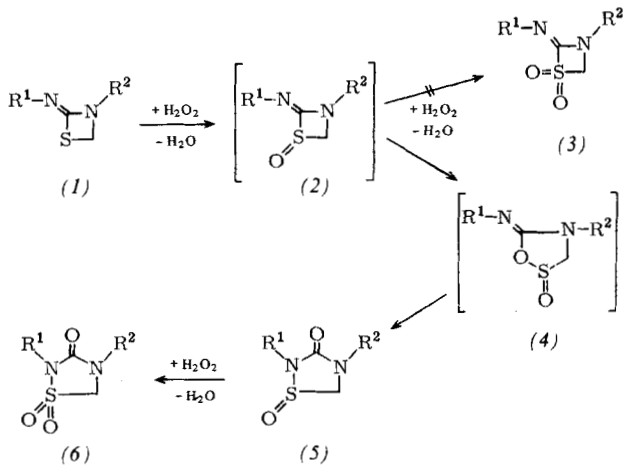

Table 1. Data for compounds *(5)* and *(6)*. Correct analyses were obtained for all compounds.

	R^1	R^2	*(5)* Yield [%]	M.p. [°C]	IR [a] [cm^{-1}]	^{1}H-NMR [b, c] [δ, ppm] q	*(6)* Yield [%]	M.p. [°C]	IR [d] [cm^{-1}]	^{1}H-NMR [b] [δ, ppm] s
(a)	$CH(CH_3)_2$	C_6H_5	72	86	1690, 1089	4.45	35	111.5	1707, 1161	4.70
(b)	CH_3	C_6H_5	34	166	1694, 1080	4.48	31	137 (dec.)	1715, 1159	4.79
(c)	$C_6H_5CH_2$	C_6H_5	53	143	1692, 1098	4.44				
(d)	o-$CH_3C_6H_4CH_2$	C_6H_5	60	107.5	1700, 1099	4.45	13	108.5	1725, 1152	4.80
(e)	C_6H_5	C_6H_5	46	140	1700, 1105	4.62	11	120.5 (dec.)	1725, 1159	4.95
(f)	C_6H_5	p-$NO_2C_6H_4$	46	168	1725, 1092	4.73	10	254 (dec.)	1740, 1148	5.00

[a] νC=O and νS=O in KBr.
[b] Methylene groups in the heterocycle relative to HDMSO as internal standard, in $CDCl_3$.
[c] $J_{AB} = 11.0$ Hz.
[d] νC=O and νSO_2 in KBr.

A solution of *(5)* (2 mmol) in glacial acetic acid (50 ml) is treated with 1.2 equivalents of hydrogen peroxide (35% aqueous solution) and allowed to stand for 4 weeks at room temperature. The solution is evaporated under vacuum, and compound *(6)* isolated from the residue by column chromatography on silica gel (eluant: benzene/ethyl acetate 4:1). Recrystallization from ethanol affords *(6)* as white crystals.

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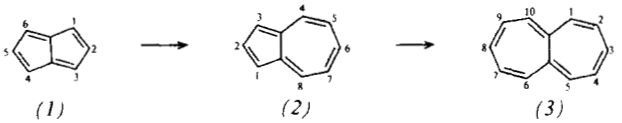
(1a), 58151-15-8; *(1b)*, 58151-16-9; *(1c)*, 50500-04-4; *(1d)*, 58151-17-0; *(1e)*, 50500-03-3; *(1f)*, 58151-18-1; *(5a)*, 58151-04-5; *(5b)*, 58151-05-6; *(5c)*, 58151-06-7; *(5d)*, 58151-07-8; *(5e)*, 58151-08-9; *(5f)*, 58151-09-0; *(6a)*, 58151-10-3; *(6b)*, 58151-11-4; *(6d)*, 58151-12-5; *(6e)*, 58151-13-6; *(6f)*, 58151-14-7

[1] *W. Ried, W. Merkel*, and *O. Mösinger*, Justus Liebigs Ann. Chem. *1973*, 1362.
[2] *W. Ried* and *O. Mösinger*, to be published.
[3] *W. Schuckmann, O. Mösinger*, and *W. Ried*, to be published.
[4] *T. Kinoshita, S. Sato, Y. Furukawa*, and *C. Tamura*, Heterocycles *3*, 1, 83 (1975).
[5] *B. A. Arbuzov, N. N. Zobova*, and *N. R. Rubinova*, Izv. Akad. Nauk SSSR, Ser. Khim. *1975*, 1438.

Cycloadditions of Pentalene and Azulene—A Facile Heptalene Synthesis[**]

By *Klaus Hafner, Herbert Diehl*, and *Hans Ulrich Süss*[*]

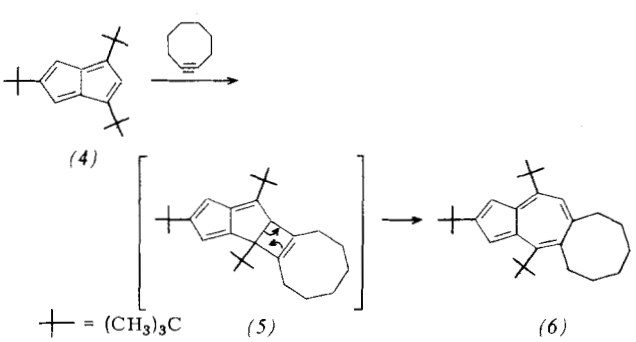
The two lowest homologs of the annulene series, *i.e.* cyclobutadiene and benzene, are known to undergo either thermally or photochemically induced [2+4] and [2+2] cycloadditions with reactive alkynes to give cyclobutene derivatives. Valence isomerization of the latter affords the next higher vinylogous annulene, *i.e.* benzene and cyclooctatetraene respectively[1,2]. A similar transformation should also be feasible



(1) *(2)* *(3)*

in the homologous series of nonalternant bicyclic hydrocarbons pentalene *(1)*, azulene *(2)*, and heptalene *(3)*, which differ from each other by possessing one additional vinylene group each, and thus provide new entries to these ring systems. Studies on transformations of cyclopent[*cd*]azulene[3], 1,3-bis-(dimethylamino)pentalene[4], and hexaphenylpentalene[5] with dimethyl acetylenedicarboxylate into derivatives of aceheptylene and azulene prompted us to investigate the ring expansion of *(1)* to *(2)* and above all that of *(2)* to *(3)*. In the course of this work we discovered a surprisingly simple and universal synthesis of stable heptalene derivatives.

Conversion of *pentalene* into *azulene:* As expected, *(4)*[6] which is the simplest pentalene derivative hitherto isolated, rapidly reacts with activated alkynes and especially with the highly strained cyclooctyne at 270 °C (presumably *via* intermediate formation of the cyclobutene derivative *(5)*) to give a 70% yield of 2,4,12-tri-*tert*-butyl-5,6,7,8,9,10-hexahydrocycloocta[*f*]azulene *(6)* (blue radial needles, m.p. 70—72 °C)[7].



(4) *(5)* *(6)*

Exclusive formation of *(6)* even at high temperatures indicates on the one hand the lack of tendency of dimerization of *(4)*, in contrast to pentalene and its methyl derivatives[8] and on the other the marked effect of substituents upon product formation. As in the dimerization of 2-methylpentalene[8] and 1,5-dimethylpentalene[9], cycloaddition in the five-membered ring of *(4)* bearing an alkyl group in position 2 (≡5) is hindered—mostly for obvious steric reasons.

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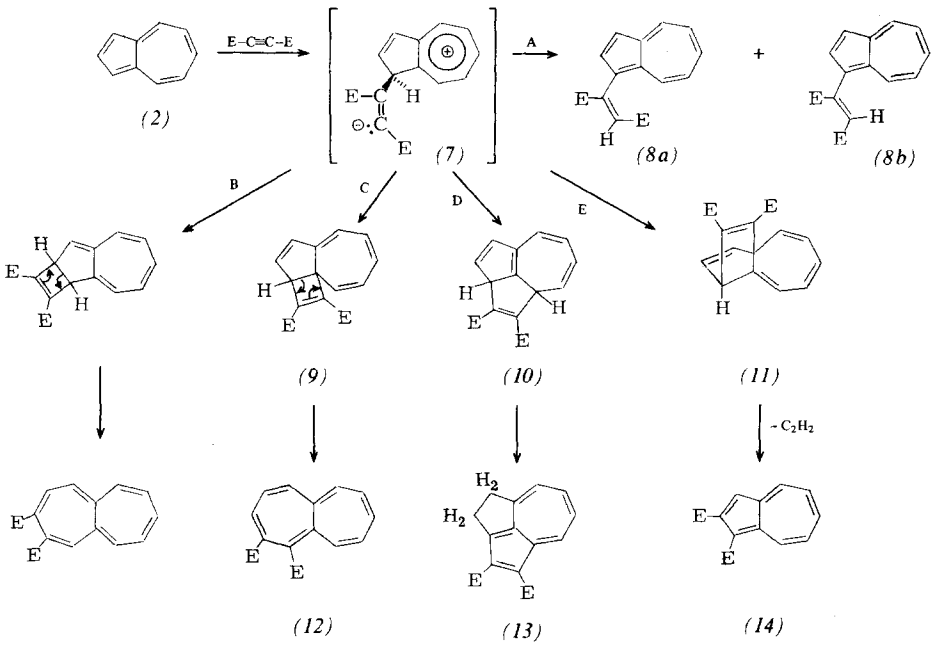
[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Conversion of *azulene* into *heptalene*: According to an observation by *W. Treibs*[10], azulene *(2)* reacts with acetylenedicarboxylic acid and its esters at elevated temperature and especially in the presence of Lewis acids *via* additive substitution to give 1-azulenylmaleic acid and its esters of type *(8b)*, the resonance stabilized dipolar intermediate *(7)* probably being formed first. It was expected that this intermediate can stabilize basically not only by re-aromatization of the azulene system to give *(8)* but also initially by formation



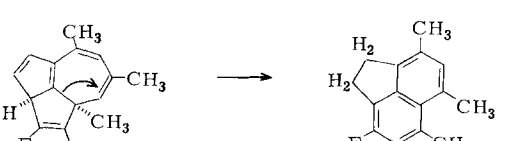
(2) *(7)* *(8a)* *(8b)* *(9)* *(10)* *(11)* *(12)* *(13)* *(14)*

of one or several cycloadducts *(9)*—*(11)*. We suspected that *(8)* is formed preferentially in the presence of proton donors or reagents promoting a proton shift, while in their absence the paths B-E may also play a role. Our experiments did confirm these expectations.

Reaction of *(2)* with dimethyl acetylenedicarboxylate in boiling tetralin in the presence of 5% trifluoroacetic acid (1 h) affords 35% of a 1:1 mixture of dimethyl 1-azulenylfumarate *(8a)* and 1-azulenylmaleate *(8b)* (olive green oil)[11] (path A). In contrast, the same reaction of *(2)* without trifluoroacetic acid added does not afford *(8)* but rather 15% of the thermally and air-stable dimethyl 1,2-heptalenedicarboxylate *(12)* [red leaflets, m.p. 114—115 °C; UV (*n*-hexane): $\lambda_{max}=204$ ($\log\varepsilon=4.36$), 266 (4.29), 337 (3.63); 60 MHz ^{1}H-NMR ([D_6]acetone): $\tau=2.73$ (d, $J=7$ Hz, H-3); 3.30—4.30 (m, 7H), 6.29 and 6.36 (s, $2COOCH_3$)] together with 1% of dimethyl 3,4-dihydro-1,2-cyclopent[*cd*]azulenedicarboxylate *(13)* (violet crystals, m.p. 138—139 °C) and 1% of dimethyl 1,2-azulenedicarboxylate *(14)* (reddish violet crystals, m.p. 49—50 °C)[12]. *(12)*—*(14)* can easily be separated by column chromatography [Al_2O_3; *n*-hexane/ether (5:1)] on account of their different R_f values and colors.

In accord with our assumption, the heptalene derivative *(12)* should result from valence isomerization of *(9)* (path C), the tricyclic species *(13)* from rearomatization of the primary adduct *(10)* to the azulenoid system (path D), and *(14)* from a cycloreversion of the adduct *(11)* with elimination of acetylene (path E). Formation of *(14)* formally resembles the [2+8] cycloaddition of heptafulvene with dimethyl acetylenedicarboxylate, which has already been observed by *Doering et al.*[12] and leads to the same azulene derivative. The surprisingly simple formation of *(12)* from *(2)*, which is also available in larger quantities, provides a convenient preparative entry to numerous derivatives of the heptalene system. That system has hardly been studied and was hitherto only accessible in very low overall yields[13]; its stabilization by two ester groups in positions 1 and 2 corresponds to that of the 3,8-heptalenedicarboxylic ester recently described by *Vogel et al.*[13b]. The spectroscopic properties of *(12)* are in agreement with the nonplanar structure of the bicyclic system, established by X-ray structure analysis[14].

Similarly to *(2)*, alkylated azulenes react with dimethyl acetylenedicarboxylate to form corresponding alkyl derivatives of *(8)*, *(12)*, *(13)*, and *(14)*. Thus the analogous reaction of 4,6,8-trimethylazulene in the presence of 5% trifluoroacetic acid yields 25% each of dimethyl 4,6,8-trimethyl-1-azulenylfumarate (violet crystals, m.p. 106—107 °C) and -maleate (violet crystals, m.p. 109—110 °C) (path A), and 5% of dimethyl 4,6,8-trimethyl-1,2-azulenedicarboxylate (reddish violet crystals, m.p. 138—139 °C) (path E). In contrast, the same reaction in the absence of protic acids leads to 45% of a mixture of thermally stable dimethyl 6,8,10-trimethyl-2,3- and 1,2-heptalenedicarboxylate[11] in the ratio 1:2.5 (paths B and C)



(15) *(16)*

besides 5% of dimethyl 4,6,8-trimethyl-1,2-azulenedicarboxylate (path E) and 4% of dimethyl 5,6,8-trimethyl-3,4-acenaphthylenedicarboxylate *(16)* (yellowish needles, m.p. 179—181 °C) arising from skeletal rearrangement and by hydrogen shift from the adduct *(15)* analogous to *(10)* (path D).

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(1), 250-25-9; *(2)*, 275-51-4; *(3)*, 257-24-9; *(4)*, 50356-52-0; *(5)*, 58150-89-3; *(6)*, 58150-90-6; *(8a)*, 58150-91-7; *(8b)*, 58150-92-8; *(9)*, 58150-93-9; *(10)*, 58150-94-0; *(11)*, 58150-95-1; *(12)*, 58150-88-2; *(13)*, 58150-96-2; *(14)*,

39479-45-3; *(15)*, 58150-97-3; *(16)*, 58150-98-4; cyclooctyne, 1781-78-8; dimethyl acetylenedicarboxylate, 762-42-5; 4,6,8-trimethylazulene, 941-81-1; dimethyl (4,6,8-trimethyl-1-azulenyl)fumarate, 58150-99-5; dimethyl (4,6,8-trimethyl-1-azulenyl)maleate, 58151-00-1; dimethyl 4,6,8-trimethyl-1,2-azulenedicarboxylate, 58151-01-2; dimethyl 6,8,10-trimethyl-2,3-heptalenedicarboxylate, 58151-02-3; dimethyl 6,8,10-trimethyl-1,2-heptalenedicarboxylate, 58151-03-4

[1] *L. Watts, J. D. Fitzpatrick*, and *R. Pettit*, J. Am. Chem. Soc. *87*, 3253 (1965); *G. Maier*, Angew. Chem. *86*, 491 (1974); Angew. Chem. Int. Ed. Engl. *13*, 425 (1974).

[2] *D. Bryce-Smith, A. Gilbert*, and *J. Grzonka*, Chem. Commun. *1970*, 498.

[3] *K. Hafner* and *R. Fleischer*, Angew. Chem. *82*, 217 (1970); Angew. Chem. Int. Ed. Engl. *9*, 247 (1970); *H. Diehl* and *K. Hafner*, Angew. Chem. *88*, 124 (1976); Angew. Chem. Int. Ed. Engl. *15*, 107 (1976).

[4] *K. Hafner*, Pure Appl. Chem. *28*, 153 (1971).

[5] *E. LeGoff*, J. Am. Chem. Soc. *84*, 3975 (1962).

[6] *K. Hafner* and *H. U. Süss*, Angew. Chem. *85*, 626 (1973); Angew. Chem. Int. Ed. Engl. *12*, 575 (1973).

[7] Correct elemental analyses and UV, NMR, and MS spectra were obtained for all substances not described in detail.

[8] *R. Bloch, R. A. Marty*, and *P. deMayo*, Bull. Soc. Chim. Fr. *1972*, 2031; *K. Hafner, R. Dönges, E. Goedecke*, and *R. Kaiser*, Angew. Chem. *85*, 362 (1973); Angew. Chem. Int. Ed. Engl. *12*, 337 (1973).

[9] *R. Dönges*, Dissertation, Technische Hochschule Darmstadt 1976.

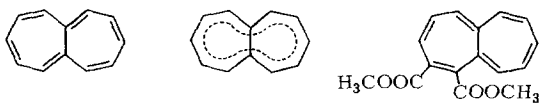
[10] *W. Treibs*, Naturwissenschaften *52*, 452 (1965).

[11] The isomeric mixture could be identified by analysis and NMR spectroscopy but not separated by chromatography.

[12] *W. v. E. Doering* and *W. W. Wiley*, Tetrahedron *11*, 183 (1960).

[13] a) *H. J. Dauben* and *D. J. Bertelli*, J. Am. Chem. Soc. *83*, 4659 (1961); *E. Vogel, H. Königshofen, J. Wassen, K. Müllen*, and *J. F. M. Oth*, Angew. Chem. *86*, 777 (1974); Angew. Chem. Int. Ed. Engl. *13*, 732 (1974); *E. Vogel* and *J. Ippen*, Angew. Chem. *86*, 778 (1974); Angew. Chem. Int. Ed. Engl. *13*, 734 (1974); b) *E. Vogel* and *F. Hogrefe*, Angew. Chem. *86*, 779 (1974); Angew. Chem. Int. Ed. Engl. *13*, 735 (1974).

[14] *H. J. Lindner* and *B. Kitschke*, Angew. Chem. *88*, 123 (1976); Angew. Chem. Int. Ed. Engl. *15*, 106 (1976).



(1a) *(1b)* *(2)*

the bicyclic system from the ^{1}H-NMR spectrum of heptalene[2]. *Vogel, Oth, et al.* synthesized heptalene and stabilized heptalenes, and found heptalene to undergo a fast π-bond shift with an activation energy of 14.7 kJ mol^{-1}[3].

We have performed an X-ray structure analysis on dimethyl 1,2-heptalenedicarboxylate *(2)*[4] which is stabilized by ester groups and has been synthesized by *Hafner* and *Diehl*. Compound *(2)* forms monoclinic red leaflets of m. p. 114—115 °C; $a = 1242 \pm 1$, $b = 818 \pm 1$, $c = 1396 \pm 1$ pm, $\beta = 105.14 \pm 0.05°$, $V_{UC} = 1370 \times 10^6$ pm^3, $Z = 4$, $d_{X\text{-ray}} = 1.310$ g cm^{-3}, $d_{exp} = 1.315$ g cm^{-3}, space group $P2_1/a$.

2160 reflections *hkl* ($0 \le k \le 6$) have been measured with $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å) on a two-circle diffractometer. The structure was solved and refined ($R = 0.098$) with the program system of *Sheldrick*[5].

The heptalene system in *(2)* (Fig. 1a) consists of two boat-shaped seven-membered rings with structural angles of $\alpha = 36.8°$, $\beta = 22.0°$ (substituted ring) and $\alpha = 37.3°$, $\beta = 22.7°$. Although smaller than in other seven-membered rings with three localized double bonds[6], these structural angles nevertheless lead to pronounced deformation of the bicyclic system. The ester groups are twisted by 30° (position 1) and 25° (position 2) relative to the ring. They are arranged in such a way that the slightest mutual approach will lead to maximal

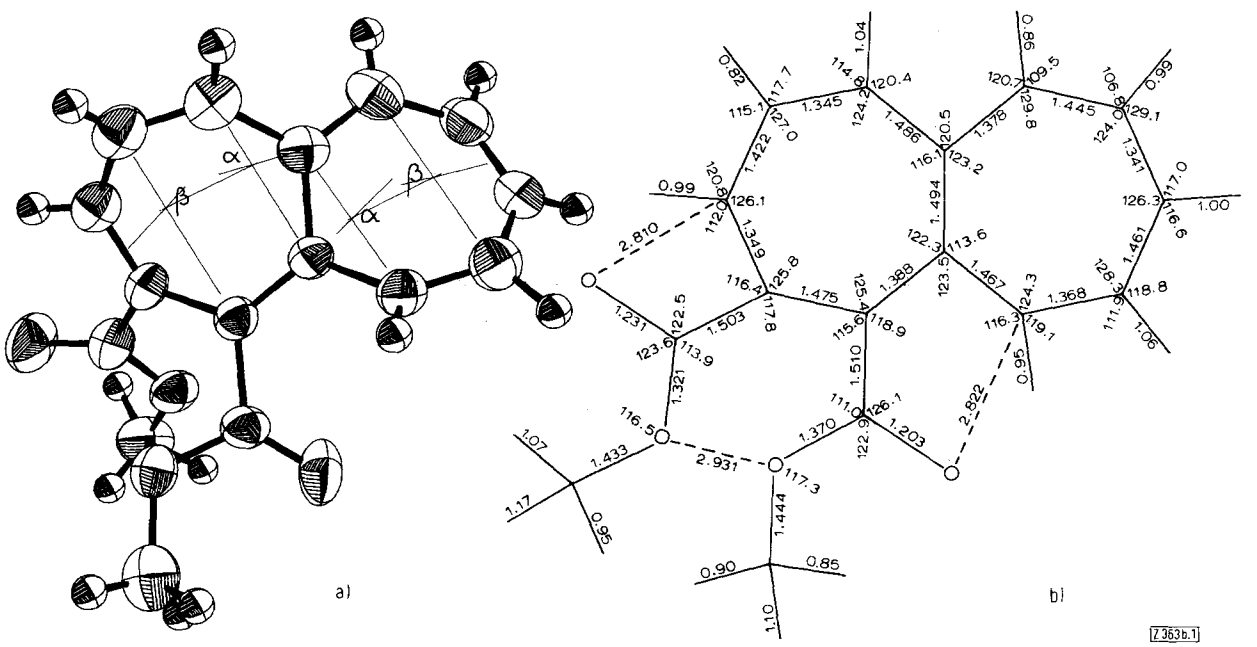


Fig. 1. a) Molecular structure of *(2)*; b) bond lengths and angles (bond lengths in 10^2 pm). Standard deviations: $\sigma_{XX} = 0.8$ pm; $\sigma_{XH} = 7$ pm; $\sigma_{XXX} = 0.5°$; $\sigma_{XXH} = 3.0°$ (X = C, O).

Crystal and Molecular Structure of Dimethyl 1,2-Heptalenedicarboxylate[**]

By *Hans Jörg Lindner* and *Brigitte Kitschke*[*]

Theoretical studies have shown that the localized heptalene structure *(1a)* is energetically preferred over the delocalized structure *(1b)*[1]. *Bertelli* deduced a nonplanar structure of conjugative interaction with the ring system. The bond lengths and angles (Fig. 1b) show an alternance already apparent from the form of the heptalene system.

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[1] *G. Binsch*, Jerusalem Symp. Quantum Chem. Biochem. *3*, 25 (1971); *T. Nakajima, A. Toyota*, and *H. Yamaguchi*, *ibid. 3*, 227 (1971); *T. Nakajima*, Fortschr. Chem. Forsch. *32*, 1 (1972).

[2] *D. J. Bertelli*, Jerusalem Symp. Quantum Chem. Biochem. *3*, 326 (1971).

[3] *E. Vogel, H. Königshofen, J. Wassen, K. Müllen*, and *J. F. M. Oth*,