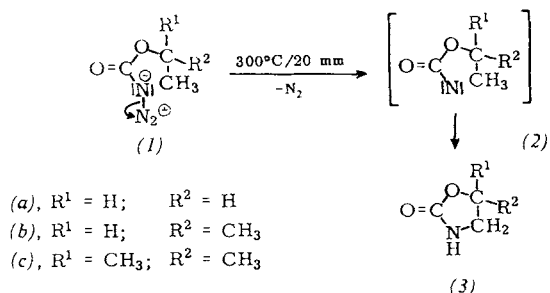


Pyrolysis of Alkyl Azidoformates in the Gas Phase [1]

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Photolysis or thermolysis of alkyl azidoformates (1) causes elimination of nitrogen leading to alkoxycarbonylazenes (2), which insert themselves into C-H bonds or dehydrogenate the solvent to form the corresponding alkylurethanes [2]. In order to avoid these secondary reactions, we investigated the pyrolysis of alkyl azidoformates in the gas phase in the presence of nitrogen as inert diluent. At 300°C/20 mm, the ethyl, isopropyl, and t-butyl esters (1a)-(1c) release nitrogen to form oxazolidones (3) in yields of 45-75%.



When ethyl azidoformate was thermolysed in carbon tetrachloride or 1,1,2-trichlorotrifluoroethane, it is not the oxazolidone (3a) that is formed [2a]; instead, two molecules of the azido ester interact with loss of nitrogen to form diethyl azodicarboxylate [2a, 3]. This compound could not so far be detected during pyrolysis in the gas phase. We assume that the concentration of (1) and (2) in the gas phase is so small as a result of the dilution with nitrogen that the dimerization observed in solution cannot occur [4].

In contrast, t-butyl azidoformate (1c) reacts exclusively intramolecularly to form the oxazolidone (3c) in solution as well. It seems that the t-butyl group shields the azene nitrogen and that the close proximity of the methyl group promotes the cyclization [2a, 2b].

According to Smolinsky and Feuer [5], thermal decomposition of (S)-2-methylbutyl azidoformate in the gas phase yields 4-ethyl-4-methyl-2-oxazolidone. The configuration of the asymmetric carbon atom remains unchanged during this reaction.

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- [1] Pyrolysis of Organic Azides, Part 2. - Part 1: R. Kreher and D. Kühling, Angew. Chem. 76, 272 (1964); Angew. Chem. internat. Edit. 3, 309 (1964).
- [2a] R. Puttner and K. Hafner, Tetrahedron Letters 1964, 3119.
- [2b] R. Kreher and G. H. Bockhorn, Angew. Chem. 76, 681 (1964); Angew. Chem. internat. Edit. 3, 589 (1964).
- [2c] D. S. Breslow et al., Tetrahedron Letters 1964, 2483, 2945.
- [2d] J. Hora, Collect. czechoslov. chem. Commun. 29, 1079 (1964).
- [3] Cf. the investigations by W. Lwowski, T. W. Mattingly, and T. J. Maricich (Tetrahedron Letters 1964, 1591) on the formation of diethyl azodicarboxylate from (1a) and (2a).
- [4] It remains an open question whether and to what extent the difference in behavior of (1) in the gas phase and in solution is determined by the reaction temperature and by solvation.
- [5] G. Smolinsky and B. I. Feuer, J. Amer. chem. Soc. 86, 3085 (1964).

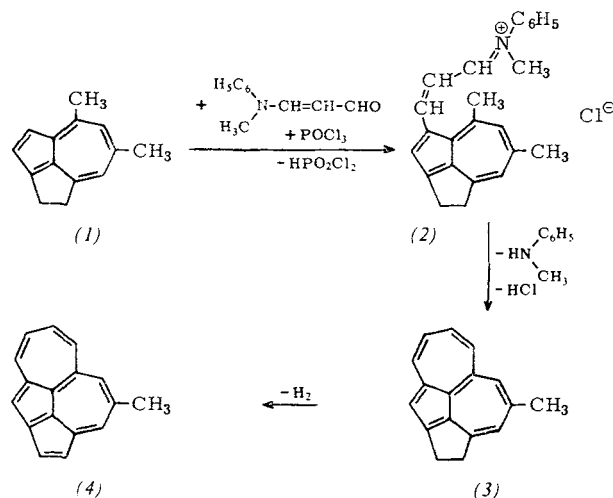
Pentaleno[2,1,6-def]heptalene - a Non-benzenoid Isomer of Pyrene

By Prof. Dr. K. Hafner, Dipl.-Chem. R. Fleischer, and K. Fritz

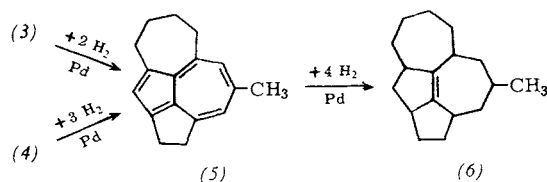
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Polycyclic conjugated non-benzenoid hydrocarbons are of great theoretical interest in connection with the question of the relationships between structure and aromaticity [1].

Starting from 4,6-dimethyl-1,8-cyclopentenoazulene (1) [2], we have prepared a non-benzenoid isomer of methylpyrene, viz. the tetracyclic hydrocarbon (4), which can formally be viewed as consisting either of a pentalene and a heptalene system or of two azulene systems. Moreover the structural elements of sesquifulvalene and heptafulvene are recognizable. Hydrocarbon (1) reacts with N-methylanilinoacrolein in the presence of phosphorus oxide chloride at 20°C to form the immonium salt (2) in 90% yield; the perchlorate of (2) forms dark violet crystals which decompose above 260°C. When (2) is heated with sodium methoxide in boiling methanol, it loses a molecule of N-methylaniline and undergoes intramolecular condensation to give (3), m.p. 62-63°C, in 35% yield; the trinitrobenzene π-complex of (3) melts at 196°C. Dehydrogenation of (3) with chloranil in benzene at 20°C produces a 65% yield of (4) as thermostable black needles, m.p. 109°C, which



dissolve in organic solvents to give wine-red solutions which exhibit a green fluorescence. The electronic spectrum of (4) in n-hexane has maxima at 255 (log ε = 4.55), 262 (4.57), 284 (4.75), 291 (4.83), 317 (4.24), 367 (3.55), 382 (3.61), 396 (3.38), 405 (3.35), 421 (3.58), 449 (3.76), 504 (2.74), 539 (3.00), 582 (3.11), 710 (2.08), and 813 mμ (1.70). Its NMR spectrum contains a multiplet for the 9 ring protons at 1.5-3.3 τ in addition to a singlet for the methyl protons at 7.25 τ. Compound (4) forms a π-complex with trinitrobenzene of m.p. 209°C. When hydrogenated at normal pressure it absorbs 3 moles of hydrogen to form the azulene derivative (5) as



blue-green needles, m.p. 64 °C; the trinitrobenzene derivative of (5) melts at 139 °C. Reduction of (3) also gives rise to (5). Further catalytic hydrogenation of (5) at normal pressure leads to an uptake of 4 moles of hydrogen, presumably to yield the hydrocarbon (6), whose double bond can be detected with bromine or tetranitromethane. Although (4) is a cyclic conjugated system with 4n π-electrons (n = 4), it is surprisingly inert toward electrophilic reagents. It dissolves in 70% perchloric acid and can be recovered unchanged from the solution by dilution at 0 °C.

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[1] K. Hafner, Angew. Chem. 75, 1041 (1963); Angew. Chem. internat. Edit. 3, 165 (1964).

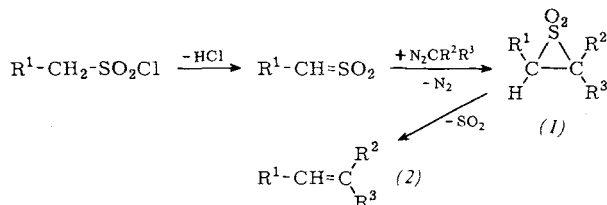
[2] K. Hafner and J. Schneider, Liebigs Ann. Chem. 624, 37 (1959).

Synthesis of Olefins from Sulfoxes and Diazoalkanes via Episulfones

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Diazomethane and sulfur dioxide react to form ethylene sulfone [1], which yields ethylene by elimination of SO₂. The reaction of higher diazoalkanes and sulfur dioxide leads via the corresponding episulfones to symmetrically substituted olefins [2].

We have now found that sulfoxes R¹-CH=SO₂ [3], which are produced by dehydrochlorination of primary alkane-sulfonyl chlorides with triethylamine, react readily *in situ* with diazoalkanes at 0 °C to form isolable episulfones (1). Thermal elimination of SO₂ from the latter produces unsymmetrically substituted olefins (2) in good yields.



	R ¹	R ²	R ³	Yield [%]	M.p. [°C] (B.p. [°C/mm])
(1a)	H	H	H	64	19
(1b)	C ₂ H ₅	H	H	95	(80/0.2; decomp.)
(1c)	C ₆ H ₅	H	H	35	39 (decomp.)
(2c)	C ₆ H ₅	H	H	67	
(1d)	C ₆ H ₅ CH ₂	H	H	99	49–51
(2d)	C ₆ H ₅ CH ₂	H	H	97	(44/10)
(2e)	C ₆ H ₅ CH ₂	H	CH ₃	91	(62/10)
(1f)	C ₆ H ₅ CH ₂	CH ₃	C ₂ H ₅	76	77–78
(1g)	7,7-Dimethyl- 2-oxobicyclo- [2,2,1]hept-1- yl	H	H	94	83–85
(2g)		H	H	74	63–64
(1h)	[2,2,1]hept-1- yl	H	CH ₃	36	77–79
(2h)		H	CH ₃	64	(62/0.02)
(2i)		CH ₃	C ₂ H ₅	71	(67/0.02)

When phenylethanesulfonyl chloride is added slowly to a solution of diazomethane and triethylamine cooled in ice, triethylamine hydrochloride is precipitated with simultaneous evolution of nitrogen, and allylbenzene episulfone (1d) is formed. The solution is filtered at room temperature and the ether evaporated from the filtrate leaving 99% (1d) as colorless crystals, m.p. 49–51 from petroleum ether, which release SO₂ slowly at room temperature and rapidly on heating to 80 °C to afford a 97% yield (based on the original sulfonyl chloride) of allylbenzene (2d). The episulfones (1a), (1b), (1c), (1d), (1f), (1g), and (1h) have bands in the infrared at 3080 cm⁻¹ due to the C–H vibration from the three-membered ring and intense sulfone bands at 1160 and 1305 cm⁻¹.

The olefin forms without isomerization, even when – as in the examples (2d)–(2f) – isomerization would lead to an increase in conjugation and hence in resonance energy. The synthesis of olefins by this method may be of preparative use. This is shown by the reaction of the readily available D-camphor-10-sulfonyl chloride to give the 10-alkylidene derivatives (2g)–(2i) of camphor whose synthesis by other methods is probably extremely difficult.

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German version: Angew. Chem. 77, 41 (1965)

[1] G. Hesse, E. Reichold, and S. Majmudar, Chem. Ber. 90, 2106 (1957); G. Hesse and S. Majmudar, *ibid.* 93, 1129 (1960).

[2] H. Staudinger and F. Pfenninger, Ber. dtsh. chem. Ges. 49, 1941 (1916); L. von Vargha and E. Kovács, *ibid.* 75, 794 (1942); N. P. Neurieter and F. G. Bordwell, J. Amer. chem. Soc. 85, 1209 (1963).

[3] G. Opitz and K. Fischer, Z. Naturforsch. 18b, 775 (1963).

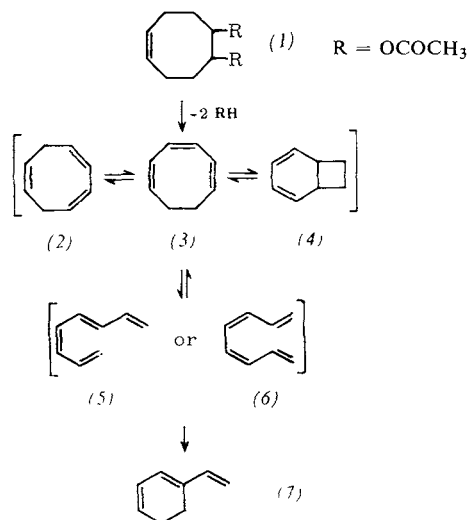
Preparation of 1-Vinylcyclohexa-1,3-diene from 5,6-Diacetoxycyclooctene

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Following pyrolysis of 5,6-diacetoxycyclooctene (1), b.p. 103–105 °C/1.5 mm, n_D²⁰ = 1.4731, at 500 °C/20 mm under nitrogen, refinement of the products by distillation affords a hydrocarbon fraction, b.p. 47 °C/20 mm, n_D²⁰ = 1.5400, in about 50% yield which consists mainly of an olefin of the composition C₈H₁₀ and a little styrene. The olefin can be isolated in about 40% yield based on (1) by chromatography with n-pentane on a column (2 m long) of Al₂O₃. This hydrocarbon (n_D²⁰ = 1.5377) is colorless, is polyunsaturated, and polymerizes readily when pure; it is not 1,3,6-cyclooctatriene (2), 1,3,5-cyclooctatriene (3), bicyclo[4,2,0]octa-2,4-diene (4) [1], *trans,trans*-1,3,5,7-octatetraene [2], nor *cis,trans*-1,3,5,7-octatetraene (5) [3]. Its elemental composition, its ultraviolet, infrared, NMR, and mass spectra, its oxidative degradation, and its hydrogenation to ethylcyclohexane identify the compound as the hitherto unknown 1-vinylcyclohexa-1,3-diene (7), λ_{max} = 288 (ε = 8340), 298 (8420), and 310 mμ (4980) in isoctane.

The results of the pyrolysis of the diacetate (1) can be explained by intermediate formation of the valence-bond isomers (2) or (3) or of (4), which is in equilibrium with these two, and of *cis,trans*- (5) or *cis,cis*-1,3,5,7-octatetraene (6) [4].



The formation of styrene can be explained by dehydrogenation of (7), probably *via* ethylbenzene as isomerization product.