Fulvenes as Isomers of Benzenoid Compounds

BY PROF. DR. K. HAFNER, DR. K. H. HÄFNER, DR. C. KÖNIG, DR. M. KREUDER, DR. G. PLOSS, CAND. CHEM. G. SCHULZ, CAND. CHEM. E. STURM, AND DR. K. H. VÖPEL

CHEMISCHES INSTITUT DER UNIVERSITÄT MARBURG/LAHN (GERMANY) AND INSTITUT FÜR ORGANISCHE CHEMIE DER UNIVERSITÄT MÜNCHEN (GERMANY)

With regard to the nature of their bonding and reactivity, fulvenes occupy a position intermediate between their benzenoid isomers and the olefins. The chemical and physical behavior of the fulvenes is determined either by the diene character of the cross-conjugated system or by the cyclic conjugation in the five-membered ring, depending on the type of substituent at the exocyclic carbon atom. In addition to several new substitution reactions, a description is given of the syntheses and reactions of 6-amino- and 6-hydroxyfulvenes, isomeric with anilines and phenols, the derivatives of which can be used for the preparation of new types of nonbenzenoid cyclic conjugated systems such as carbocyclic and heterocyclic azulenes, pseudoazulenes, thiepines, dihydropyridazines, and s-indacene.

Introduction

In connection with the question of the nature and origin of "aromatic character", recent interest has centered chiefly on nonbenzenoid cyclic conjugated compounds. The cyclopentadienyl anion *(1)* [1] and the tropylium cation *(2)* [2], although discovered at the turn of the century, have acquired within the last decade special significance as the parent structures of a multitude of "quasiaromatic" systems, as a consequence of the suggestion, more than thirty years ago, by *Robinson* [3] and *Ingold* [4] and especially *Hückel* [5] of the close relationship to benzene engendered by the common π-electron

(1)   *(2)*

sextet. The realization, that various carbocyclic nonbenzenoid compounds might possess aromatic character — earlier *Bamberger* [6], indicated the benzene-like behavior of several five-membered heterocycles and interpreted this as being due to the presence of six "potential valences" — stimulated the preparation of many new types of carbocyclic and heterocyclic conjugated nonbenzenoid systems and led to investigations of the relationships between their structures and their chemical and physical properties as a means of obtaining further information on the correlation between constitution and "aromatic character" [7].

In this respect, special importance must be allocated to compounds which are isomers of benzene and its derivatives, namely the fulvenes *(3)*. These cross-conjugated systems were prepared for the first time by *Thiele* [8] at the turn of the century by condensing cyclopentadiene with aldehydes and with ketones in the presence of bases. Their dipole moments of approx. 1.5 D [9] and the resonance energy of the cross-conjugated system of about 12 kcal/mole [10] (nearly one-third of the resonance energy of benzene) indicate their intermediate position between benzenoid and olefinic compounds.

Day [11] and *Bergmann* [12] have reviewed the progress of fulvene chemistry up to 1955. In the present paper, we shall report only the results of our own investigations. These results reveal with unusual clarity contrasting and common features of the benzenoid and fulvenoid systems.

Fulvenes as Nonbenzenoid Cyclic Conjugated Systems

The nature of the bonding in fulvenes *(3)* can be described qualitatively as a mesomeric superposition of the covalent structure A and the polar structure B. The contribution of the dipolar structure B to the resonance

[1] *J. Thiele*, Ber. dtsch. chem. Ges. *34*, 69 (1901).

[2] *G. Merling*, Ber. dtsch. chem. Ges. *24*, 3108 (1891); *W. v. E. Doering*, and *L. H. Knox*, J. Amer. chem. Soc. *76*, 3203 (1954).

[3] *J. W. Armit* and *R. Robinson*, J. chem. Soc. (London) *127*, 1604 (1925).

[4] *C. K. Ingold* and *E. H. Ingold*, J. chem. Soc. (London) *1926*, 1310.

[5] *E. Hückel*, Z. Physik *70*, 204 (1931); Grundzüge der Theorie ungesättigter und aromatischer Verbindungen. Verlag Chemie, Berlin 1938.

[6] *E. Bamberger*, Ber. dtsch. chem. Ges. *24*, 1758 (1891); Liebigs Ann. Chem. *273*, 373 (1893).

[7] Reviews: *W. Baker* and *J. F. W. McOmie*, in *J. W. Cook*: Progress in Organic Chemistry. Butterworths, London 1955, vol. 3, p. 44. *D. Ginsburg*: Non-Benzenoid Aromatic Compounds. Interscience, New York 1959; *W. v. E. Doering*: Theoretical Organic Chemistry. Butterworth, London 1959; *M. E. Vol'pin*, Russian Chem. Reviews *29*, 129 (1960).

[8] *J. Thiele*, Ber. dtsch. chem. Ges. *33*, 666 (1900).

[9] *G. W. Wheland* and *D. E. Mann*, J. chem. Physics *17*, 264 (1949); this value applies to 6,6-dialkylfulvenes.

[10] *J. H. Day* and *Ch. Oestreich*, J. org. Chemistry *22*, 214 (1957).

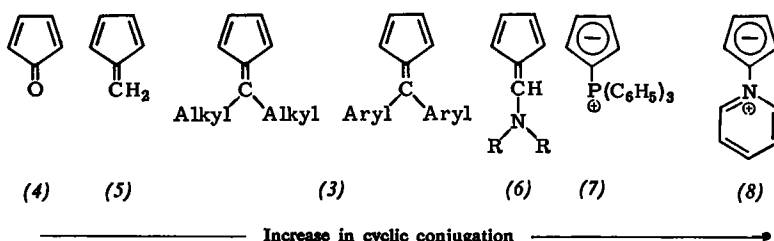[11] *J. H. Day*, Chem. Reviews *53*, 167 (1953).

[12] *E. D. Bergmann* in *J. W. Cook*: Progress in Organic Chemistry. Butterworth, London 1955, vol. 3, p. 81.

of (3) in the ground state amounts to only 5–10%, as may be assessed easily from the dipole moments [9] of 6,6-dialkylfulvenes and 6,6-diarylfulvenes. This contribution is larger in the excited state and is responsible for a de-

A   (3)   B
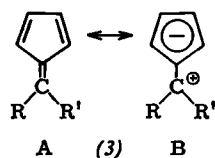
R = R' = H, Alkyl, Aryl

crease in the energy difference between the excited and ground state, and thus for the fact that fulvenes absorb at long wavelengths (compared with isomeric benzenoid systems). With the increasing electron-donating character of a substituent at carbon atom 6, the polar structure B becomes more significant [13,14]. This can be explained in accordance with Hückel's rule [5] by stabilization through the cyclic conjugated system of six π-electrons, which is present in this structure just as it is in cyclopentadienyl-metal compounds [1] and in cyclopentadiene ylides [15]. In agreement with this concept, the bond character of the fulvenes can be shifted either towards the olefinic or towards the "cyclic conjugated" side by variation of the substituents at carbon atom 6. The effect of substituents on the "aromatization tendency" of the cross-conjugated system can be studied in this manner.

itself (5) [17] as well as to 6,6-dialkyl- or 6,6-diaryl-fulvenes (3), and fulvenes containing functional groups at carbon atom 6, e.g. (6). Of these compounds, the 6,6-dialkyl- and 6,6-diarylfulvenes and the parent compound itself (5) have been especially well characterized. The latter is apparently thermally unstable and very susceptible to autoxidation. The readiness of fulvenes to undergo Diels-Alder reactions, both as dienes and dienophiles, to add on halogens, and to form peroxides (all characteristic olefinic properties) have been reported.

Being cyclic conjugated isomers of benzenoid compounds, these cross-conjugated systems may also undergo substitution reactions. Some of the fulvene derivatives thus obtained strongly resemble the isomeric benzene derivatives and prove to be valuable starting materials for the synthesis of both known and novel polycyclic conjugated nonbenzenoid compounds.

Substitution Reactions Involving 6,6-Dialkylfulvenes and 6,6-Diarylfulvenes

Besides the tendency to 1,4-additions already mentioned, which is due to the pronounced olefinic character of fulvenes alkylated or arylated at carbon atom 6 (3), the fulvenes also undergo reactions with nucleophilic and electrophilic reagents which reveal the participation of

(4)   (5)   (3)   (6) (7)   (8)

—————— Increase in cyclic conjugation ——————•

The complete replacement of carbon atom 6 by electron-attracting atoms or groups leads to fulvenoid systems with pronounced diene properties. A characteristic representative of this group is cyclopentadienone (4) [16], which undergoes a Diels-Alder condensation with itself in the nascent state. On the other hand, exchange of carbon atom 6 for electron-releasing atoms or groups results in nearly complete cyclic conjugation within the five-membered ring. This is manifested in the benzene-like behavior of cyclopentadiene ylides [15] of the type (7) and (8). The fulvenes themselves may be placed between these two fulvenoid systems, which differ so strongly in their fine structures. Depending on their degree of polarization, the fulvenes more or less combine the properties of both extremes. This applies to fulvene

the polar structure B. Thus, organolithium compounds add to fulvenes as first observed by Ziegler and co-workers [18]. In agreement with calculations of its elec-

(3)   (9)

(10)

[13] G. Kresze and H. Goetz, Chem. Ber. 90, 2161 (1957).

[14] K. Hafner, Angew. Chem. 74, 499 (1962); K. H. Häfner, Ph. D. thesis, Universität Marburg, 1962.

[15] D. Lloyd and J. S. Sneezum, Chem. and Ind. 1955, 1221; Tetrahedron 3, 334 (1958); F. Ramirez and S. Levy, J. org. Chemistry 21, 488 (1956); J. Amer. chem. Soc. 79, 67 (1957).
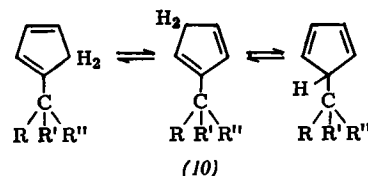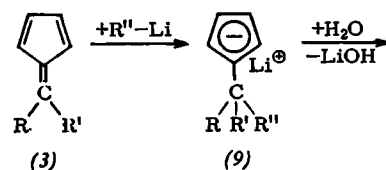
[16] K. Hafner and K. Goliasch, Chem. Ber. 94, 2909 (1961); C. H. DePuy, M. Isaks and K. L. Eilers, Chem. and Ind. 14, 429 (1961); C. H. DePuy, B. W. Ponder and J. D. Fitzpatrick, Angew. Chem. 74,489 (1962) and previous publications; E. Vogel and E.-G. Wyes, ibid. 74, 489 (1962).

[17] J. Thiele and H. Balhorn, Liebigs Ann. Chem. 348, 1 (1906); J. Thiec and J. Wiemann, Bull. Soc. chim. France 1956, 177; 1957, 366; 1960, 1066; see also H. J. F. Angus and D. Bryce-Smith, J. chem. Soc. (London) 1960, 1409.

[18] K. Ziegler, F. Croessmann, H. Kleiner, and O. Schäfer, Liebigs Ann. Chem. 473, 1 (1929); K. Ziegler and W. Schäfer, ibid. 511, 101 (1934); see also D. Lavie and E. D. Bergmann, Bull. Soc. chim. France 18, 250 (1951); R. C. Fuson and F. E. Mumford, J. org. Chemistry 17, 255 (1952); R. C. Fuson and O. York, ibid. 18, 570 (1953); D. Taber, E. J. Becker, and P. E. Spoerri, J.Amer. chem. Soc. 76, 776 (1954); A. G. Bonagura, M. B. Meyers, S. J. Storter, and E. J. Becker, ibid. 76, 6122 (1954).

124

tron density distribution [19], the nucleophilic reagent attacks the fulvene at the exocyclic carbon atom to form an alkylcyclopentadienyl-lithium compound *(9)*.

The driving force behind this reaction is the gain in resonance energy originating from the transition of the cross-conjugated system to the cyclic conjugated state. Metal hydrides react similarly with these fulvenes [20]. Hydrolysis of *(9)* leads to alkylated cyclopentadienes *(10)*. Thus, alkylating or arylating reduction of the exocyclic double bond supplements the synthesis of substituted cyclopentadienes from cyclopentadiene- metal compounds and alkyl halides [21].
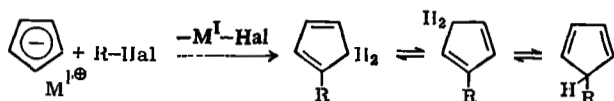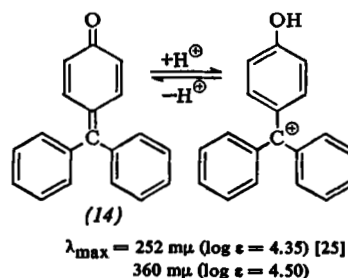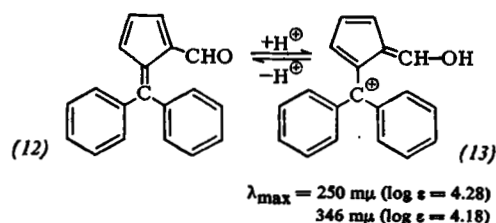

Electrophilic substitution in fulvenes has not attracted much attention, since such experiments have so far been of doubtful success [22]. In fact, however, fulvenes are as susceptible to electrophilic substitution as other nonbenzoid cyclic conjugated compounds. Thus, 6,6-diphenylfulvene *(3)*, R = R'= C$_6$H$_5$, is formylated with ease and in high yield by treatment with Vilsmeier's complex *(11)*, obtained from dimethylformamide and phosphorus oxychloride [23,24]. Again, in accordance with the theoretically derived electron density distribution [19], the electrophilic reagent attacks at carbon
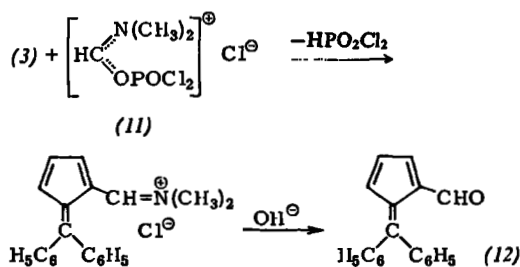

atom 2 of the cross-conjugated system to yield the aldehyde *(12)*, the structure of which has been confirmed by its nuclear magnetic resonance spectrum (ABX). This stable red fulvenaldehyde resembles its isomer fuchsone *(14)*. Like the latter, it is readily and reversibly protonated at the carbonyl oxygen to give the conjugated acid

(13). The ultraviolet spectrum of aldehyde *(12)* largely resembles that of the fuchsone.

$\lambda_{max} = 250$ mµ (log ε = 4.28)
346 mµ (log ε = 4.18)

$\lambda_{max} = 252$ mµ (log ε = 4.35) [25]
360 mµ (log ε = 4.50)

6,6 - Diphenylfulvene and 6,6 - dimethylfulvene *(3)*, R=R'=CH$_3$, also undergo protonation, alkylation, and nitrosation at temperatures as low as −80 °C [14], σ-complexes of type *(15)*, which are stable only at −80 °C,
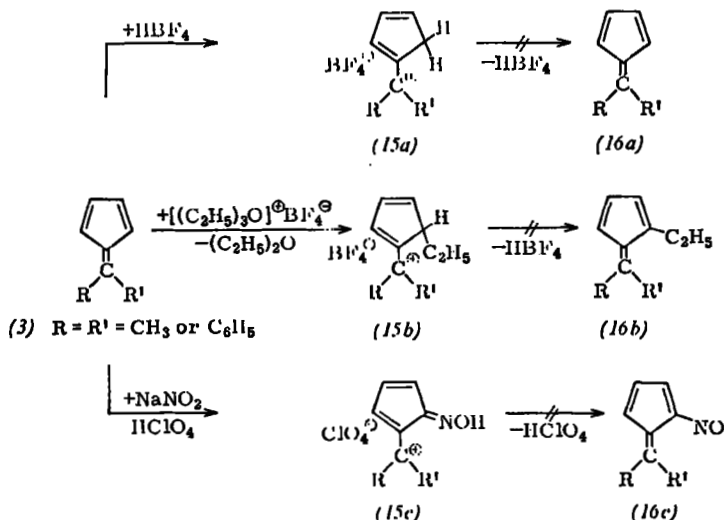
being obtained first as colorless salts. The conversion of these fulvenium salts into substituted fulvenes *(16)* has not yet been accomplished, polymeric products *(18)* being formed instead. Ionic polymerization of the possible intermediary 1,3-dipole *(17)* probably competes with the conversion of the carbonium salts *(15)* into the cross-conjugated substitution products *(16)*, since this change is associated with only a slight energy gain. *Thiec* and *Wiemann* [17] observed a similar polymerization with unsubstituted fulvene.

Moreover, the dark red polymethine dye salts *(19)* and *(20)*, which are obtained respectively from the fulvenium salts *(15a)* and benzaldehyde and from 6,6-diphenylfulvene-2-aldehyde *(12)* by an acid-catalyzed

[19] *G. Berthier* and *B. Pullmann*, Bull. Soc. chim. France [4] *16*, D 461 (1949).

[20] *K. Ziegler*, Angew. Chem. *64*, 323 (1952); *K. Ziegler, H. G. Gellert, H. Martin, K. Nagel*, and *J. Schneider*, Liebigs Ann. Chem. *589*, 91 (1954); *K. Hafner*, ibid. *606*, 79 (1957); Angew. Chem. *70*, 419 (1958); *H. Dohm*, Ph. D. thesis, Universität Marburg, 1958.

[21] *K. Alder* and *H. Holzrichter*, Liebigs Ann. Chem. *524*, 145 (1936); *H. Dohm*, Ph. D. thesis, Universität Marburg, 1958; *R. Riemschneider* and *E.-B. Grabitz*, Mh. Chem. *89*, 748 (1958); *R. Riemschneider* and *R. Nehring*, ibid. *90*, 568 (1959).

[22] *E. Bergmann* and *A. v. Christiani*, Ber. dtsch. chem. Ges. *63*, 2559 (1930); *64*, 1481 (1931); *J. H. Day* and *C. Pidwerbesky*, J. org. Chemistry *20*, 89 (1955).

[23] *A. Vilsmeier* and *A. Haack*, Ber. dtsch. chem. Ges. *60*, 119 (1927); *Ch. Jutz*, Chem. Ber. *91*, 850 (1958); *H. H. Bosshard* and *Hch. Zollinger*, Angew. Chem. *71*, 375 (1959); Helv. chim. Acta *42*, 1659 (1959); *H. Bredereck, R. Gompper, K. Klemm*, and *H. Rempfer*, Chem. Ber. *92*, 837 (1959).

[24] *K. H. Vöpel*, Ph. D. thesis, Universität Marburg, 1960; *K. Hafner* and *K. H. Vöpel*, Angew. Chem. *71*, 672 (1959); *K. Hafner*, ibid. *72*, 574 (1960).

[25] *E. Walton, A. F. Wagner, F. W. Bachelor, L. H. Peterson, F. W. Holly*, and *K. Folkers*, J. Amer. chem. Soc. *77*, 5144 (1955).

Angew. Chem. internat. Edit. | Vol. 2 (1963) | No. 3

125

aldol condensation [*] polymerize rapidly under the action of nucleophilic reagents. This behavior indicates that the sextet stabilization of the fulvenes forming the

workers [27] were the first to succeed in preparing 6-(dimethylamino)fulvene *(22)*; they obtained it by condensing *N,N*-dimethyldiethoxymethylamine *(23)* (which
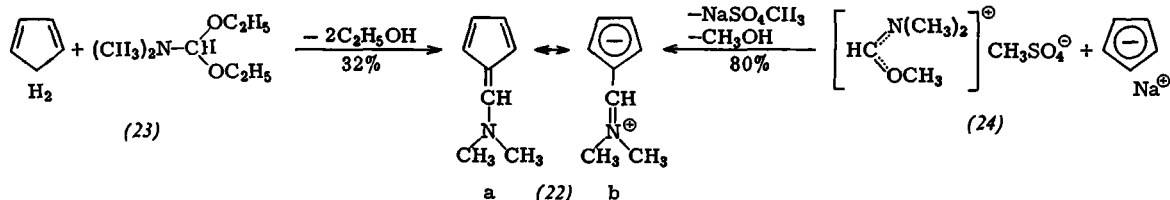
basic structure of the fulvenium salts *(15)*, *(19)*, and *(20)* is weak. Thus, these salts differ from their benzenoid isomers and from other nonbenzenoid cyclic conjugated systems, e.g., azulene [26] and 6-aminofulvenes, which give addition products that often rearrange spontaneously into cyclic conjugated systems.

jugated systems, e.g., azulene [26] and 6-aminofulvenes, which give addition products that often rearrange spontaneously into cyclic conjugated systems.

they discovered) with cyclopentadiene. We also obtained this fulvene, which is an isomer of and chemically similar to *N,N*-dimethylaniline, in over 80 % yield by treating cyclopentadienylsodium with the carbonium immonium methosulfate *(24)* [28], prepared from dimethylformamide and dimethyl sulfate. Its dipole moment of 4.5 D [29], indicates that there is considerable participation (approx. 25 %) of the dipolar cyclic conjugated structure *(22b)* in the ground state; this explains the slight tendency of this fulvene to behave as a 1,3-diene. Electrophilic substitution at the five-membered ring proceeds readily. Thus, just like its benzenoid isomer, this compound adds on tetracyanoethylene *(25)* to yield 2-tricyanovinyl-6-dimethylaminofulvene
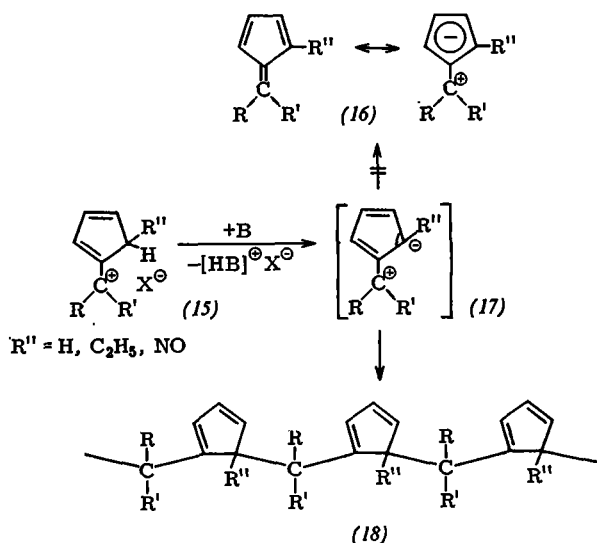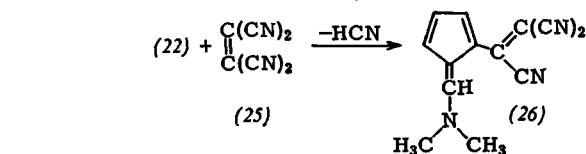
(26) [30] and, on acylation, gives mono- and diacyl derivatives. Moreover, the slight solvatochromism exhibited by solutions of *(22)* when nonpolar n-hexane is replaced by water as solvent indicates a strong polarization cor-
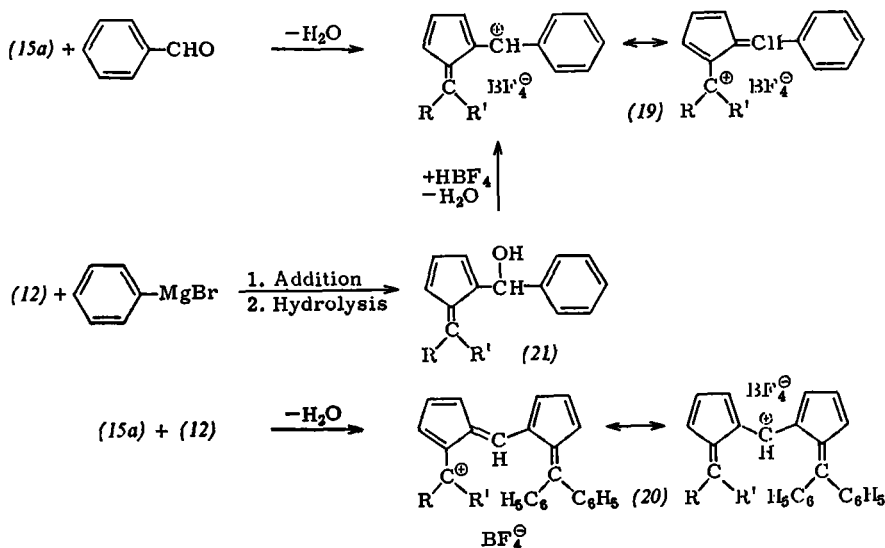
6-Amino- and 6-Hydroxyfulvenes

Fulvenes with functional groups at carbon atom 6 have only very recently become known. *Meerwein* and co-

responding to structure *(22b)*. On the other hand, vinylogous fulvenes *(27)*, n = 1—3, which are readily acces-

[*] The product *(19)* may also be obtained by the reaction of the fulvenaldehyde *(12)* with phenylmagnesium bromide, yielding the carbinol *(21)*.

[26] *K. Hafner*, Angew. Chem. *70*, 419 (1958).

[27] *H. Meerwein, W. Florian, N. Schön*, and *G. Stopp*, Liebigs Ann. Chem. *641*, 1 (1961).

[28] *H. Bredereck, F. Effenberger*, and *G. Simchen*, Angew. Chem. *73*, 493 (1961).

[29] *K. Hafner, K. H. Vöpel, G. Ploß*, and *C. König*, Liebigs Ann. Chem. *661*, in the press.

[30] *G. Schulz*, diploma thesis, Universität München, in preparation.

126

Angew. Chem. internat. Edit. / Vol. 2 (1963) / No. 3

sible from cyclopentadiene and ω-dimethylaminopoly-
enals, show considerable increases in solvatochromism
with increasing n. This is especially evident in the shifts
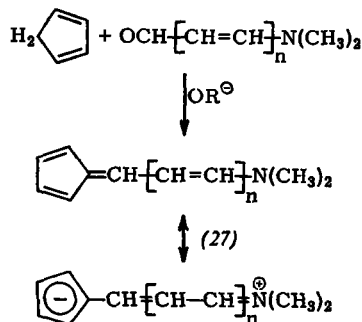
of the absorption band of longest wavelength (Table 1)
and is to be attributed to the transition of these fulvenes
to a polar excited state [31].

Table 1. Absorption spectra of vinylogous aminofulvenes (27)

Amino-fulvene (27)	Main absorption band [mμ (log ε)] in			
	n-hexane	methanol	formamide	methanol/ H₂SO₄ (1 %)
n = 0	316 (4.49)	322 (4.52)	326 (4.49)	318
n = 1	375 (4.67) 242 (3.70)	401 (4.68) 244 (3.79)	419	376 239
n = 2	411 (4.75) 261 (3.70)	445 (4.71) 267 (3.72)	481	422 270
n = 3	429 (4.79) 280 (3.71)	464 (4.76) 283 (3.73)		433 286

In contrast to (22), the vinylogous aminofulvenes (27)
are thermally unstable; this, in conjunction with some
of their reactions, points to a stronger 1,3-diene charac-
ter and, thus, to a weaker sextet stabilization for them.
At the same time, this finding shows in an impressive
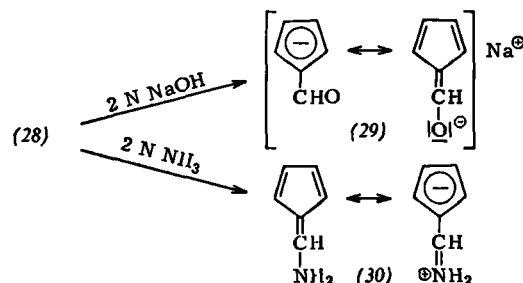manner the limitations of the vinylogue principle [32].

The fulvene (22) reacts with nucleophilic reagents ex-
clusively at the exocyclic carbon atom, e.g. with primary
or secondary amines with exchange of the amino group
or with hydroxyl ions to yield 6-hydroxyfulvene (28)
[30], which is isomeric with phenol. From its infrared
and NMR spectra, (28) appears to exist as a mixture of
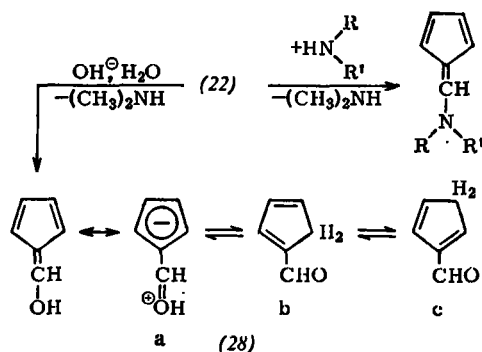
[31] K. Hafner, G. Schneider, and W. aus der Fünten, unpublished
results; see also K. Hafner, Liebigs Ann. Chem. 606, 79 (1957).
[32] Compare with corresponding observations with 6-phenyl-
fulvenes substituted in the benzene ring, G. Kresze and H. Goetz
[13]; G. Kresze, S. Rau, G. Sabelus, and H. Goetz, Liebigs Ann.
Chem. 648, 51 (1961), and with 6-furfurylfulvene and its vinyl-
ogues, C. H. Schmidt, Chem. Ber. 90, 1352 (1957).

tautomeric forms (28a, b, and c). This is the simplest
fulvene isolated so far; it is only slightly stable thermally
and is susceptible to autoxidation. Although the pKα
value of (28) is equal to that of phenol, the unionized
compound has largely the nonpolar cross-conjugated
structure and only a slight resonance contribution from
the dipolar structure. While phenol is cyclically conju-
gated only in its enolic form, the fulvenoid isomer is con-
jugated only in its anionoid carbonyl form. This ex-
plains why the sodium salt of 6-hydroxyfulvene is more
stable than the free fulvene. With bases — even with 2N
sodium hydroxide — the fulvne (28) is rapidly trans-
formed to the energetically favored formylcyclopenta-
dienyl anion (29). 6-Hydroxyfulvene, like other hydroxy-

methylene compounds, reacts with 2N ammonia to give
the stable 6-aminofulvene (30) which, like aniline, rea-
dily undergoes electrophilic substitution; it has thus
established itself as a starting material for the synthesis
of many new fulvene derivatives [30].

6-Aminofulvenaldehydes

6-Dimethylaminofulvene (22) and its derivatives not
only have a propensity for nucleophilic exchange reac-
tions at carbon atom 6, but are also highly reactive
toward electrophiles. The fulvene (22) reacts even at
−60 °C with the Vilsmeier complex (11) to yield the
immonium salt (31), which can be isolated as its per-
chlorate or iodide. Hydrolysis of (31) with alkali leads
to 6-dimethylaminofulvene-2-aldehyde (32) [29,33]. On
the other hand the fulvene (22) reacts rapidly at 20 °C
with two molecules of the formylation reagent (11) to
give the symmetrical bis-immonium salt (33), which is
extensively stabilized by resonance. Hydrolysis of (33)
with alkali yields 6-dimethylaminofulvene-3,4-dialde-
hyde (34), a fulvene derivative isomeric with N,N-di-
methylamino-o-phthaldialdehyde. At the same time, the
isomeric 6-dimethylaminofulvene-2,4-dialdehyde (35) is
also formed in low yield, apparently in dependence on
the conditions of hydrolysis.

Both fulvenaldehydes are obtained in a simpler manner
directly from cyclopentadiene and the Vilsmeier com-
plex (11). Thus, the cyclic 1,3-diene reacts even at
−20 °C with the electrophilic reagent to yield, probably,
the addition product (36), which by elimination of one
mole of hydrogen chloride and one mole of dichloro-

[33] G. Ploß, Ph. D. thesis, Universität Marburg, 1961.

phosphoric acid is then converted into the resonance-stabilized fulvene *(22)*. The latter then undergoes electrophilic substitution at position 2 in a fast subsequent step. Above 0 °C, the immonium salt *(31)* formed reacts

chlorides. Mono- or poly-alkylated or -arylated cyclopentadienes, as well as indene, also react to yield the corresponding five-membered substituted 6-(N,N-dialkylamino)fulvenemono- and dialdehydes [24,29,34]. .
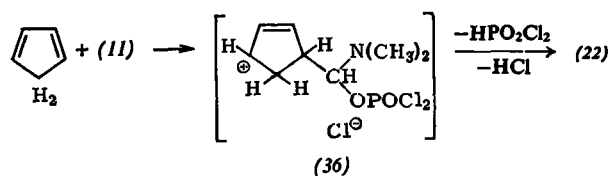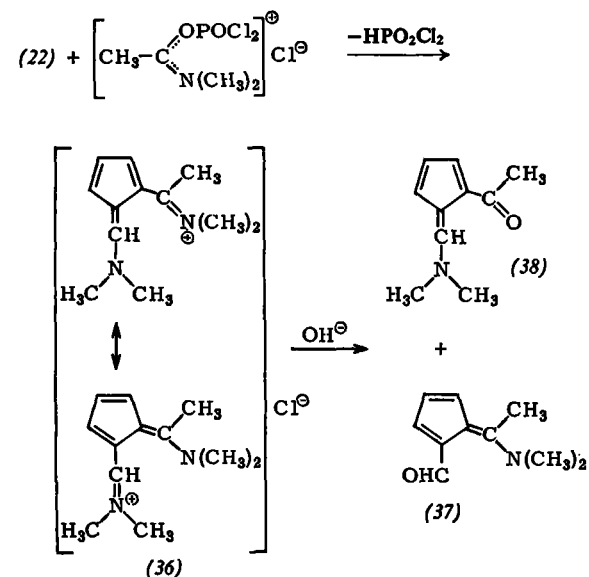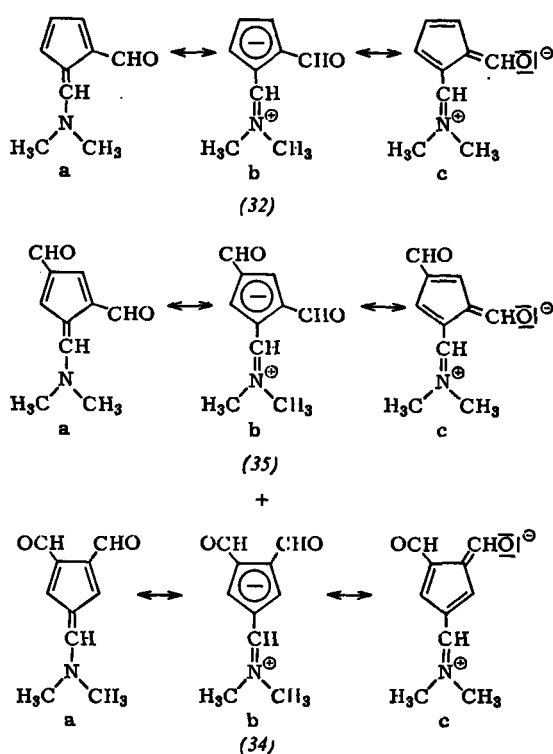
$$(22) \quad \xrightarrow[\text{−HPO}_2\text{Cl}_2]{+ (11)}$$

(31)

(32)

$$\downarrow \begin{array}{c} + (11) \\ \text{−HPO}_2\text{Cl}_2 \end{array}$$

(33)

(35)

+

(34)
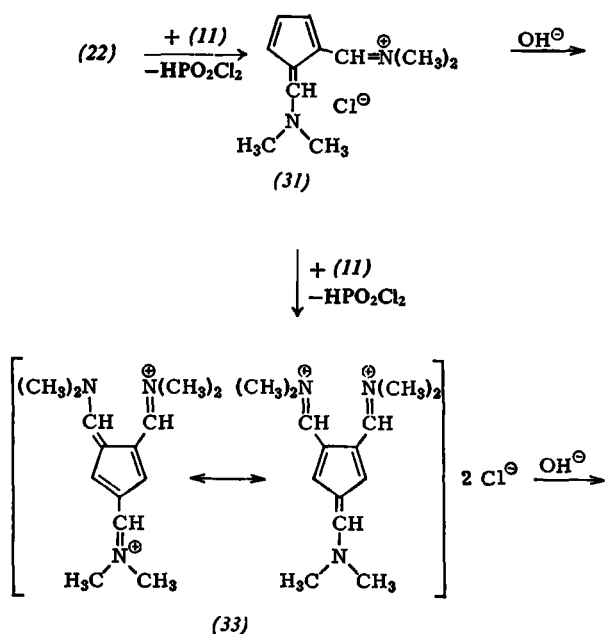
immediately with an additional mole of the Vilsmeier complex *(11)* to give the bis-immonium salt *(33)* in over 90% yield. Thus, it is possible to obtain in good yields both the fulvenemonoaldehyde *(32)* and the fulvenedi-

(36)

aldehyde *(34)* or their immonium salts directly from cyclopentadiene, dimethylformamide, and phosphorus oxychloride, phosgene, thionyl chloride, or other acid

Instead of dimethylformamide, other N,N-dialkylform-amides may also be used for this reaction with cyclopentadiene, but not the amides of homologous carboxylic acids [14,24,29]. On the other hand, 6-(N,N-dimethylamino)fulvene *(22)* reacts smoothly with the Vilsmeier complex obtained from N,N-dimethylacetamide and phosphorus oxychloride to give the immonium salt *(36)*, hydrolysis of which then leads to a mixture of the fulvenaldehyde derivative *(37)* and the methylfulvene ketone *(38)* [30]. Compound *(22)* reacts with vinylogous amides, e.g. β-(N,N-dialkylamino)acroleins, in the presence of oxalyl chloride to give immonium salts of type *(39)*, which hydrolyze to give 6-(N,N-dialkylamino)-

$$(22) + \begin{bmatrix} \text{CH}_3-\text{C} \begin{array}{c} \text{OPOCl}_2 \\ \text{N(CH}_3)_2 \end{array} \end{bmatrix} \text{Cl}^{\ominus} \xrightarrow{\text{−HPO}_2\text{Cl}_2}$$

(36)

(38)

+

(37)

$$(22) + \text{OCH−CH=CH−N} \begin{array}{c} \text{R} \\ \text{R} \end{array} \xrightarrow[\begin{array}{c}\text{−HCl}\\\text{−CO}_2\end{array}]{\text{+(COCl)}_2}$$
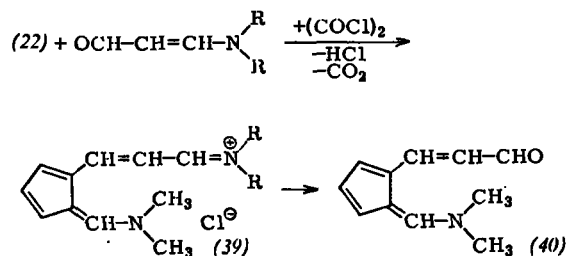
fulvene-2-prop-2'-en-1-al *(40)* [35]. Vinylogous aminofulvenes *(27)* also undergo electrophilic substitution at the five-membered ring. Thus, formylation of the fulvene derivative *(27)* where n ≈ 1, with the Vilsmeier complex *(11)* leads directly to the red fulvenedialdehyde *(42)*.

[34] After we had published these results Z. *Arnold*, Coll. Czechos. chem. Commun. *25*, 1313 (1960), also reported the reaction of cyclopentadiene with Vilsmeier's complex.

[35] M. *Kreuder*, Ph. D. thesis, Universität Marburg, 1961.

128

Angew. Chem. internat. Edit. | Vol. 2 (1963) | No. 3

Correspondingly, on reaction with β-(N,N-dialkylamino)-acroleins and oxalyl chloride, compound *(27)*, where n = 1, yields the dark red fulvene-3,4-dipropenal *(44)*. The bis-immonium salts *(41)* and *(43)*, which are formed first, can be isolated as their perchlorates or iodides [35].

(42)

$$\overset{OHC}{\underset{OHC}{}}\text{=CH-CH=CH-N(CH}_3)_2$$

↑ OH⊖

(41)

$$\left[\begin{array}{c}(CH_3)_2\overset{\oplus}{N}=CH\\(CH_3)_2\overset{\oplus}{N}=CH\end{array}=CH-CH=CH-N(CH_3)_2\right]\ 2\ Cl^\ominus$$

↑ + *(11)*
−2 HPO₂Cl₂

(27) n = 1 ◯=CH-CH=CH-N(CH₃)₂

+2 R₂N-CH=CH-CHO
+2 (COCl)₂
−2 CO₂, −2 HCl

3)

$$\left[\begin{array}{c}R\\R\end{array}\overset{\oplus}{N}=CH-CH=HC\cdots=CH-CH=CH-N(CH_3)_2\right]\ 2\ Cl^\ominus$$

↓ OH⊖

(44)

$$\overset{OCH-CH=HC}{\underset{OCH-CH=HC}{}}\text{=CH-CH=CH-N(CH}_3)_2$$

All of these new 6-dialkylaminofulvenaldehydes crystallize well. Their slight positive solvatochromism and the shift of their carbonyl stretching frequencies to lower values (1650 cm⁻¹; compared with aromatic aldehydes) suggest strong participation of the polar resonance

(34)

(45)

structures *(32b,c)*, *(34b,c)*, and *(35b,c)* in the ground state. With regard to their chemical properties, they only faintly resemble their isomeric aromatic aldehydes. They may otherwise be regarded as vinylogous amides.

(31)

(46)

(47)

(33)

Attempts to oxidize them to fulvenecarboxylic acids failed. Reduction of the dialdehyde *(34)* with lithium aluminum hydride leads to (N,N-dimethylaminomethyl) dimethylcyclopentadiene *(45)*, i.e., as in the case of amides, both carbonyl groups are reduced directly to methyl groups. Subsequently, the exocyclic double bond is also reduced [29,33]. Aldehydes *(32)* and *(34)* behave similarly to p-dimethylaminobenzaldehyde toward compounds containing acidic CH groups. For example, in the presence of basic condensing agents, these aldehydes, and more especially, their immonium salts *(31)* and *(33)*, react with diethyl malonate, malonodinitrile, or other compounds containing active methylene groups, to yield fulvene derivatives of general formulae *(46)* or *(47)* [29,33,36]. The fulvenaldehyde *(34)* reacts with hydroxylamine, depending on the reaction conditions, to yield either the dioxime *(48)*, or, with simultaneous exchange of the dimethylamino group at carbon atom 6, the N-hydroxyaminofulvenedialdoxime *(49,a,b)*. Compounds *(32)* and *(34)* react similarly with hydrazine, thiosemicarbazide, and isonicotinic hydrazide. The dialdehyde *(34)* reacts with aliphatic and aromatic amines with simultaneous exchange of the dimethylamino group at carbon atom 6 to yield Schiff bases of general formulae *(50a,b)* and *(51a,b)* [92,33,37]. The infrared and NMR spectra of these compounds as well as energy considerations indicate large contributions from structures *(50b)* and *(51b)* [38].

6-Hydroxyfulvenaldehydes

The mono- and dialdehydes *(32)* and *(34)* of 6-(N,N-dimethylamino)fulvene *(22)* react similarly to the latter with nucleophilic reagents undergoing replacement of

[36] R. Oda, T. Shono, and K. Nishida, J. chem. Soc. (Japan), 82 1422 (1961).

[37] C. König, Ph. D. thesis, Universität Marburg, 1961.

[38] H. Musso, K. Hafner, and G. Ploß, unpublished results.

the dimethylamino group. When treated with 2N sodium hydroxide, these fulvenealdehydes yield (slowly at 20 °C, rapidly when warmed) the water-soluble stable

6-alkyl- and arylfulvenes of type (56) [39], which are formed, together with o-acyl derivatives of monoacylated cyclopentadienes (57), on treating cyclopenta-


sodium salts of cyclopentadienedialdehyde and cyclopentadienetrialdehyde (52) and (53), respectively. The latter are easily converted with dilute acids into the parent 6-hydroxyfulvenaldehydes (54) and (55), which are also stable and crystallize well. Both of these hydroxymethylene compounds combine readily with amines to regenerate the corresponding 6-aminofulvenaldehydes [24, 29,33].

6-Hydroxyfulvene-2-aldehyde (54) and -2,4-dialdehyde (55) are readily volatile and strongly acidic. pK$_\alpha$ measurements give values of 1.8 ± 0.1 for the dialdehyde (55) and 4.5 ± 0.1 for the monoaldehyde. The cyclopentadiene derivatives are therefore equal in acidity to mineral acids or acetic acid [29,33]. Infrared and NMR spectroscopic investigations show that both compounds are

dienylsodium with acyl halides. Like compound (56), the 6-hydroxyfulvenaldehydes give intensely green or
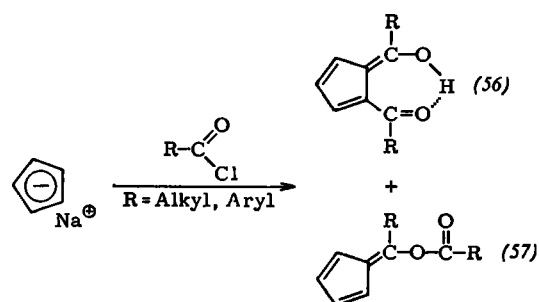
red color reactions with ferric chloride. 6-Hydroxyfulvene-2-aldehyde (54) reacts with phenylisocyanate, as
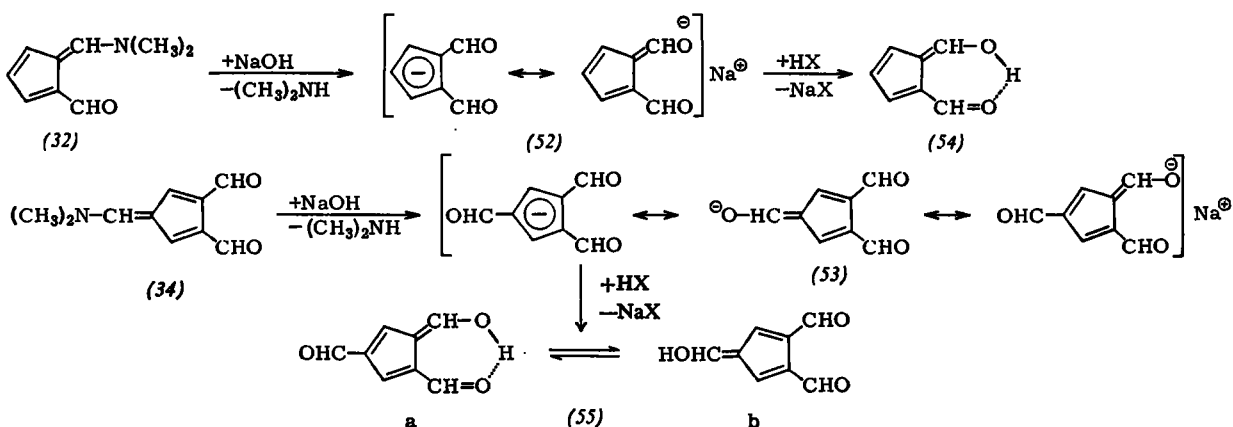

systems with almost completely symmetrical hydrogen bonds according to formulae (54) and (55a) [38]. Both fulvene derivatives have a pronounced tendency to form a π-electron sextet in the five-membered ring, which may contribute far more to the ground state resonance than the cross-conjugated fulvene structure, though the latter is certainly also involved. In their properties, the derivatives resemble the previously known 2-acyl-6-hydroxy-
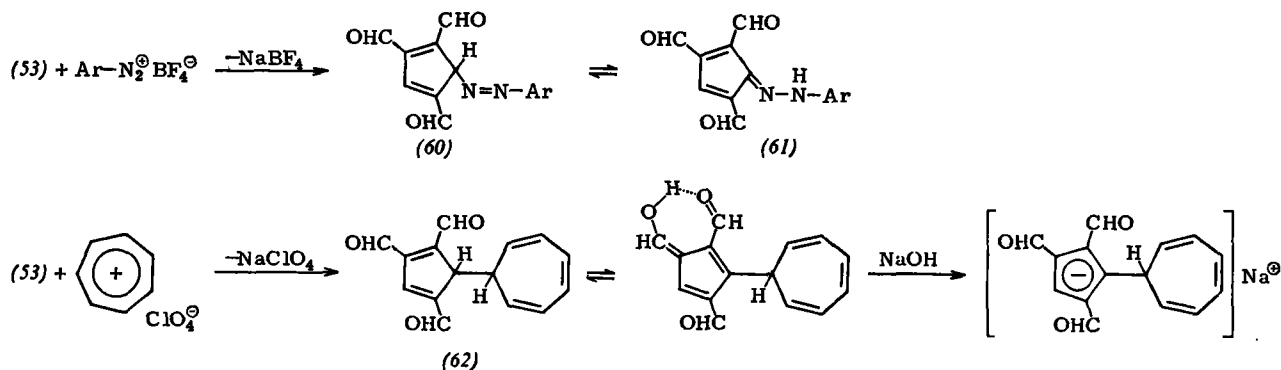
do other hydroxymethylene compounds, to give the o-carbanilide (58), which is converted directly after its formation into 6-anilinofulvenedialdehyde (59) [29,33] with evolution of carbon dioxide. The fulvenedialdehyde

[39] W. J. Hale, J. Amer. chem. Soc. 34, 1580 (1912); 38, 2535 (1916); W. J. Linn and W. H. Sharkey, ibid. 79, 4970 (1957); H. Dohm, Ph. D. thesis, Universität Marburg, 1958; R. Riemschneider and M. Krüger, Mh. Chem. 90, 573 (1959).

130

(55) undergoes substitution at the five-membered ring on treatment with electrophilic reagents. Thus, *(53)*

(54)

$$\downarrow C_6H_5-N=C=O$$

(58)

$$\downarrow -CO_2$$

(59)
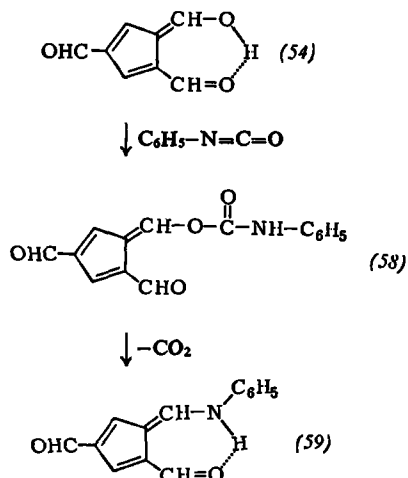
couples with diazonium salts to give a brownish-red compound, which, according to its infrared spectrum, is not the primary product *(60)* of the coupling but very

give orange-red fulvenotropone derivatives of type *(63)*, which resemble quinone methides and which were previously inaccessible. Thus, for example, on alkylation with triethyloxonium fluoborate, the quinonoid azulene

(33)
2 Cl$^{\ominus}$

(34)

(63)

$$X = COOR, COCH_3, C_6H_5, CH_3$$
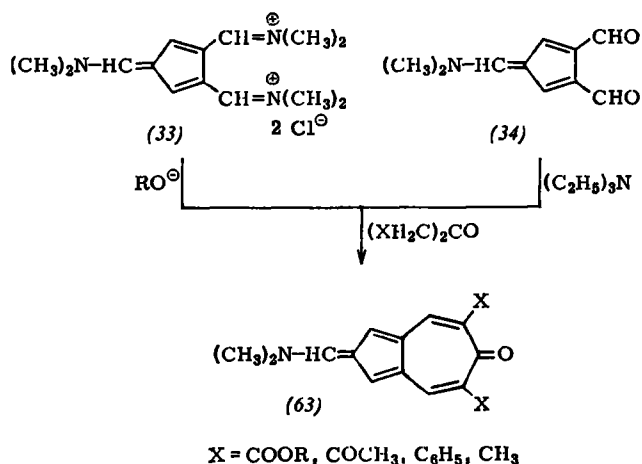
derivative *(63)*, where $R = C_6H_5$, is readily converted into the immonium salt *(64)*, which on alkaline hydrolysis gives a good yield of a blue compound, 5,7-diphenyl-6-

(53) + Ar–N$_2^{\oplus}$BF$_4^{\ominus}$ $\xrightarrow{-NaBF_4}$

(60) $\rightleftharpoons$ *(61)*

(53) + $\xrightarrow{-NaClO_4}$

(62) $\rightleftharpoons$ $\xrightarrow{NaOH}$

likely the tautomeric hydrazone *(61)* of 2,3,5-triformyl-cyclopentadienone. Alkylation of the sodium salt of tri-formylcyclopentadiene *(53)* also leads to fulvene derivatives which are substituted in the five-membered ring. Thus, 6-hydroxy-2-tropylfulvene-3,4-dialdehyde *(62)*, is formed in this way from tropylium perchlorate and easily affords a sodium salt; being a dihydrosesquifulvene derivative, *(62)* is of definite interest [29,33].

Syntheses of Bi- and Tricyclic Conjugated Ring Systems

With suitable reagents, 6-aminofulvenealdehyde *(32)* and -dialdehyde *(34)*, as well as the corresponding hydroxy compounds, readily form new cyclic conjugated systems with fulvenoid structures.
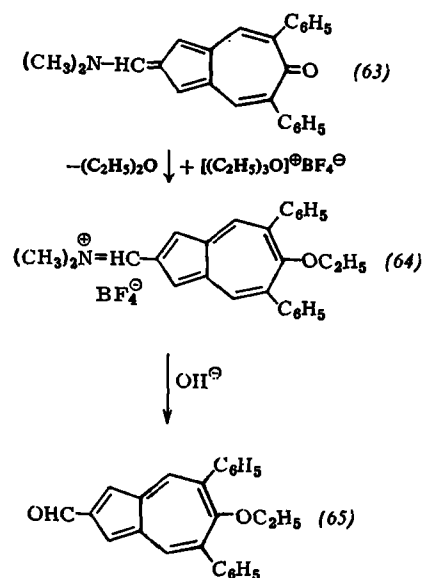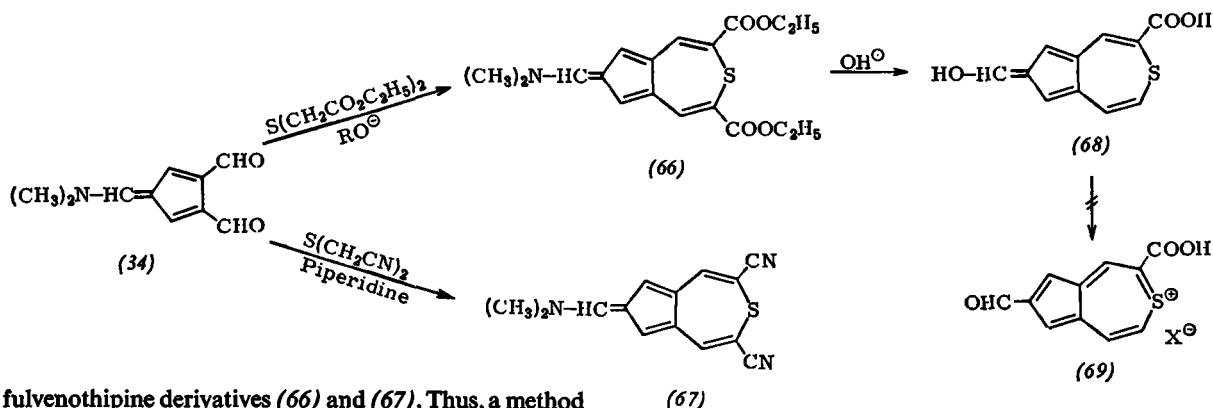
Azulenes

6-(*N,N*-Dimethylamino)fulvene-3,4-dialdehyde *(34)*, which condenses with malonic acid derivatives or their immonium salts *(33)*, also condenses with diethyl aceto-nedicarboxylate, dibenzyl ketone, or diethyl ketone to

ethoxyazulene-2-aldehyde *(65)*. The synthesis of this azulene derivative simultaneously confirms the struc-

(63)

$$-(C_2H_5)_2O \downarrow + [(C_2H_5)_3O]^{\oplus}BF_4^{\ominus}$$

(64)

$$\downarrow OH^{\ominus}$$

(65)

ture of the preliminary step in the synthesis of the ful-venedialdehyde *(34)*, viz. the bis-aldimmonium salt *(33)* [24,29,37].

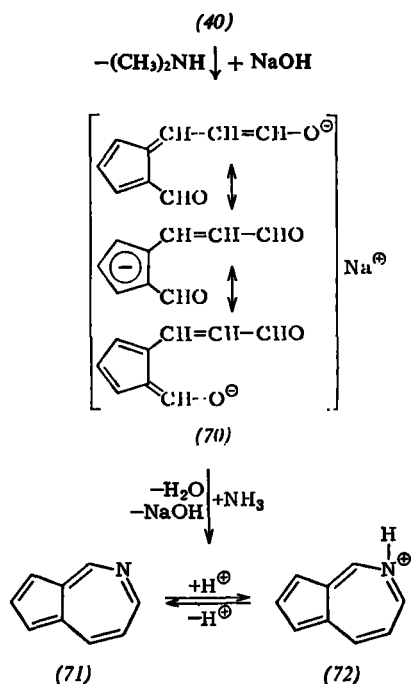*Angew. Chem. internat. Edit. | Vol. 2 (1963) | No. 3*

131

Thiepines

In the presence of alkaline condensing agents, the ful-venedialdehyde *(34)* reacts with diethyl thiodiglycolate or thiodiacetonitrile to yield systems with condensed five- and seven-membered rings, such as the red-brown

presentative of a bicyclic azulene with a hetero atom in the seven-membered ring and, being an azepine deri-vative, is of special interest. Chemically and physically, it resembles carbocyclic azulene and pyridine. Its ultra-violet and visible absorption spectrum resembles that of

(66)

(68)

(67)

(69)

fulvenothipine derivatives *(66)* and *(67)*. Thus, a method has become available for the first time for the synthesis of thiepines condensed with a five-membered ring. On treatment with methanolic potassium hydroxide, com-pound *(66)* is converted by hydrolysis and decarboxyl-ation into compound *(68)*, which so far has resisted all efforts to transform it into the cyclic conjugated sulfon-ium salt *(69)* [37], an isomer of the 1- or 2-thianaphthal-enium ion [40].

5-Aza-azulene

The hydroxyfulvene derivative *(70)* is easily accessible by treating 6-(N,N-dimethylamino)fulvene-2-prop-2'-en-1'-al *(40)* with sodium hydroxide and on treatment with aqueous ammonia, leads to new types of azulene derivatives. In this reaction, a 77% yield of the violet 5-aza-azulene *(71)* is obtained directly; this is the first re-

(40)

$-(CH_3)_2NH \downarrow + NaOH$

(70)

(71)   *(72)*

azulene, especially in its fine structure, the absorption maxima being, however, hypsochromically shifted by 35 mμ; this corresponds to theoretical predictions by *H. Kuhn* [41]. On treatment with protons or alkylating agents, it is converted into the red azulene-immonium salt *(72)*, the protonation being reversed by bases. As expected, protonation or alkylation of the nitrogen — just as the presence of electronegative substituents at carbon atom 5 or carbon atom 7 of the azulene — effects a further hypsochromic shift of the absorption maxima [35,42].

As with pyridine, nucleophilic reagents add onto the carbon atoms adjacent to the nitrogen to yield the cor-responding dihydro derivatives *(73)* [43].

(73)
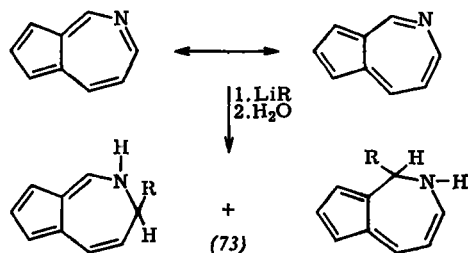
Pseudo-azulenes

It has been known for a long time that, on replacement of a —CH=CH— group in cyclic conjugated systems by a hetero atom (sulfur, oxygen, NH group) possessing free electron pairs, the cyclic conjugation is more or less preserved. Thus, the heterocyclic systems *(74)* and *(75)* are closely related to electronically isosteric azulene deri-vatives. *Armit* and *Robinson* [3,44] as well as *Boyd* [45]

[40] *A. Lüttringhaus* and *N. Engelhard*, Chem. Ber.*93*, 1525 (1960).

[41] *H. Kuhn*, personal communication; see also *H. Kuhn*, Helv. chim. Acta *34*, 2371 (1951); Chimia*4*,203 (1950); Fortschr. Chem. org. Naturstoffe (Wien) *16*, 169 (1958); *17*, 404 (1959).
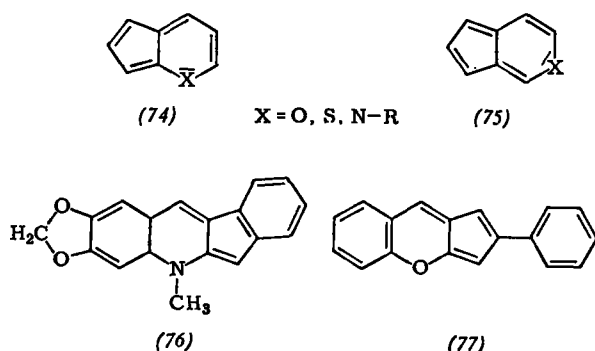
[42] *K. Hafner* and *M. Kreuder*, Angew. Chem. *73*, 657 (1961).

[43] *M. Kreuder*, unpublished results.

[44] *J. W. Armit* and *R. Robinson*, J. chem. Soc. (London) *121*, 827 (1922).

[45] *G. V. Boyd*, J. chem. Soc. (London) *1958*, 1978; *1959*, 55.

132

Angew. Chem. internat. Edit. / Vol. 2 (1963) / No. 3

and *Treibs* and co-workers [46] have already prepared polycyclic compounds of type *(76)* and *(77)* that are

(74)   X = O, S, N–R   *(75)*

(76)   *(77)*

based on these pseudoazulenes. By dehydrogenation of the corresponding octahydro derivatives, *Anderson* et al. [47] and *R. Mayer* [48] recently obtained simple representatives of this class of compounds, such as the two isomeric cyclopentathiapyrans *(74)* and *(75)*, where X = S, and *N*-phenyl-2-pyridine *(75)*, where X = NC₆H₅.

It is much simpler to prepare these pseudoazulenes by condensing 6-hydroxyfulvene-2-aldehyde *(32)* with the ethyl ester of sarcosine to give the aminofulvene *(78)*,
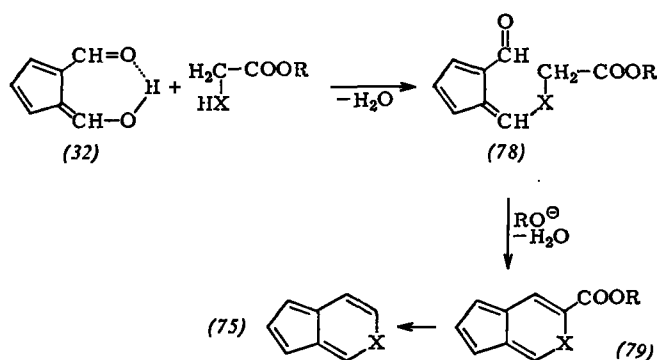
which, in the presence of basic condensing agents, subsequently undergoes intramolecular ring closure. A 76 % yield of *(79)*, where X = NCH₃ and R = C₂H₅, is thus obtained.

Dihydropyridazines

By another simple cyclic condensation, hydrazine reacts with 6-dimethylaminofulvene-2-aldehyde *(32)* or 6-hydroxyfulvene-2-aldehyde *(54)* to yield 2*H*-cyclopenta[*d*]pyridazine *(80)*, a compound previously unknown except in the form of its derivatives [39] and possessing a ring system isoelectronic with that of 5-aza-azulene. With bases, this bicyclic system easily affords an anion *(81)*, which is stabilized by cyclic conjugation

and can be isolated, for example, as its sodium salt. It reacts with alkylating agents to yield dihydropyridazine derivatives *(82)* which are alkylated at nitrogen atom 2 and which may also be obtained directly by the reaction of monosubstituted hydrazines and *(32)* or *(54)* [33].

(54)   *(32)*

$$\left[-2H_2O \right. \qquad \left. -H_2O \right] -(CH_3)_2NH$$

$$+H_2N-NH_2$$

(80)

OH⁽⁾

(81)

+RX
–X⊖

(82)
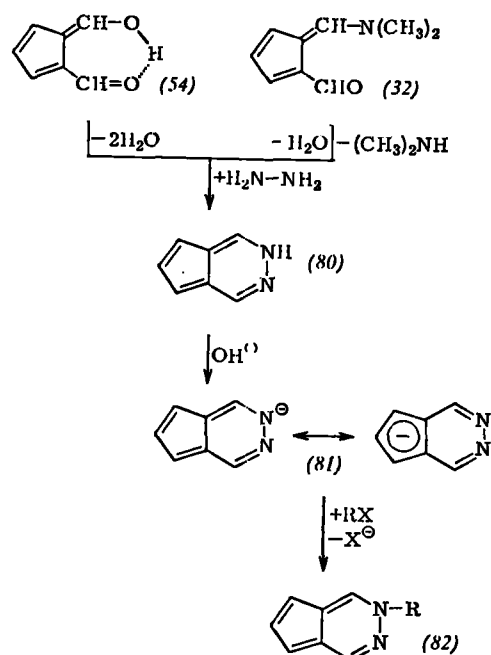
s-Indacene

Using the aminofulvenaldehyde *(32)* as the starting material, a new member of the fulvene series of non-benzenoid cyclic conjugated systems, viz. *s*-indacene *(84)* [49], was prepared. Treatment of the aldimmonium perchlorate *(31)* with cyclopentadienylsodium in tetrahydrofuran at –40 °C yields 6-[6′-dimethylamino-fulvene-2′-yl]fulvene *(83)* which undergoes rapid intramolecular ring closure, also below 0 °C, with elimination of an additional mole of dimethylamine. The hydro-

(31)   *(83)*

(85)   *(84)*

+3 Br₂

(86)

[46] *W.Treibs, W. Schroth, H.Lichtmann,* and *G.Fischer,* Liebigs Ann. Chem. *642,* 97 (1961); *W.Treibs* and *J.Beger, ibid. 652,* 192, 204, 212 (1962).

[47] *A. G. Anderson Jr., W. F. Harrison, R.G. Anderson,* and *A. G. Osborne,* J. Amer. chem. Soc. *81,* 1255 (1959); *A. G. Anderson Jr.* and *W. F. Harrison,* Tetrahedron Letters *1960,* No. 2, p. 11.
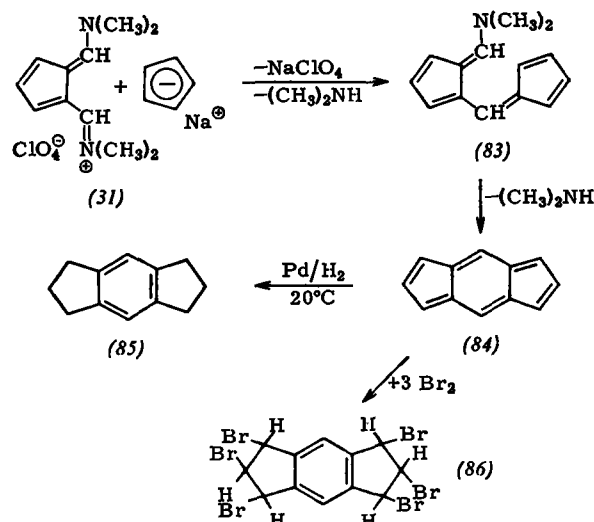
[48] *R. Mayer,* Angew. Chem. *69,* 481 (1957); *R. Mayer* and *U. Weise,* Naturwissenschaften *45,* 312 (1958).

[49] *E. Sturm,* diploma thesis, Universität München, in preparation; *R. D. Brown,* J. chem. Soc. (London) *1951,* 2391.

carbon is isolated as a red oil but has low thermal stability and is susceptible to autoxidation. On catalytic hydrogenation under mild conditions, it absorbs three moles of hydrogen to form the previously reported compound *s*-hydrindacene *(85)* [50]. Bromination of *s*-indacene to give hexabromo-*s*-hydrindacene *(86)* is also associated with a transition of the quinonoid system *(84)* to the energetically favored benzenoid system of *s*-hydrindacene *(85)*.

s-Indacene *(84)*, which is closely related to the still unreported compound pentalene [7], is a nonalternating hydrocarbon (like heptalen [51]) with twelve π-electrons. In agreement with theoretical considerations, *s*-indacene behaves more like a cyclopolyolefin than a nonbenzenoid "aromatic" system.

Conclusion

Discussions of "aromatic character" have resulted in recent years in fruitful theoretical proposals and in the synthesis of numerous nonbenzenoid cyclic conjugated

systems. Despite systematic and critical attack from both the theoretical and experimental standpoint, the concept of "aromatic character" still remains to be precisely defined. The blurred boundary between distinctly olefinic and classical "aromatic" systems makes interpretation of the phenomenon difficult, and hard and fast divisions are meaningless. Nevertheless, the cyclic conjugation, electron delocalization energy, and chemical reactivity of any given compound have proved to be useful criteria for investigation of the relationships between its constitution and "aromatic character." This has been confirmed by the results reported in the present paper. By considering the fulvenes and several carbo- and heterocyclic systems derived from them as examples, the existence of some relationships between fine structure and chemical behavior in benzenoid and nonbenzoid compounds has been indicated. Furthermore, the great variety of reactivities of cross-conjugated systems has been demonstrated.

[50] R. T. Arnold and E. Rondestvedt, J. Amer. chem. Soc. 67, 1265 (1945).
[51] H. J. Dauben and D. J. Bertelli, J. Amer. chem. Soc. 83, 4659 (1961).

Organic Derivatives of Mica-Type Layer-Silicates

BY PROF. DR. ARMIN WEISS

INSTITUT FÜR ANORGANISCHE CHEMIE DER UNIVERSITÄT HEIDELBERG (GERMANY)

Dedicated to Prof. Dr. Ulrich Hofmann on the occasion of his 60th birthday

Mica-type layer-silicates such as montmorillonite and vermiculite are capable of exchanging their cations for other (including organic) cations, just like the zeolites. These derivatives swell in a variety of liquids. This paper presents a survey of the structures of organic derivatives of mica-type layer-silicates and illustrates some possibilities for their industrial utilization.

Introduction

One-dimensional intracrystalline swelling of the clay mineral montmorillonite was discovered just thirty years ago by *U. Hofmann, Endell,* and *Wilm* [1]. Since then, the phenomenon has been repeatedly reinvestigated [2].

This intensive research on montmorillonite is due primarily to its industrial utilization as a binder for molding sand, its uses in oil well drilling and in the production of catalysts, and its importance as a model substance in swelling studies [3]. In the past ten years, organic derivatives of montmorillonite have been developed and employed in the manufacture of thixotropic lacquers, thermostable lubricants, emulsion stabilizers, etc. [4].

In mica-type layer-silicates of composition represented by the limiting formulae

[1] U. Hofmann, K. Endell, and D. Wilm, Z. Kristallogr., Mineralog. Petrogr. Abt. A 86, 340 (1933); Angew. Chem. 47, 539 (1934).
[2] In this connection, see K. Jasmund: Die Tonminerale. 2nd Edit., Verlag Chemie, Weinheim 1955; P. F. Kerr and P. K. Hamilton: Reference Clay Minerals. Amer. Petrol. Inst. Research Project 49 (1949); G. Brown: The X-Ray Identification and Crystal Structures of Clay Minerals. Mineralogical Soc., London 1961; R. C. Mackenzie: The Differential Thermal Investigations on Clays. Mineralog. Soc., London 1957; R. E. Grim: Clay Mineralogy, McGraw-Hill, London 1953; R. E. Grim: Applied Clay Mineralogy. McGraw-Hill, London 1962; M. Déribéré and A. Esme: La Bentonite. 3rd Edit., Dunod, Paris 1952.

[3] U. Hofmann, Angew. Chem. 68, 53 (1956).
[4] O. P. Müller, J. W. Jordan, and J. J. Brancato, Official Digest Federation Paint and Varnish Production Clubs No. 294, 451 (1949); E. P. Peterson and O. P. Muller, US-Patent 2531825 (1950); J. W. Jordan, US-Patent 2531440 (1950); E. A. Hauser, US-Patent 2531427 (1950); L. W. Carter, J. G. Hendricks, and D. S. Bolly, US-Patent 2531396 (1950).