

solution was filtered; the filtrate was concentrated to half its original volume and stored overnight at 0° under carbon monoxide. The orange crystals were filtered and the filtrate was cooled in a bath of Dry Ice-acetone, whereupon a yellow precipitate was obtained. The crystals and the second crop of precipitate were recrystallized separately from *n*-pentane and proved to be identical. After four such recrystallizations, orange crystals melting at 93–94° with slight decomposition were obtained.

Anal. Calcd. for $C_{11}H_5CoFeHgO_6$: C, 24.13; H, 0.91; mol. wt., 547. Found⁷: C, 24.14; H, 1.14; mol. wt.,⁸ 523.

The X-ray emission spectrum showed bands corresponding to Hg $L\alpha_1$ at 35.90, Co $K\alpha_1$ at 52.75, and Fe $K\alpha_1$ at 57.47°.

It is soluble in most organic solvents but insoluble in water. It is air stable as a solid but decomposes slowly in solution on exposure to air. On treatment with an aqueous iodine solution (KI + I₂ in water) 4 moles of CO are evolved per mole of the compound, and π -C₅H₅Fe(CO)₂I,⁹ m.p. 118–120° dec., is recovered. I reacts with excess triphenylphosphine in hexane solution with the evolution of 1 mole of CO per mole of I to yield a bright yellow, insoluble, air-stable compound. This compound was difficult to purify because of its limited solubility.

The infrared spectra in the C–O stretching region of I and II in carbon tetrachloride solution showed the following bands: I (cm.⁻¹): 1952 (m), 1972 (sh), 1983 (s), 1990 (s), 2008 (s), 2054 (sh, w), and 2066.6 (s); II (cm.⁻¹): 1830 (m), 1961 (sh), 1985 (s), 2021 (s), 2063 (m), 2075 (s), and 2130 (w).

I probably has the geometry of two trigonal bipyramids connected at corners through mercury. It may be considered as being derived from half of Hg[π -C₅H₅Fe(CO)₂]₂ and half of Hg[Co(CO)₄]₂, both of which are also probably trigonal bipyramids. However, the spectrum of I shows some interesting differences from the two moieties above and this will be the subject of a future paper.

Acknowledgment.—We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of the above research. We also thank Frank Rizzo for help with the X-ray emission spectra.

(7) Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(8) Determined in benzene using a Mechrolab vapor pressure osmometer.

(9) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

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MILTON ORCHIN

RECEIVED JULY 30, 1964

Crystallographic Studies of Krypton Difluoride¹

Sir:

The identification of KrF₂ has been established by Turner and Pimentel² and MacKenzie.³ Samples of the difluoride, prepared by J. Malm and F. Schreiner in this laboratory, have been found to be sufficiently

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. J. Turner and G. C. Pimentel, *Science*, **140**, 974 (1963).

(3) D. R. MacKenzie, *ibid.*, **141**, 3586 (1963).

stable to enable us to obtain some crystallographic information.

Single crystal oscillation and Weissenberg patterns indicate that the symmetry is tetragonal, with $a = 6.533$ and $c = 5.831$ Å. The calculated X-ray density, assuming four molecules in the cell, is 3.24 g./cm.³.

It is not possible to establish the space group on the basis of the available X-ray data. However, the cell appears to be primitive, and KrF₂ is therefore not isostructural with XeF₂. The latter is also tetragonal, with $a = 4.315$ and $c = 6.990$ Å., but is based on a body-centered cell with space group I4/mmm.

The quality of the X-ray patterns is poor because of a tendency for the crystals to decompose upon irradiation. Hence, the assignment of the symmetry is tentative until further structural studies are completed.

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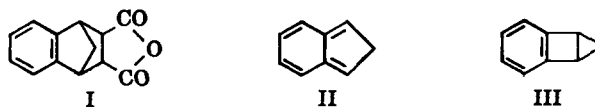
STANLEY SIGEL
ELIZABETH GEBERT

RECEIVED JULY 20, 1964

Formation and Capture of a Reactive Intermediate Related to Dimethylpseudoindene¹

Sir:

The formation of benzonorbornene derivatives (*e.g.*, I) from the reaction of maleic anhydride with indene^{2–4} (or from the zinc debromination of 1,3-dibromoindane in the presence of maleic anhydride³) and the thermal 1,5-hydrogen rearrangements of indene⁵ are readily interpreted on the assumption that isoindene (II)



intervenes as an intermediate. The possibility that a valency tautomer, pseudoindene (III, benzobicyclo[2.1.0]pentene), may be capable of existence prompted the present study.

Pseudoindene (III) is a formal cycloaddition product of benzyne and cyclopropene. In attempting to realize this type of addition in practice, we observed that 1,2,3-triphenylcyclopropene⁶ (IV) and benzyne⁷ (V) did not react in this sense but instead gave the substitutive addition product 1,2,3,3-tetraphenylcyclopropene (VI), m.p. 177–178°, in 60–70% yield.¹⁰ The structure of VI was assigned on the basis of its elemental composition. *Anal.* Calcd. for C₂₇H₂₀: C, 94.15; H, 5.85; mol. wt., 344. Found: C, 93.85; H, 5.97; mol. wt. 383, 325 (osmometric). Spectral peaks appeared at: ultraviolet λ_{\max} (ethanol) 229, 303, 316,

(1) The support of this work by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, through Grant No. AF-AFOSR-389-63, and by the National Science Foundation through a fellowship, is gratefully acknowledged.

(2) K. Alder, F. Pascher, and H. Vagt, *Ber.*, **75**, 1501 (1942).

(3) K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).

(4) J. A. Berson and G. B. Aspelin, *ibid.*, in press.

(5) W. R. Roth, *Tetrahedron Letters*, No. 17, 1009 (1964).

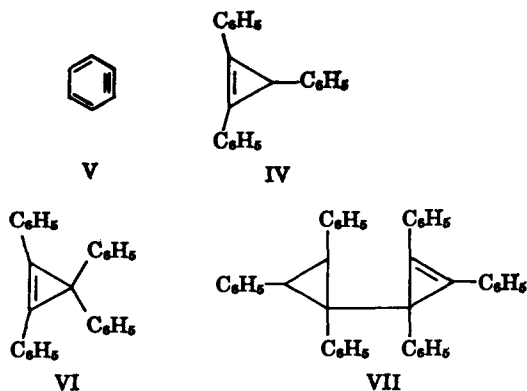
(6) R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, **85**, 2729 (1963).

(7) Generated *in situ* from an ethylene chloride suspension of *o*-benzenediazonium carboxylate according to a modification⁸ of the Stiles⁹ procedure. We are indebted to Prof. L. Friedman for details.

(8) L. Friedman, private communication.

(9) M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963).

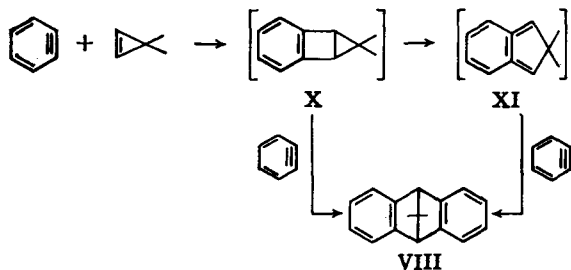
(10) This kind of process seems to be analogous to the thermal dimerization of IV to VII.⁶



and 333 $m\mu$; $\log \epsilon$ 4.52, 4.32, 4.36, and 4.32; compare IV, λ_{\max} 228, 305 sh, 314, and 331 $m\mu$; $\log \epsilon$ 4.44, 4.37, 4.45, and 4.33; infrared spectrum: λ_{\max} (carbon tetrachloride) 5.5 μ ; compare IV, λ_{\max} 5.5 μ ; 60 Mc. n.m.r. (carbon tetrachloride): only aromatically bound protons, $\delta \sim 7.3$ and 7.7 p.p.m. relative to tetramethylsilane as internal standard. The only reasonable alternative structure, tetraphenylallene, m.p. 164–165°, is a known compound¹¹ and has properties quite different from those of VI.

Although the possibility of substitutive addition now was precluded, tetraphenylcyclopropane (VI) nevertheless still failed to add benzyne; it was recovered unchanged in >95% yield after exposure to decomposing *o*-benzenediazonium carboxylate in ethylene chloride. Under the same conditions, the same batch of *o*-benzenediazonium carboxylate reacted with anthracene in a parallel experiment to give a 66% yield of triptycene.

Blocking the 3,3 positions and leaving the 1,2 positions of the cyclopropane unsubstituted had a fruitful result. When a cold suspension of ~ 7 mmoles of *o*-benzenediazonium carboxylate in a solution of 3 mmoles of 3,3-dimethylcyclopropane¹² in ethylene chloride was gradually warmed to 55°, there was obtained a complex mixture of products, from which was isolated biphenylene (m.p. 110–110.5°, ultraviolet and infrared spectra identical with those reported¹³) and, as the major component of the volatile fraction, an approximately 5% yield of a new hydrocarbon, 7,7-dimethyldibenzonorbornadiene (VIII), m.p. 127.8–128°. *Anal.* Calcd. for $C_{17}H_{16}$: C, 92.68; H, 7.32;



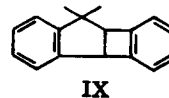
mol. wt., 220. Found: C, 92.90; H, 7.25; mol. wt., 219 (osmometric incarb on tetrachloride). Spectral peaks appeared at: n.m.r., symmetrical pattern centered

(11) (a) D. Vorländer and C. Siebert, *Ber.*, **39**, 1027 (1906); (b) W. Otting, *ibid.*, **87**, 611 (1954).

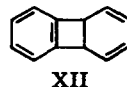
(12) G. L. Closs, L. E. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3706 (1963).

(13) W. Baker, M. P. V. Boarland, and J. F. W. McOmie, *J. Chem. Soc.*, 1476 (1954); C. G. Cannon and G. B. M. Sutherland, *Spectrochim. Acta*, **4**, 373 (1951).

about $\delta \sim 6.9$ p.p.m. (aromatic protons, area 8); sharp singlet at δ 3.63 p.p.m. (bridgehead protons, area 2); sharp singlet at δ 0.90 p.p.m. (methyl protons, area 6); ultraviolet λ_{\max} (95% ethanol) 274 and 281 $m\mu$; $\log \epsilon$ 3.25 and 3.37; compare dibenzonorbornadiene, λ_{\max} 272 and 278 $m\mu$; $\log \epsilon$ 3.30 and 3.41.¹⁴ The extreme simplicity of the n.m.r. spectrum precludes assignment to the new substance of an unsymmetrical structure such as IX.



The formation of VIII is most simply explained as a cycloaddition of benzyne to 3,3-dimethylcyclopropane to give 2,2-dimethylpseudoindene (X), followed by reaction with a second mole of benzyne, either directly on X or after a preliminary isomerization of X to 2,2-dimethylisindene (XI). The latter isomerization is only formally analogous to that proposed¹⁵ for the presumed dihydrobiphenylene intermediate (XII) in the benzene-benzyne reaction that leads to benzocyclooctatetraene. Closer analogies are the thermolyses of benzocyclobutene (XIII) in the presence of



diene acceptors. These processes, which seem to proceed *via* *o*-xylylene (XIV) or a closely related species, are quite slow at 150°,^{3,16,17} in sharp contrast to the hypothetical $X \rightarrow XI$ reaction which, if it occurs, must be rapid at 55°.

A remarkable feature of the present results is the apparent capture of an extremely reactive substance (X and/or XI) by a trapping agent (very probably benzyne¹⁸) which itself has only a fleeting existence.

(14) W. R. Vaughan and M. Yoshimine, *J. Org. Chem.*, **22**, 7 (1957).

(15) R. G. Miller and M. Stiles, *J. Am. Chem. Soc.*, **85**, 1798 (1963).

(16) M. P. Cava and D. R. Napier, *ibid.*, **80**, 2255 (1958).

(17) F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Letters*, No. 1, 15 (1962).

(18) It is conceivable that the reactive entity is not benzyne but some other transient species derived from *o*-benzenediazonium carboxylate. Experiments like those reported⁹ for other additions using substituted *o*-benzenediazonium carboxylates might clarify this point.

(19) National Science Foundation Postdoctoral Fellow, 1963–1964.

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RECEIVED JULY 23, 1964

Pentaethoxyphosphorus

Sir:

Compounds containing five atoms bonded to phosphorus are relatively rare. During the past few years Ramirez and co-workers¹ have described the preparation of substances containing five oxygens bonded to phosphorus. Because of the method of preparation two of these oxygen atoms always comprise part of a five-membered ring. Materials without a ring are generally unknown.² We wish to report the prepara-

(1) (a) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **85**, 3252 (1963); (b) F. Ramirez, N. B. Desai, and N. Ramanathan, *ibid.*, **85**, 1874 (1963); (c) F. Ramirez, N. Ramanathan, and N. B. Desai, *ibid.*, **85**, 3465 (1963); and references cited in these papers.

(2) I. N. Zhmurova and A. V. Kirsanov, *Zh. Obshch. Khim.*, **29**, 1687 (1959); *Chem. Abstr.*, **54**, 8689 (1960). have reported briefly on penta-phenoxyphosphorus.