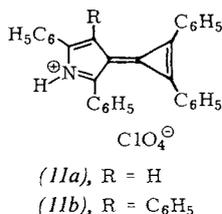
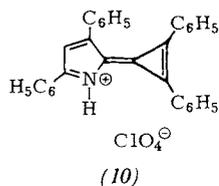
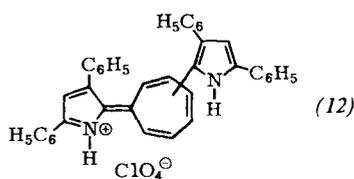


azatriafulvalenium salts (10), m.p. 222 °C (dec.); $\lambda_{\text{max}}^{\text{CH}_3\text{CN}} = 390 \text{ nm}$, $\log \epsilon = 4.70$; $\nu_{\text{C}=\text{C}} = 1835 \text{ cm}^{-1}$, (11a), m.p. 235 °C (dec.); $\lambda_{\text{max}}^{\text{CH}_3\text{CN}} = 372 \text{ nm}$, $\log \epsilon = 4.18$; $\nu_{\text{C}=\text{C}} = 1840 \text{ cm}^{-1}$, and (11b), m.p. 205 °C (dec.); $\lambda_{\text{max}}^{\text{CH}_3\text{CN}} = 362 \text{ nm}$ (shoulder), $\log \epsilon = 4.09$, $\nu_{\text{C}=\text{C}} = 1825 \text{ cm}^{-1}$, are obtained in yields of 79, 50, and 59% respectively. They are deprotonated to give the



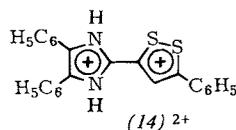
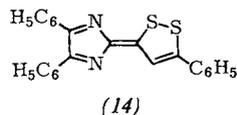
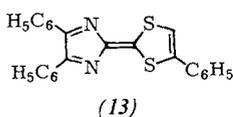
azacalicyenes (10') [$\lambda_{\text{max}}^{\text{CH}_3\text{CN}} = 384 \text{ nm}$, $\log \epsilon = 4.63$; $\nu_{\text{C}=\text{C}} = 1835 \text{ cm}^{-1}$], (11a') [unstable red oil], and (11b') [dark red solution]; (10) and (11a) by Hünig base in methylene chloride, (11b) by potassium *tert*-butoxide.

The action of tropylium perchlorate on 2,4-diphenylpyrrole under various conditions always gives a 1:2 adduct in a yield of about 15%. This adduct can be isolated as the perchlorate (12), m.p. 282 °C (dec.); $\lambda_{\text{max}}^{\text{CH}_3\text{CN}} = 554 \text{ nm}$, $\log \epsilon = 4.83$. The free base is obtained from (12) with Hünig base (m.p. 279 °C; $\lambda_{\text{max}}^{\text{CH}_3\text{CN}} = 520 \text{ nm}$, $\log \epsilon = 4.67$). Compound (12) gives a red-violet anion with potassium *tert*-butoxide.



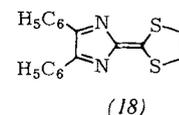
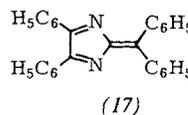
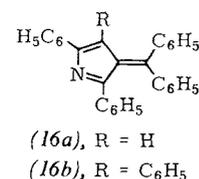
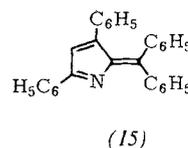
Benzoheterofulvalenes are obtained by reaction of pyrroles and indoles with the benzo-derivatives of the cations (1)–(3).

The Na salt of 4,5-diphenylimidazole, which is prepared by heating diphenylimidazole with NaH in benzene in the presence of a little diglyme, reacts surprisingly smoothly with (1) and (2) in boiling benzene to form the diazadithiafulvalenes (13) (red needles, m.p. 210 °C, yield 35%) and (14) (m.p. 205 °C; $\lambda_{\text{max}}^{\text{CH}_3\text{CN}} = 565 \text{ nm}$, $\log \epsilon = 4.60$; yield 49%). (14) forms a perchlorate [m.p. 280 °C (dec.); $\lambda_{\text{max}}^{\text{CH}_3\text{CN}} = 520 \text{ nm}$, $\log \epsilon = 4.57$]; reaction with an excess of perchloric



acid gives the dication (14)²⁺ ($\lambda_{\text{max}}^{\text{CH}_3\text{CN}-\text{HClO}_4} = 460 \text{ nm}$, $\log \epsilon = 4.40$). Compound (13) behaves in a similar manner.

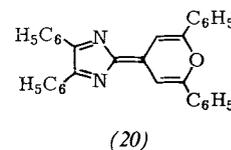
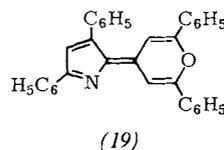
Di- and triphenylpyrroles react with benzophenone dichloride in acetonitrile at room temperature to give the azafulvenes (15) and (16), which are isolated as the perchlorates and are deprotonated with Hünig base. In the presence of two equivalents of NaH, 4,5-diphenylimidazole reacts with benzophenone dichloride in boiling benzene to give the tetraphenyldiazafulvene (17), which has already been synthesized by another route^[3], and with 2-methylthio-1,3-dithiolanylium methyl sulfate to form the 6,6-dithiodiazafulvene (18).



| Compound [a] | Yield (%) | M.p. (°C) | λ_{max} [b] (nm) | $\log \epsilon$ |
|---------------------|-----------|-----------|---------------------------------|-----------------|
| (15) | | | 380 | 4.20 |
| (15 ⁺) | 62 | 265 [c] | 300–500 [d] | |
| (16a) | | 187 | 466 | 3.60 |
| | | | 347 | 4.12 |
| (16a ⁺) | 80 | 226 [c] | 550 | 3.76 |
| | | | 374 | 4.21 |
| (16b) | 55 | 208 | 300–450 [d] | ca. 4 |
| (17) | 30 | 174 | 410 | 4.52 |
| (18) | 30 | 235 | | |

[a] (X⁺) = perchlorate. [b] In acetonitrile. [c] With decomposition. [d] Broad band.

2,4-Diphenylpyrrole can be converted into the O analog (19) of a sesquifulvalene [m.p. 173 °C; $\lambda_{\text{max}}^{\text{CH}_3\text{CN}} = 490 \text{ nm}$, $\log \epsilon = 4.64$; yield 69%]. Perchlorate: m.p. 306 °C (dec.); $\lambda_{\text{max}}^{\text{CH}_3\text{CN}} = 499 \text{ nm}$, $\log \epsilon = 4.78$] by heating in benzene with 4-methylthio-2,6-diphenylpyrylium perchlorate in the presence of one



equivalent of NaH. (20) is obtained in the same way from 4,5-diphenylimidazole [m.p. = 227–228 °C; $\lambda_{\text{max}}^{\text{CH}_3\text{CN}} = 550$, 518 nm. Perchlorate: m.p. 277 °C (dec.); $\lambda_{\text{max}}^{\text{CH}_3\text{CN}} = 507 \text{ nm}$. Dication: $\lambda_{\text{max}}^{\text{CH}_3\text{CN}-\text{HClO}_4} = 450 \text{ nm}$].

Received: January 22, 1968 [Z 715 1E]
German version: Angew. Chem. 80, 277 (1968)

[*] Prof. Dr. R. Gompper and Dipl.-Chem. R. Weiss
Institut für Organische Chemie der Universität
8 München 2, Karlstr. 23 (Germany)

[1] R. Gompper and E. Kutter, Chem. Ber. 98, 1365 (1965).

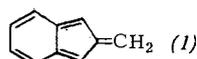
[2] Cf. W. Rohr and H. A. Staab, Angew. Chem. 77, 1077 (1965); Angew. Chem. internat. Edit. 4, 1073 (1965); U. Mayer, H. Baumgärtel, and H. Zimmermann, Angew. Chem. 78, 303 (1966); Angew. Chem. internat. Edit. 5, 311 (1966); Tetrahedron Letters 1966, 5221; H. Behringer and U. Türck, Chem. Ber. 99, 1815 (1966).

[3] J. H. M. Hill, J. org. Chemistry 32, 3214 (1967).

Isobenzofulvenes

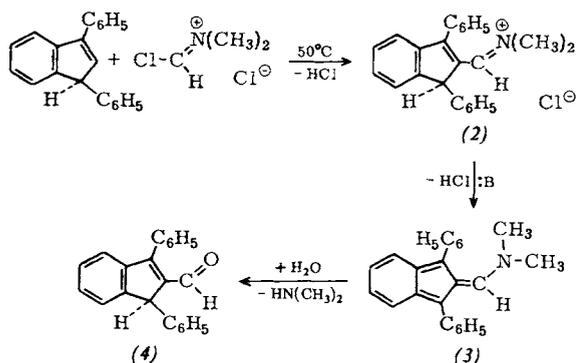
By K. Hafner and W. Bauer[*]

The hitherto unknown isobenzofulvenes (benzo[c]fulvenes) are of interest as being isosteric with isobenzofuran, isobenzothiophene, and isoindole, as well as with the still hypothetical nonafulvenes (cyclononatetraenefulvenes). Like fulvene, isobenzofulvene (1) should be stabilized by electron donors on the exocyclic C atom^[1].

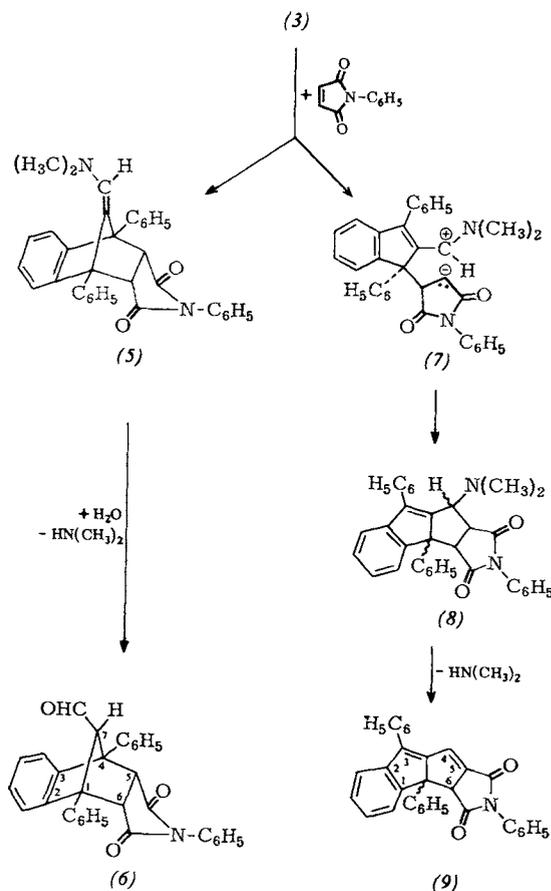


We have been able to confirm this assumption by the synthesis of *N,N*-dimethyl-*N*-(1,3-diphenyl-2-indenylidene-methyl)amine (3) [2].

1,3-Diphenylindene [3] reacts with chloromethylenedimethyliminium chloride in chloroform at 50 °C (about 8 days) to form *N,N*-dimethyl-*N*-(1,3-diphenyl-2-indenylmethylene)iminium chloride (2) in 83 % yield [light yellow crystals, dec. p. > 75 °C; UV spectrum in CH₂Cl₂: λ_{max} = 248 nm (ε = 9800), 270 (3200), 328 (11000), 379 (15400)]. The reaction of a suspension of (2) in ether/tetrahydrofuran (1:1) with diisopropylethylamine at -35 °C gives a deep blue solution. Removal of the solvent in a high vacuum gives (3) as dark blue, shiny prisms having m.p. 145–147 °C (from ether) [yield: 82 %; UV spectrum in tetrahydrofuran: λ_{max} = 250 nm (ε = 14900), 260 (14900), 339 (24800), 403 (26500), 593 (3540)]. The NMR spectrum (in CDCl₃ at 37 °C), which proves the structure of (3), contains a singlet at τ = 2.01 (arising from the proton on the exocyclic C atom) and a multiplet centered at τ = 2.63 for the ten phenyl protons and the four protons of the fused benzene ring, as well as two singlets at τ = 6.89 and 7.36 for the two methyl groups of the tertiary amino group; in the NMR spectrum of (3) at 59 °C, the two signals combine to give one broad singlet at τ = 7.12.



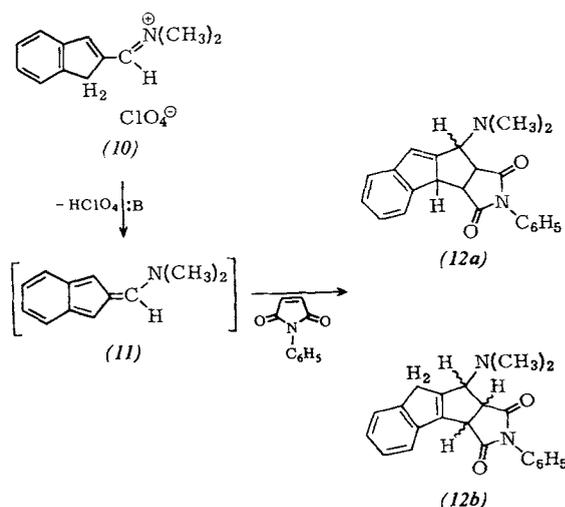
The mass spectrum of (3), in addition to the molecular ion at *m/e* = 323, contains characteristic decomposition products at *m/e* = 246 (M⁺-C₆H₅), 279 (M⁺-N(CH₃)₂), 308 (M⁺-CH₃) [4]. While (3) is stable by itself for a long time at room temperature in the absence of air, solutions of (3) in inert, aprotic solvents react rapidly with atmospheric oxygen to form a yellow resin; in the presence of water, (3) is hydrolyzed to 1,3-diphenylindene-2-carbaldehyde (4) [yield: 88 %; pale yellow prisms having m.p. 94–96 °C; UV spectrum in *n*-hexane: λ_{max} = 234 nm (ε = 18700), 239 (18500), 260 (8250), 265 (8100), 270 (7900), 307 (13500); NMR spectrum in CDCl₃: singlet at τ = 0.14 (CHO), multiplet centered at τ = 2.65 (aromatic protons), singlet at τ = 5.0 (H-1)]. Compound (3) combines with *N*-phenylmaleimide at 0 °C in ether/tetrahydrofuran (1:1) to form a green-yellow mixture, from which the products (6) [m.p. 238–240 °C; UV spectrum in dioxane: λ_{max} = 258 nm (ε = 1295), 264 (1015), 301 (75); NMR spectrum in CDCl₃: doublet at τ = 0.59 (*J* = 1.3 Hz) (CHO), multiplets centered at τ = 2.10 (four protons of the fused benzene ring) and at τ = 3.0 (15 aromatic protons of the three phenyl groups), singlet at τ = 5.39 (H-5, H-6), doublet at τ = 5.81 (*J* = 1.3 Hz) (H-7)] and (9) [m.p. 205–207 °C; UV spectrum in dioxane: λ_{max} = 222 nm (ε = 28400), 254 (22700), 375 (15800); NMR spectrum in CDCl₃: multiplet centered at τ = 2.47 (19 aromatic protons and H-4), doublet at τ = 6.0 (*J* = 2.6 Hz, allyl coupling, H-6)] formed by hydrolysis and by elimination of dimethylamine from the initially formed 1:1 adducts (5) and (8) could be separated by thin layer chromatography [silica gel PF₂₅₄, CCl₄-cyclohexane-isopropanol (30:30:1)].



The existing data are insufficient for a decision as to whether the compound (6) is the *exo* or the *endo* isomer. By analogy with the formation of corresponding Diels-Alder adducts of *N*-substituted isoindoles [5], the *endo* adduct (5) or its further reaction product (6) is probably formed first in the reaction of (3).

The 1,3-cycloaddition to form (8) that accompanies the Diels-Alder reaction of (3) with *N*-phenylmaleimide probably proceeds by a two-step mechanism. A primary Michael addition with formation of the dipolar intermediate (7) is followed by the intramolecular cyclization of (7) to form the adduct (8), which is stabilized by loss of dimethylamine to form (9). A synchronous *cis* addition (1,3-dipolar cycloaddition) with formation of (8) [6] is incompatible with the Hoffmann-Woodward rules [7].

N,N-Dimethyl-*N*-(2-indenylmethylene)iminium perchlorate (10) [8] reacts with diisopropylethylamine in the same way as



the aldiminium salt (2), with deprotonation. The expected *N,N*-dimethyl-*N*-(2-indenylidene)methyl)amine (11) has not yet been isolated as such, because of its low thermal stability.

Compound (11), which is yellow-brown in solution (UV spectrum in CH_2Cl_2 : $\lambda_{\text{max}} = 364, 376 \text{ nm}$) reacts with *N*-phenylmaleimide at -40°C to give a colorless 1:1 adduct having m.p. $215\text{--}216^\circ\text{C}$. The UV spectrum (in *n*-hexane) [$\lambda_{\text{max}} = 211 \text{ nm}$ ($\epsilon = 28000$), 217 (26000), 223 (23200), 258 (10100), 262 (9940), 267 (9000), 280 (3000), 286 (1100)] corresponds to that of an equimolar mixture of *N,N*-dimethyl-*N*-(2-indenylmethyl)amine and *N*-phenylsuccinimide, and so points to the formation of a 1,3 adduct having the constitution (12a) or (12b); the NMR spectrum (in CDCl_3) of the adduct [multiplets centered at $\tau = 2.55$ (9 H), 5.80 (3 H), 6.64 (2 H), and a singlet at $\tau = 7.68$ (6 H)] is in agreement with a mixture of epimers of (12b).

Received: January 26, 1968 [Z 716 IE]
German version: Angew. Chem. 80, 312 (1968)

[*] Prof. Dr. K. Hafner and Dipl.-Chem. W. Bauer
Institut für Organische Chemie der Technischen Hochschule
61 Darmstadt, Schlossgartenstr. 2 (Germany)

[1] K. Hafner, K. H. Häfner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm, and K. H. Vöpel, Angew. Chem. 75, 35 (1963); Angew. Chem. internat. Edit. 2, 123 (1963); K. Hafner, K. H. Vöpel, G. Ploss, and C. König, Liebigs Ann. Chem. 661, 52 (1963); K. Hafner, G. Schulz, and K. Wagner, Liebigs Ann. Chem. 678, 39 (1964); a quantum-chemical calculation of (1) has been carried out by A. J. Sadlej, Acta phys. Polon. 27, 859 (1965).

[2] The compound (3) is based on 1,3-diphenyl-2*H*-indene, whose 2,2-dimethyl derivative was prepared by K. Alder and M. Fremery, Tetrahedron 14, 190 (1961).

[3] K. Ziegler, K. Richter, and B. Schnell, Liebigs Ann. Chem. 443, 161 (1925).

[4] We are grateful to Dr. D. Jung for recording and discussing the NMR spectra, and to Dr. N. Neuner-Jehle for the mass-spectroscopic examination of (3).

[5] R. Kreher and J. Seubert, Angew. Chem. 78, 984 (1966); Angew. Chem. internat. Edit. 5, 967 (1966).

[6] R. Huisgen, Angew. Chem. 75, 742 (1963); Angew. Chem. internat. Edit. 2, 633 (1963).

[7] R. Hoffmann and R. B. Woodward, J. Amer. chem. Soc. 87, 4388 (1965), and earlier communications.

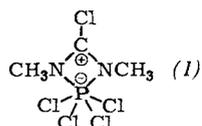
[8] Z. Arnold, Coll. czechoslov. chem. Commun. 30, 2783 (1965); (10) can be isolated in a yield of about 50% as an intermediate in the Vilsmeier formylation of indene.

A Four-Membered Ring System Containing Hexacoordinated Phosphorus

By H. P. Latscha and P. B. Hormuth[*]

The reaction of *N,N'*-dimethylurea with phosphorus pentachloride (PCl_5)^[1] in an inert solvent leads to the formation of a substance having the composition $\text{C}_3\text{H}_6\text{Cl}_5\text{N}_2\text{P}$. The compound is white, very sensitive to moisture, and melts at 129°C after recrystallization from cyclohexane.

The ^1H -NMR spectrum in benzene against TMS as internal standard shows six equivalent methyl protons ($\delta = 2.67 \text{ ppm}$, $J_{\text{PH}} = 20.8 \text{ Hz}$). The ^{31}P -NMR spectrum contains a signal at $202 \pm 1 \text{ ppm}$ (based on 85% H_3PO_4 as external standard), $J_{\text{PH}} = 20 \pm 1 \text{ Hz}$. This indicates a phosphorus atom having a coordination number of 6^[2], and together with the elemental analysis, molecular weight, and IR spectrum, points to a 2,2,2,2,4-pentachloro-1,3-dimethyl-1,3-diaza-2-phosphonia^{VI}-cyclobutane (1).



Procedure:

1. For the preparation of *N,N'*-dimethylchloroformamidine hydrochloride see reference^[1].

2. *N,N'*-Dimethylchloroformamidine hydrochloride is refluxed for five hours with PCl_5 (molar ratio 1:1) in CCl_4 . The crude, slightly greenish product crystallizes out on concentration of the reaction solution. Recrystallization from anhydrous cyclohexane gives white crystals having m.p. 129°C . The yield is almost quantitative.

Received: November 28, 1967 and February 12, 1968 [Z 717 IE]
German version: Angew. Chem. 80, 281 (1968)

[*] Dr. H. P. Latscha and P. B. Hormuth
Anorganisch-Chemisches Institut der Universität
69 Heidelberg, Tiergartenstr. (Germany)

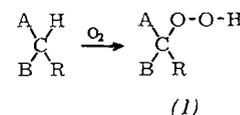
[1] H. Ulrich and A. A. R. Sayigh, Angew. Chem. 76, 647 (1964); Angew. Chem. internat. Edit. 3, 585 (1964).

[2] H. P. Latscha, Z. Naturforsch., in press.

Autoxidation of Dimedone Derivatives

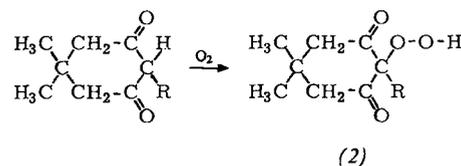
By H. Brederbeck, R. Franz, and G. Bauer[*]

Hydroperoxides have until now been assumed to occur as intermediates in the initiation of the radical polymerization of vinyl monomers by means of CH-active compounds, atmospheric oxygen, Cu^{2+} , and Cl^- ^[1-3]. We have now



A and B = electron-withdrawing groups, R = H, alkyl

established their formation when dimedone derivatives are used as CH-active compounds. Dimedone hydroperoxides (2) were prepared for the first time by oxidation of dimedones with oxygen in benzene at room temperature.



| (2), R = | Reaction time (h) | Crude yield (%) | M.p. ($^\circ\text{C}$) |
|-----------------------------------|-------------------|-----------------|---------------------------|
| CH_3 | 12 | 40-50 | 55 (decomp.) |
| C_2H_5 | 12 | 35 | 81 (decomp.) |
| <i>i</i> - C_3H_7 | 12 | 40 | 116 (decomp.) |
| <i>i</i> - C_4H_9 | 15 | 30 | 90 (decomp.) |
| $\text{C}_6\text{H}_5\text{CH}_2$ | 2 | 70 | 119 (decomp.) |

The hydroperoxides form colorless crystals that cannot be stored for long periods. They were identified by elemental analysis, iodometric titration, their reaction with lead tetraacetate, and their IR and NMR spectra.

The hydroperoxides that we have assumed to be formed during polymerization can decompose either thermally or on reaction with the cocatalysts Cu^{2+} and Cl^- ^[3,4]. For this reason we were able to isolate the hydroperoxides formed on autoxidation of dimedone derivatives only in the absence of these cocatalysts. In the case of benzyl dimedone, however, we obtained the hydroperoxide also in the presence of Cu^{2+} and Cl^- because the extremely low solubility of the substance caused its immediate precipitation.