[CONTRIBUTION No. 723 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

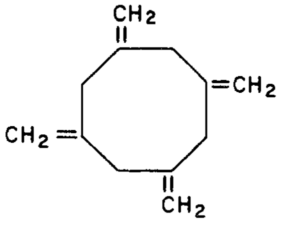
Transannular 1,7-Addition of Tetracyanoethylene to 1,3,5,7-Tetramethylenecycloöctane

BY J. K. WILLIAMS AND R. E. BENSON

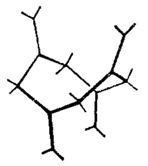
RECEIVED NOVEMBER 18, 1961

Tetracyanoethylene has been found to undergo 1,7-addition with allene tetramer (1,3,5,7-tetramethylenecycloöctane, I) to give the tricyclic compound III formed by a transannular reaction.

The formation of a tetrameric product by the catalyzed cyclization of allene with bis-(triphenyl phosphite)-nickel dicarbonyl has been reported[1] from this Laboratory. The compound was assigned the structure 1,3,5,7-tetramethylenecyclooctane (I) on the basis of elemental and spectral analyses. Recently, studies of I with molecular models (Dreiding stereomodels) indicated that the conformation I-a places opposite pairs of double bonds parallel to one another at a distance of about 2.7 Å. It appeared that at this distance there should be appreciable π-orbital interaction of the double bonds in each pair and thus the compound might exhibit enhanced reactivity of a kind associated with conjugated systems.

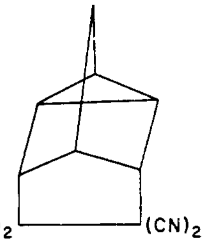


I



I-a

Tetracyanoethylene was selected as the reagent to establish the interaction of the pairs of opposite double bonds in I, since it has been shown[2,3] to react readily with bicycloheptadiene, a formally non-conjugated structure, to give the nortricyclene product II.[4]



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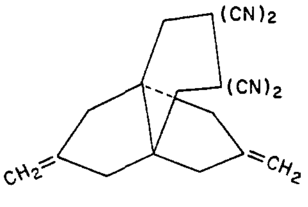
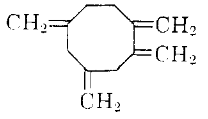


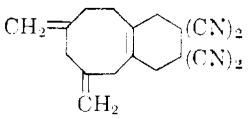
III

When equimolar quantities of allene tetramer and tetracyanoethylene were mixed in tetrahydrofuran solution, an exothermic reaction took place and a 1:1 adduct (m.p. 222–223°) was isolated in 85% yield. This adduct showed no maxima in the ultraviolet and had infrared absorption characteristic of unconjugated CN (4.43 μ), C=C (6.08 μ) and terminal methylene (11.00 μ with overtone at 5.50 μ). The adduct formed a tetrabromo derivative, m.p. 217.5–218°, that had no absorption in the infrared in the 6 μ region usually associated with carbon–carbon unsaturation. In deuterioacetone solution the adduct exhibited a simple proton n.m.r. spectrum with unsplit resonance peaks of equal intensity at τ-values[5] of 5.12 (unsaturated proton), 6.67 and 6.83 (*exo* and *endo* protons of 5-membered ring) and 7.70 (protons of 6-membered ring). The data are consistent for the adduct having the structure III. Although transannular reactions brought about by ionic reagents in 8-membered ring systems are well known,[6,7] this appears to be the first example in which transannular bond formation can be directly attributed to the proximity of exocyclic methylene groups.[8]

Furthermore, the identification of the tetracyanoethylene adduct of allene tetramer as III establishes the identity of allene tetramer as I rather than the alternative structure IV.[9] The latter would be expected to undergo facile reaction with tetracyanoethylene as was observed for I, but the proton n.m.r. spectrum of the anticipated adduct V would be expected to be quite complex with at least an A_2B_2 pattern resulting from spin-spin coupling.[10] Presumably, the high end absorption observed[1] in the ultraviolet at 210 mμ for I is attributable to transannular interaction of the exomethylene groups.



IV



V

Experimental

3,3,4,4-Tetracyano-8,11-dimethylenetricyclo[4.3.3.0]-dodecane (III).—A solution of 4.2 g. of allene tetramer in 25 ml. of tetrahydrofuran was mixed with a solution of 3.3 g. of tetracyanoethylene in 25 ml. of tetrahydrofuran. The mixture became warm and the initial amber color faded. After 1.5 hours, the solvent was removed under reduced pressure.

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[1] R. E. Benson and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **81**, 4247 (1959).

[2] A. T. Blomquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959).

[3] D. E. Applequist and D. C. England, U. S. Patent 2,940,984 (1960).

[4] Maleic anhydride with bicycloheptadiene also yields the nortricyclene-type adduct.[3] However, tetracyanoethylene is the more avid dienophile in Diels–Alder reactions, as shown by the recent studies of J. Sauer (Sudwestdeutsche Chemie-Dozenten-Tagung, Munich, May, 1961; *Angew. Chem.*, **73**, 545 (1961)).

[5] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[6] A. C. Cope, G. A. Berchtold, P. E. Peterson and S. H. Sharman, *J. Am. Chem. Soc.*, **82**, 6366 (1960), and preceding publications.

[7] V. Prelog and S. Borcic, *Helv. Chim. Acta*, **41**, 199 (1958), and preceding publications.

[8] Reaction of the adduct III with tetracyanoethylene under these mild conditions does not proceed further, since the exocyclic methylene groups in III are not in close proximity.

[9] Footnote 2 of ref. 1.

[10] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959.

The solid that remained was crystallized from acetonitrile with treatment with charcoal to give 6.4 g. (85%) of III, m.p. 214–216°. A sample was prepared for analysis by an additional crystallization from acetonitrile to give white crystals, m.p. 222–223°.

Anal. Calcd. for $C_{18}H_{16}N_4$: C, 75.0; H, 5.59; N, 19.4; mol. wt., 288. Found: C, 74.9; H, 5.62; N, 19.5; mol. wt., 294.

3,3,4,4-Tetracyano-8,11-dibromo-8,11-bis-(bromomethyl)-tricyclo[4.3.3.0]dodecane.—To a solution of 1.44 g. of the adduct III in 75 ml. of warm chloroform was added 1.6 g. of bromine. Solid began to separate after 10 minutes. After 30 minutes the bromine color had faded and 1.9 g. of solid was collected by filtration. Crystallization of 1.6 g. of the crude product from acetonitrile gave 0.9 g. of 3,3,4,4-tetracyano-8,11-dibromo-8,11-bis-(bromomethyl)-tricyclo-[4.3.3.0]-dodecane, m.p. 217.5–219°. An additional crystallization from the same solvent gave a sample for analysis melting at 218.5–220°.

Anal. Calcd. for $C_{18}H_{16}N_4Br_4$: C, 35.6; H, 2.65; N, 9.22; Br, 52.6. Found: C, 35.7; H, 2.68; N, 9.53; Br, 53.1.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

The Mechanism of Reductive Furan Formation

BY CHARLES F. WILCOX, JR., AND MALCOLM P. STEVENS[1]

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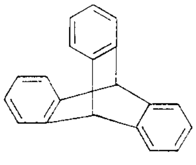
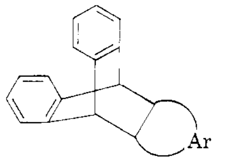
During the attempted preparation of heteroatom analogs of triptycene, reductive furan formation from 2-ene-1,4-diones has been observed. The mechanism of this type of reaction is re-examined and a modified formulation in terms of a Lewis acid and a reducing agent is proposed. From this study two new syntheses of furans are suggested.

Introduction

Previous work from this Laboratory[2-4] has been concerned with the preparation and interpretation of the ultraviolet spectra of triptycene (I) and its derivatives. These compounds are of interest because they permit the study of chromophore interaction through space with molecules of relatively fixed and certain geometry. One extension of this study to be developed was the preparation of triptycene analogs (II) in which one of the benzene rings has been replaced by another aromatic nucleus.



I

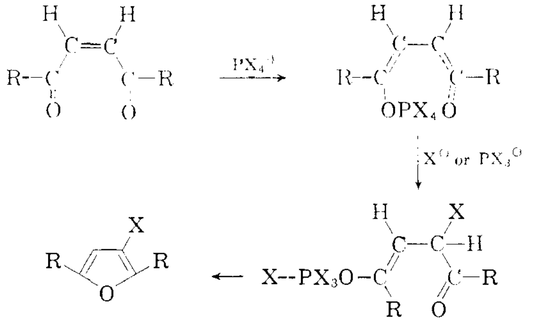


II

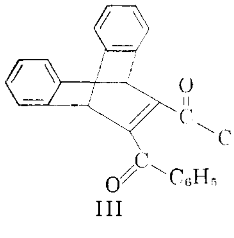
During the attempted preparation of such compounds, several interesting reactions have been observed which shed new light on the recently proposed mechanism of Newman[5] for the abnormal reaction of PBr_5 with certain ketones to give furans. This paper will be concerned solely with these reactions, the modification they require in the mechanism for abnormal furan formation and their potential extrapolation to a new furan synthesis. A subsequent paper will discuss the interpretation of the ultraviolet spectra of the various compounds described here.

Discussion

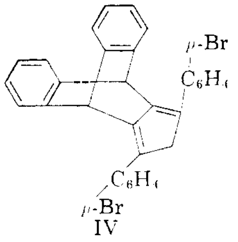
When α,β-unsaturated 1,4-diketones like 1,4-diphenylbutene-1,4-dione are treated with PCl_5 or PBr_5 a chlorinated or brominated furan results. These cyclizations have been tentatively interpreted by Newman and Wood[5] in their general PX_5–ketone reaction mechanism as involving first the equilibrium formation of PX_4^+ and PX_6^- followed by attack of the PX_4^+ on the ketone to yield the furan in the manner



A dominating feature of this mechanism is the addition of a halide ion to the initially formed Lewis salt so that a halogenated furan inevitably results. With this in mind, it is interesting to observe that when III, an unsaturated 1,4-diketone incapable of such halogenation, was treated with PBr_5 at 200°, the furan IV was formed in 67% yield (after purification).



III



IV

The identity of this product was established by: (1) a comparison of its physical properties with those previously reported for the compound prepared by a different route,[6] (2) its nitric acid oxida-

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[1] Taken from a dissertation submitted by M. Stevens to Cornell University in partial fulfillment of the requirements for the Ph.D. degree, June, 1961.

[2] A. C. Craig and C. F. Wilcox, Jr., *J. Org. Chem.*, **24**, 1619 (1959).

[3] C. F. Wilcox, Jr., *J. Chem. Phys.*, **33**, 1874 (1960).

[4] C. F. Wilcox, Jr., and A. C. Craig, *J. Org. Chem.*, **26**, 2491 (1961).

[5] M. S. Newman and L. L. Wood, Jr., *J. Am. Chem. Soc.*, **81**, 4300 (1959), and references therein.

[6] P. Baumgarten and G. Hugel, *Bull. soc. chim. France*, **21**, 1105 (1954).