[Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Mass.]

Photochemical Reactions. XII.[1,2] Addition Reactions of Olefins and Acetylenes with Benzonitrile

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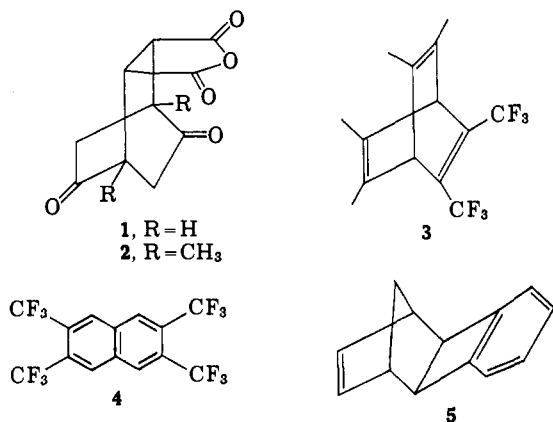
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Irradiation of benzonitrile and 2-methyl-2-butene produced a 1:1 adduct which was shown to be 7,8,8-tri-methylbicyclo[4.2.0]octa-2,4-diene-1-carbonitrile. The structure of the photoadduct was established using chemical and spectroscopic arguments. It was not stable to ultraviolet light and easily reverted to benzonitrile and olefin. Pyrolysis caused primarily ring cleavage to a conjugated tetraene. Dialkylacetylenes could be added to benzonitrile photochemically. The 1:1 adducts isolated were 2,3-disubstituted cycloöctatetraene-carbonitriles.

Introduction

Condensation of aromatic compounds with olefins and acetylenes usually does not lead to formation of an additional ring, but to Friedel–Crafts type alkylation products when acidic catalysts are used. The well known and facile Diels–Alder reactions of anthracene,[4] however, represent an exception. Similar 1,4-addition reactions to benzene and naphthalene have been attempted under forcing conditions, but only few successful examples are known.

In a series of papers[5a,b,c] Takeda and his co-workers described the thermal condensation of various hydroxybenzenes and of β-naphthol[5a] with maleic anhydride. From hydroquinone[5b] and 2,5-dimethylhydroquinone[5c] the adducts 1 and 2, respectively, were obtained. Catechol, resorcinol, 2-methylhydroquinone, 2,6-dimethylhydroquinone, 2-methyl-5-isopropylhydroquinone, and 2,3,5,6-tetramethylhydroquinone gave no adducts. Preparation and structure proof of the adduct 1 were described also by Cookson.[6] Conjugate addition to an aromatic nucleus occurred when bis-(trifluoromethyl)-acetylene was heated with various benzenes and naphthalenes. Thus, durene gave the adduct 3, while from benzene there was obtained the naphthalene 4 as the major product.[7]

1, R = H
2, R = CH₃

3

4

5

The only thermal condensation in which 1,2-addition to an aromatic ring occurred seems to be the reaction of benzyne with bicyclo[2.2.1]hepta-2,5-diene which

yielded the exo-adduct 5.[8] No analogous reactions have been reported with aromatic compounds proper, but in this paper we wish to report the light-catalyzed 1,2-addition of olefins[9] and acetylenes to benzonitrile.

Results

Photochemical addition of nitriles to olefins might be expected to lead to the unknown 1-azetines in analogy to the formation of oxetenes from aromatic aldehydes and acetylenes.[10] However, in the case of benzonitrile, addition occurred mainly at the benzene ring. Irradiation of benzonitrile and 2-methyl-2-butene (1:1) for 7–14 days with a mercury arc yielded a mixture of neutral and basic materials. Examination of the n.m.r. spectrum of the neutral portion indicated that it was composed of one major and two minor isomers. Analysis of the product was in agreement with the formula $C_{12}H_{15}N$, corresponding to a 1:1 adduct. This adduct crystallized spontaneously when stored at $-20°$ and a pure isomer (m.p. 26–30°) was isolated in 63% yield.

Intensity measurements in the n.m.r. spectrum of the original mixture and in the spectrum of crystalline material showed the mixture to be composed of 77% of one isomer and 23% of two other isomers. Degradative and spectral evidence outlined below prove the major adduct to be 7,8,8-trimethylbicyclo[4.2.0]octa-2,4-diene-1-carbonitrile (6).[9]

An infrared spectrum of a crystalline sample had bands at 3040 and 2950 cm.⁻¹, characteristic of vinyl and aliphatic C–H bonds, respectively. Absorption at 2230 cm.⁻¹ confirmed the presence of a nitrile group and bands at 1585 and at 690 cm.⁻¹ indicated the presence of a conjugated cis-disubstituted double bond. Comparison of the ultraviolet spectrum of the photoadduct 6 [λ_{max}^{EtOH} 273 mμ (ε 3450), λ_{min} 229 mμ (ε 446)] with that of bicyclo[4.2.0]octa-2,4-diene[11] [$\lambda_{max}^{C_6H_{12}}$ 274 mμ (ε 3340), λ_{min} 232 mμ (ε 374)] suggested the presence of identical chromophores and the bicyclic nature of the adduct was confirmed by hydrogenation over Adams' catalyst in acetic anhydride which furnished the crystalline, saturated amide 7.

6

7

Condensation of the photoadduct with dimethyl acetylenedicarboxylate led to a crystalline compound whose spectra [λ_{sh}^{EtOH} 215 mμ (ε 4500) [compare with

(1) Part XI: G. Büchi, C. W. Perry and E. W. Robb, J. Org. Chem., 27, 4106 (1962).

(2) Part of a program of research supported by a grant from the Godfrey L. Cabot Fund, Publication No. 76, M.I.T. Solar Energy Conversion Project.

(3) National Science Foundation Predoctoral Fellow, 1955–1957.

(4) M. C. Kloetzel in R. Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 1.

(5) (a) K. Takeda, S. Nakagura and K. Kitahonoki, Pharm. Bull. (Japan), 1, 135 (1953); (b) K. Takeda, K. Kitahonoki and K. Igarashi, ibid., 4, 12 (1956); (c) K. Takeda and K. Kitahonoki, Ann., 606, 153 (1957).

(6) R. C. Cookson and N. S. Wariyar, J. Chem. Soc., 327 (1957).

(7) C. G. Krespan, B. C. McKusick and T. L. Cairns, J. Am. Chem. Soc., 83, 3428 (1961).

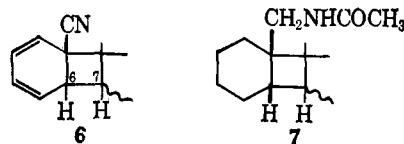(8) H. E. Simmons, ibid., 83, 1657 (1961).

(9) First described in a patent to D. E. Ayer and G. H. Büchi, U. S. Patent 2,805,242 (1957) [Chem. Abstr., 52, 2904a (1958)].

(10) G. Büchi, J. T. Kofron, E. Koller and D. Rosenthal, J. Am. Chem. Soc., 78, 876 (1956).

(11) A. C. Cope, A. C. Haven, Jr., F. I. Ramp and E. R. Trumbull, ibid., 74, 4867 (1952).

dimethyl dimethylmaleate (9),[12] λ_{max}^{EtOH} 212.5 mμ (ϵ 8900); $\nu_{max}^{CCl_4}$ 2220 ($-C\equiv N$), 1740 ($-COOCH_3$) 1640 and 1605 cm.$^{-1}$ ($C=C$)] were consistent with structure **8**.

Pyrolysis[13] of the Diels–Alder adduct **8** at 160–170° gave dimethyl phthalate (identified as phthalic anhydride) and the α,β-unsaturated nitrile **10** which was catalytically hydrogenated over Pd–SrCO$_3$[14] to a mixture of the epimeric 2,2,3-trimethylcyclobutanecarbonitriles **12**. The same mixture of nitriles was prepared by catalytic hydrogenation of 2,2-dimethyl-3-methylenecyclobutanecarbonitrile (**11**).[15,16] These mixtures were compared by vapor phase chromatography, infrared and n.m.r. spectra. It was not possible to separate the epimers by vapor phase chromatography on four different types of column packings. Formation of dimethyl phthalate in the pyrolysis of **8** proves that the four carbon atoms of the cyclohexadiene ring in the photoadduct were unsubstituted. Because the olefinic portion of the retro-Diels–Alder reaction was the cyclobutene **10**, the complete structure of the photoadduct is defined as **6**.
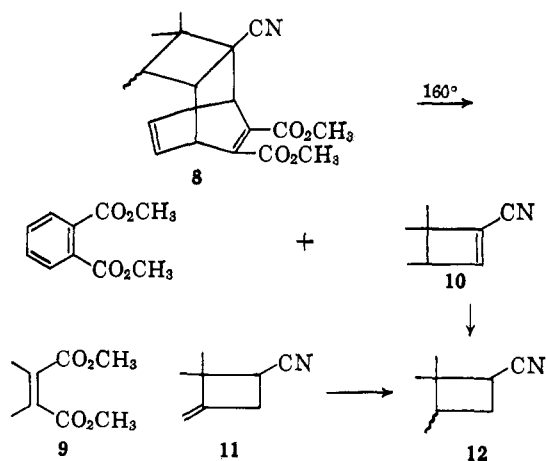

In the Diels-Alder reaction between photoadduct **6** and dimethyl acetylenedicarboxylate, varying amounts of a monomeric nitrile were produced. It was not identical with starting material because there was strong absorption in the ultraviolet spectrum at 300 mμ and consequently the thermal stability of nitrile **6** had to be investigated.

Chromatographic analysis of **6** in the vapor phase on silicone grease or XF-1150 columns indicated the presence of only one component. As the temperature of the preheater was raised gradually from 185 to 280°, pyrolytic decomposition of the material occurred and increasing amounts of benzonitrile and 2-methyl-2-butene (retention times compared with those of authentic samples) were observed, along with five other products with retention times of the order of magnitude of the original adduct. A sample of the adduct was then heated in benzene at 128° for 38 hours and 60% of the material was recovered by distillation. It consisted of starting material (53%), benzonitrile (6%) and a tetraene (41%). An n.m.r. spectrum of the crude tetraene had five peaks in the region of 8 ± 0.2 τ, indicating that it probably was a mixture of cis and trans isomers of 2-

(12) R. F. Rekker, P. J. Brombacker, H. Hamann and W. T. Nauta, *Rec. trav. chim.*, **73**, 410 (1954).

(13) K. Alder and H. F. Rickert, *Ann.*, **524**, 180 (1936).

(14) S. M. McElvain and R. E. Starn, Jr., *J. Am. Chem. Soc.*, **77**, 4571 (1955).

(15) H. N. Cripps, J. K. Williams and W. H. Sharkey, *ibid.*, **80**, 751 (1958).

(16) We are indebted to Dr. W. H. Sharkey, du Pont Co., for a generous sample of **11**.

methyl-3-cyano-2,4,6,8-decatetraene (**13**). A portion of the tetraene crystallized and had λ_{sh}^{EtOH} 295 mμ (ϵ 38,000), λ_{max}^{EtOH} 307 and 322 mμ (ϵ 45,000 and 41,000) while 2,4,6,8-decatetraene (**14**)[17] has maxima at 272, 283, 296 and 310 mμ. The tetraene unfortunately could not be characterized further because it turned into an insoluble polymer within a few hours at room temperature under nitrogen.

In contrast to pyrolysis, irradiation of the photoadduct caused almost complete reconversion (90%) to benzonitrile and 2-methyl-2-butene while formation of tetraene **13** occurred to the extent of 8–10%. A small but finite amount of the photoadduct was present in the crude irradiation mixture as evidenced by low intensity but sharp peaks in the n.m.r. spectrum at 8.17 and 8.87 τ corresponding to the *gem*-dimethyl groups (see below).
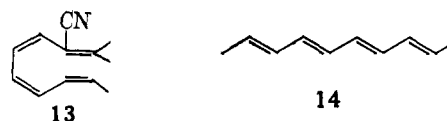
Nuclear magnetic resonance spectra[18] of the photoadduct **6** (Fig. 1) and of its Diels–Alder condensation product **8** (Fig. 2) confirm the structures assigned. The geminal methyl groups in the photoadduct appear as sharp singlets at 8.70 and 8.87 τ while the tertiary protons at C$_6$ and C$_7$ and the methyl group at C$_7$ form a readily identified ABX$_3$[19] system, with J_{AB} = 10.0 c.p.s., J_{BX} = 6.8 c.p.s. and J_{AX} = 0 c.p.s. The centers of the A multiplet (the allylic proton), of the B octet, and of the X$_3$ doublet were calculated from the spectrum and are located at 7.11, 7.61 and 9.06 τ, respectively. The A proton exhibits further fine structure due to extensive coupling with the vinyl protons which appeared as complex multiplets centered at 3.92, 4.20, 4.28 and 4.50 τ. It was not possible to assign chemical shifts to particular protons. The large coupling constant (10 c.p.s.) for the two tertiary protons may indicate that the dihedral angle between them is near 0 or 180°.[20a] The latter is not possible on a cyclobutane ring, whereas an angle of 0° is that expected for *cis* substituents. In one case[20b] *cis*- and *trans*-1,2-proton coupling constants were found to be 8 and 4 c.p.s., respectively, but measurements on other cyclobutanes[20c] showed a reverse order and in one case the difference was only 1.2 c.p.s. Furthermore, the coupling constants seem to depend on the nature of the substituents[20c] and we conclude that the configuration of the methyl group in the photoadduct **6** can be assigned with confidence only when its epimer becomes available for n.m.r. measurement. Incidentally, the alternative structure **6a** is excluded because of the large coupling observed although the rather unusual spectrum of the amide **15** revealed a coupling constant of 7 c.p.s. for the protons at C$_5$ and C$_6$. In the corresponding epimer the coupling was 0 c.p.s. As emphasized by the authors[21] this represents a special case of a folded cyclobutane ring and no long range interactions of similar

(17) E. A. Braude, in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 148.

(18) Nuclear magnetic resonance spectra were obtained at 60 Mc. using tetramethylsilane as an internal reference, τ = 10.00.

(19) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 90.

(20) (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959). (b) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962). The author has kindly informed us that the *cis–trans* coupling constants in footnote 9 should be inverted. (c) J. K. Williams, D. W. Wiley and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962).
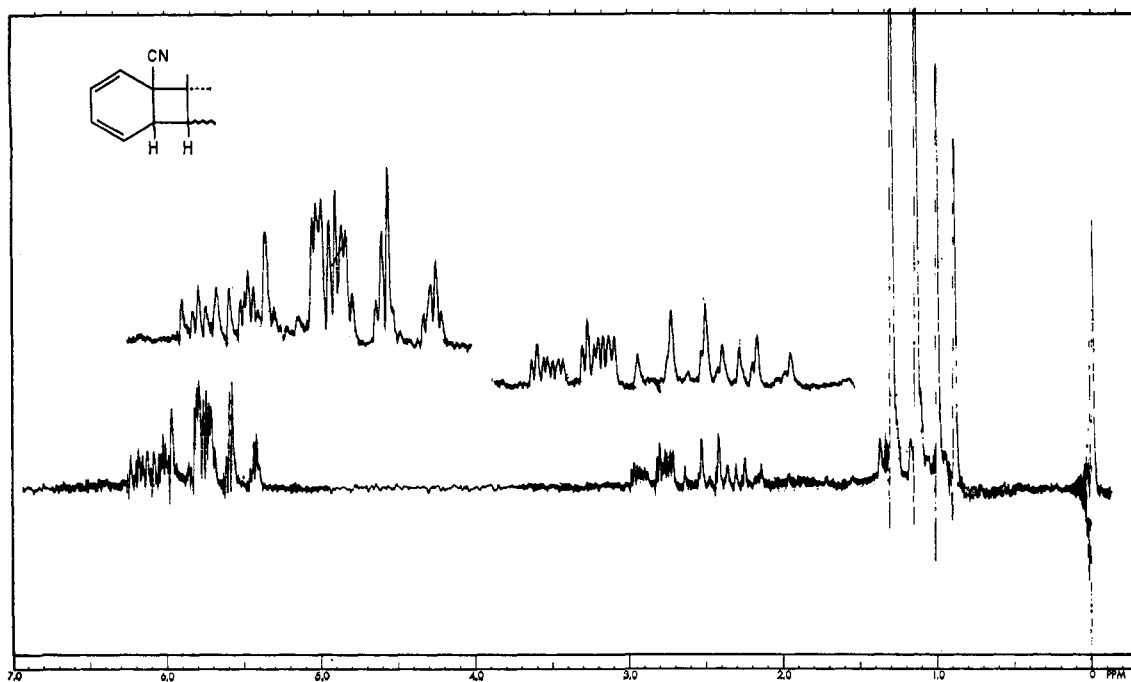
(21) J. Meinwald and A. Lewis, *ibid.*, **83**, 2769 (1961).

Fig. 1.—60-Mc. n.m.r. spectrum of 7,8,8-trimethylbicyclo[4.2.0]octa-2,4-diene-1-carbonitrile (6) as 25% solution in CCl₄ with tetramethylsilane as an internal reference (0 p.p.m.). Inserts are twofold expansions of the vinyl and tertiary protons.
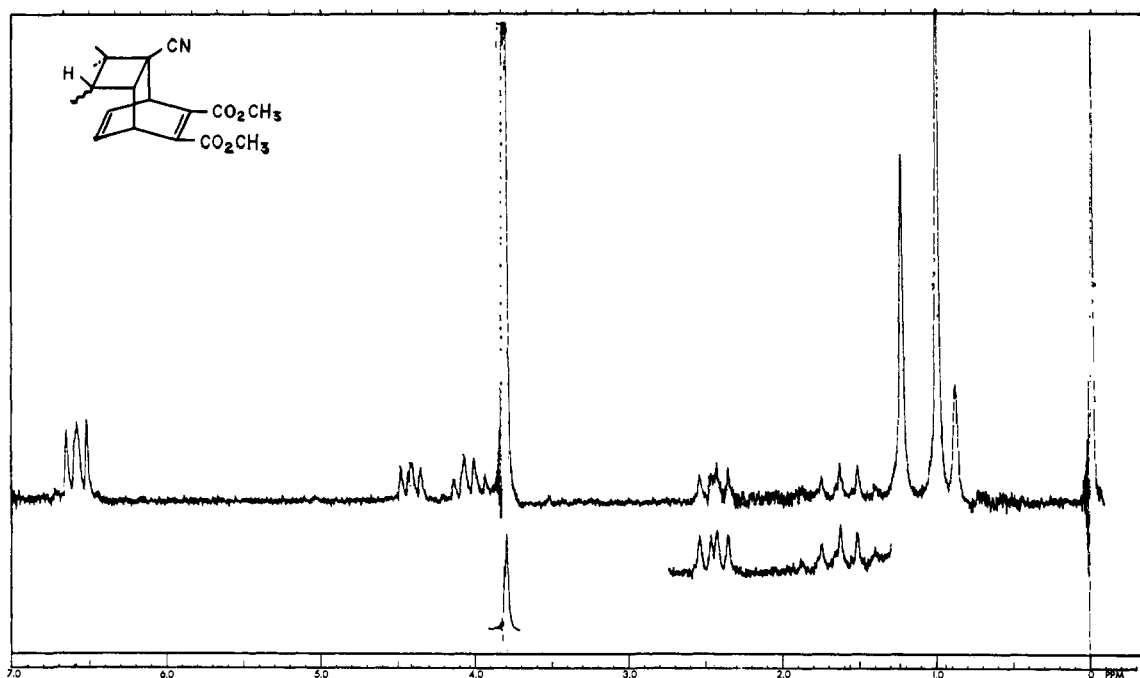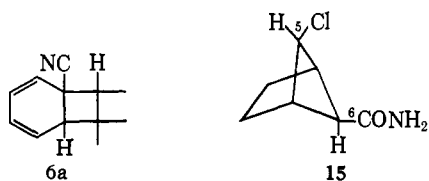

Fig. 2.—60-Mc. n.m.r. spectrum of the Diels–Alder condensation product 8 as a 20% solution in CDCl₃ with tetramethylsilane as an internal reference (0 p.p.m.).

magnitude have been observed in essentially planar cyclobutanes.

The spectrum of the Diels–Alder adduct (Fig. 2, Table I) does not differentiate between structures 8 and

8a, but the latter seems excluded since its formation would require attack of the dienophile on the more hindered, *endo* side of the bicyclo[4.2.0]octa-2,4-diene skeleton.
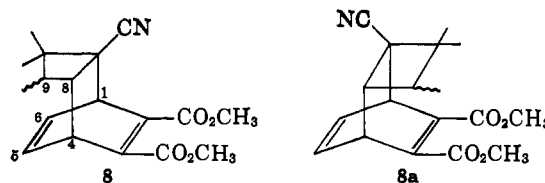
TABLE I

N.M.R. SPECTRUM[18] OF DIELS–ALDER ADDUCT 8

Protons	τ-Value (center of multiplet)	Pattern	J-Values, c.p.s.
gem-Dimethyl	8.77, 8.98	Singlets	...
C_9–CH_3	9.05	Doublet	6.8
C_9	8.37	Pentuplet	6.8
C_8	7.55	2 Doublets	$J_{89} = 6.8$ $J_{84} = 4$
–OCH_3	6.21	Singlets	...
C_4	5.97	Quartet	$J_{48} = J_{45} = J_{46} = 4$
C_1	5.50	Triplet	$J_{16} = J_{15} = 4$
C_5, C_6	3.42	Triplet	$J_{54} = J_{51} = J_{64} = J_{61} = 4$

In one irradiation benzophenone was added as a sensitizer in an attempt to increase the yield of the photoadduct.[22] There was isolated only 0.05% of photoadduct along with 54% (based on benzophenone) of a white crystalline compound. This proved to be 16 and the structure assigned is in agreement with the nuclear magnetic resonance spectrum. The low (5.47 τ) position of the tertiary proton indicates that it is adjacent to the ring oxygen and the orientation observed is in agreement with previous results.[23]

16

17
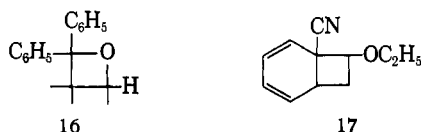
Several other olefins were irradiated in the presence of benzonitrile including ethyl vinyl ether, vinyl acetate, maleic anhydride and cis-1,2-dichloroethylene. Of these, only ethyl vinyl ether gave a 1:1 adduct which we believe to be 8-ethoxybicyclo[4.2.0]octa-2,4-diene-1-carbonitrile (17).

Photochemical addition of benzonitrile to acetylenes might be expected to lead, initially, to derivatives of bicyclo[4.2.0]octa-2,4,7-triene-1-carbonitrile, which could isomerize to substituted cyclooctatetraenes. Both 3-hexyne and 5-decyne did indeed add to benzonitrile in methanol solution[24] and the 1:1 adducts isolated are 2,3-diethylcyclooctatetraene-1-carbonitrile (18) and 2,3-di-n-butylcyclooctatetraene-1-carbonitrile (19), respectively

18, R = C_2H_5
19, R = n-C_4H_9

20

20a
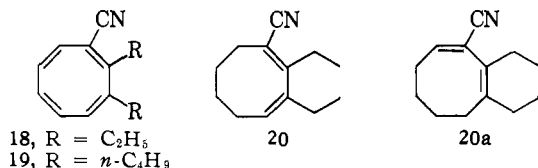
The infrared spectrum of the adduct 18 exhibited bands at 2200 (–C≡N), 1620 (conj. C=C) and 725 (cis-H–C=C–H) cm.$^{-1}$ and the ultraviolet spectrum (in ethanol) had a single maximum at 214 mμ (ϵ 21,500). The mass spectrum[25] shows a strong parent peak at m/e 185, the molecular weight calculated for a 1:1 adduct.

A n.m.r. spectrum of adduct 18 had three regions of resonance corresponding to vinyl, methylene and methyl protons in the ratios 4.5:3.5:6.0, respectively; calculated 5:4:6. Details of the spectrum are summarized

(22) G. O. Schenck and R. Steinmetz, Tetrahedron Letters, No. 21, 1 (1960).

(23) G. Büchi, C. G. Inman and E. S. Lipinsky, J. Am. Chem. Soc., 76, 4327 (1954).

(24) Irradiation of the pure liquids yielded no adduct. Methyl acetate was unsatisfactory as a solvent because of formation of acidic materials.

(25) Mass spectra were obtained through the courtesy of Professor Klaus Biemann of the Department of Chemistry at M. I. T.; the instrument used was a CEC 21-103C spectrometer.

in Table II. The relative intensities observed excluded a bicyclic structure for the adduct. Further evidence in favor of a monocyclic structure was forthcoming when the adduct was found to be stable to pyrolysis at 440° and when prolonged hydrogenation over platinum oxide in acetic anhydride solution resulted in absorption of 5.7 equivalents of hydrogen.

TABLE II

N.M.R. SPECTRUM OF 2,3-DIETHYLCYCLOÖCTATETRAENE-1-CARBONITRILE (18)

Proton on	τ-Value (center of multiplet)	Pattern	J-Values, c.p.s.
Ring	3.75	Fine splitting	...
Ring	3.93	Fine splitting	...
Methylene group	7.07	Sextet (?)	7.8
Methylene group	7.63	Quartet	7.8
Methyl group	8.87	Triplet	7.8
Methyl group	8.91	Triplet	7.8

Hydrogenation of 18 over Pd–SrCO$_3$[14] gave a mixture of two reduction products and a mass spectrum revealed parent peaks at m/e 189 and 191, corresponding to tetrahydro (20) and hexahydro compounds, respectively. The major constituent (20) was purified by v.p.c., ozonized in chloroform at –25°, and subsequently oxidized with aqueous hydrogen peroxide. Adipic acid was isolated (see Experimental) and identified by melting point, mixture melting point and infrared spectrum. Propionic and formic acids were present in the mixture after peroxide oxidation, as indicated by paper chromatography.

A n.m.r. spectrum[18] of the pure tetrahydro derivative 20 exhibited three areas of resonance: (a) two overlapping triplets, centered at 9.03 and 9.10 τ, with separation between the triplets of about 4 c.p.s., and a coupling constant in each of 7.5 c.p.s.; (b) a complex series of sharp peaks, centered at 7.83 τ, and ranging from 90 to 174 c.p.s.; (c) a symmetrical triplet, centered at 4.40 τ, with a coupling constant of 7.3 c.p.s.

Area measurements on n.m.r. curves of diene 20 gave the following ratios of vinyl to methylene to methyl protons: 1.0:14.3:7.8; the calculated ratios being 1:12:6. The spectrum does not differentiate between structures 20 and 20a, but the latter is excluded by the formation of adipic acid on ozonolysis.

An analogous structure (19) is assigned to the adduct from benzonitrile and 5-decyne on the basis of the similarity of its spectra and physical properties with those of the adduct from 3-hexyne.

The irradiation of benzonitrile and acetylene was investigated, using methanol as solvent, and cooling the reaction mixture to –20° to increase the solubility of acetylene, but no cyclooctatetraenecarbonitrile was formed. Similarly, benzonitrile and ethoxyacetylene gave no 1:1 adduct. Irradiation of benzene and 3-hexyne and of methyl benzoate and 3-hexyne under conditions used for the preparation of 18 produced no adducts.

The recent literature on photochemical reactions contains several independent reports of the light-induced reaction of an olefin or an acetylene with an aromatic compound, to form, initially, a 1:1 adduct containing the bicyclo[4.2.0]octane skeleton.

A 2:1 adduct of benzene and maleic anhydride has been obtained[26,27] and shown to have structure 21 with the stereochemistry indicated.[27] Similar irradiations have produced 2:1 adducts from maleic anhydride and toluene, o-xylene and chlorobenzene.[22] The use of

(26) H. J. F. Angus and D. Bryce-Smith, J. Chem. Soc., 4791 (1960).

(27) E. Grovenstein, D. V. Rao and J. W. Taylor, J. Am. Chem. Soc., 83, 1705 (1961).

benzophenone as a sensitizer increased the yield five-fold in 3 hours,[22] whereas acetone had no apparent effect.[26] More recently[28] a 1:1 adduct between maleic anhydride and phenanthrene has also been reported and structure 22 was assigned to it; benzophenone and benzil sensitized this irradiation also.


21   **22**   **23**
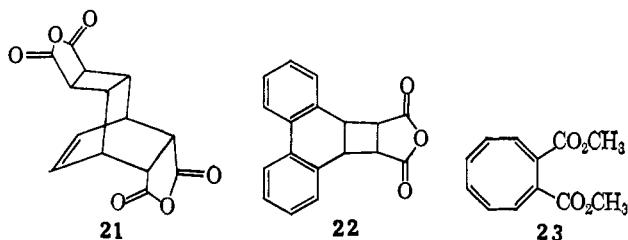
Irradiation of benzene in the presence of various acetylenes has been found to produce substituted cyclooctatetraenes,[29,30] e.g., dimethyl 1,8- (or 1,2-)cyclooctatraenedicarboxylate (23) from dimethyl acetylenedicarboxylate and benzene.[29] From benzene and methyl propiolate or phenylacetylene there is obtained methyl cyclooctatetraenecarboxylate and phenylcyclooctatetraene, respectively.[30]

Mechanism

The structures of the products obtained are in agreement with the hypothesis[23] that the product arises from the diradical (triplet) intermediate of greatest stability. Thus from benzonitrile and 2-methyl-2-butene, intermediate 24 would be the most stable of the four possible intermediates. Similarly, in the formation of the trimethylene oxide 16, the most stable diradical would be that which leads to the structure observed.

24
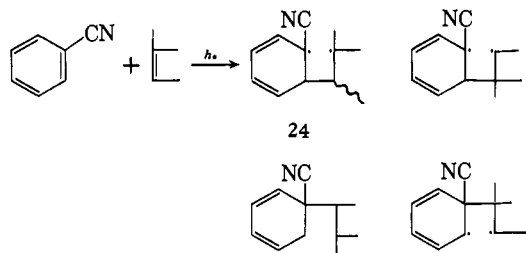
The interesting contrast between pyrolysis and photolysis of the bicyclooctadiene 6 has no ready explanation. In a pyrolytic reaction the intermediate 25 is expected to be the most stable diradical and would probably form more easily than 24; such an intermediate could easily decompose to give the tetraene 13. When light is the source of energy, the bond which breaks initially need not be the one which is thermally most labile; thus 24 may be the intermediate produced in the light-catalyzed reaction. Although the photochemical cleavage of 6 was run in a solvent rather than with the neat liquid, it is reasonable to assume that an equilibrium is set up between the starting materials and the product. Such an equilibrium would explain the low conversion observed. Benzophenone may catalyze cleavage more efficiently than addition and this would account for the low yield of photoadduct when benzophenone was present.


24   **6**   **25**
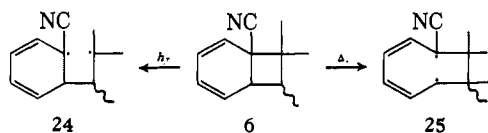
(28) D. Bryce-Smith and B. Vickery, *Chem. Ind.* (London), 429 (1961).
(29) E. Grovenstein and D. V. Rao, *Tetrahedron Letters*, **No. 4**, 148 (1961).
(30) D. Bryce-Smith and J. E. Lodge, *Proc. Chem. Soc.*, 333 (1961).

Formation of cyclooctatetraenes from aromatic compounds and acetylenes presumably proceeds through a bicyclo[4.2.0]octa-2,4,7-triene intermediate which rapidly isomerizes to a cyclooctatetraene. No conclusions concerning the radical intermediates can be made since the only acetylenes which gave successful reactions were symmetrical.

$\longrightarrow$ **18**
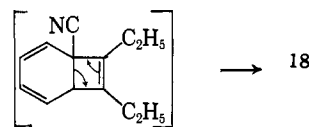
Experimental

Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Box 25, Herlev, Denmark, and Dr. S. M. Nagy and Associates of the Massachusetts Institute of Technology. Melting points were taken on a Kofler hot-stage and are corrected; boiling points are uncorrected. Woelm neutral alumina and Davison activated silica gel were used for chromatograms. Infrared spectra were recorded on a Perkin–Elmer model 137 Infracord and a Perkin–Elmer model 21 spectrophotometer in the media indicated. Infrared bands are listed as weak (w), medium (m) or strong (s). Ultraviolet spectra were obtained on a Cary recording spectrophotometer, model II.

The irradiation lamp was a quartz-contained mercury arc ("Labortauchelampe S 81," Quartzlampengesellschaft Hanau). The irradiation vessels were of two types: a flask fitted with an inlet tube for the lamp, a reflux condenser and a fritted disk in the bottom of the flask through which nitrogen was bubbled, and a 500-ml. Kjeldahl flask with a side-arm. Irradiations in the latter were stirred with a magnetic bar under a positive pressure of nitrogen. The flask was immersed in a running water bath to provide cooling.

Irradiation of Benzonitrile and 2-Methyl-2-butene.—Benzonitrile (232 g., 2.25 moles) and 2-methyl-2-butene (175 g., 2.50 moles) were placed in an irradiation vessel, a few crystals of catechol added, and nitrogen was bubbled through for 20 minutes before turning on the lamp. After 11 days irradiation excess olefin was removed by distillation through a Vigreux column, first at atmospheric pressure and finally at 45 mm., the temperature of the oil-bath being kept below 80°; recovery, 117 g. (67%). Excess benzonitrile was removed at 42° (1.7 mm.); recovery, 212.5 g. (91%). The dark residue was distilled immediately, b.p. 80–95° (0.1 mm.), to yield 17.5 g. of a light yellow oil. This was dissolved in 100 ml. of ether and washed with 4 × 50 ml. of ice-cold 5% hydrochloric acid–20% sodium chloride solution, followed by 3 × 50 ml. of cold 5% sodium bicarbonate solution saturated with sodium chloride. The aqueous layers were extracted with fresh ether and the combined ether solutions dried over sodium sulfate. The solvent was removed and the yellow oil distilled through a short column to yield three colorless fractions: (1) b.p. 37–42° (1.0 mm.), 4.2 g., benzonitrile; (2) b.p. 70–80° (1.0 mm.), 5.6 g., photoadduct; (3) b.p. 65–70° (0.6 mm.), 5.0 g., photoadduct; yield 10.6 g. (42% based on benzonitrile consumed, 2.7% conversion of benzonitrile), λ_{max}^{EtOH} 273 mμ (ϵ 3200), λ_{min} 236 mμ (ϵ 782). The second fraction crystallized after several weeks storage in a freezer. It was purified by recrystallization from small amounts of pentane at −20°, followed by short-path distillation. A sample of the liquid was induced to crystallize in a melting-point capillary and had m.p. 26–30°; λ_{max}^{EtOH} 273 mμ (ϵ 3450), λ_{min} 229 mμ (ϵ 446); ν_{max}^{liquid} 3040(m), 2950(s), 2970(m), 2230(m), 1740(w, broad), 1640(w, broad), 1585(m, sharp), 1470, 1455, 1390, 1375(all s), 890(m), 770(m), 690(s) cm.$^{-1}$; n.m.r., see Fig. 1.

Anal. Calcd. for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.09. Found: C, 83.08; H, 8.65; N, 8.21.

In one photochemical experiment, 10 g. of benzophenone was added to the solution and on chromatography of the reaction mixture 7.5 g. of crude 2,2-diphenyl-3,3,4-trimethyloxetane (17) was obtained. One recrystallization from ethanol gave a product with m.p. 109–110°, unchanged by further recrystallization; λ_{max}^{EtOH} 222, 248, 253, 259 and 266 mμ (ϵ 12,000, 318, 405, 454 and 343, respectively); ν_{max}^{KBr} 3040, 3020, 2940, 2860, 1600(w), 1490, 1470, 1450, 1390, 1370 (all medium) 990(s) and 710(s) cm.$^{-1}$; n.m.r.[18] (20% CDCl$_3$, τ-values refer to multiplet centers; measured relative areas in brackets), 8.98 τ (5.2), singlet; 8.77 τ (3.0), doublet, J = 7.0 c.p.s.; 5.47 τ (0.80), quartet, J = 7.0 c.p.s.; 2.60 τ (8.80), complex multiplet; calcd. relative areas: 6:3:1:10.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.69; H, 7.99. Found: C, 85.62; H, 7.92.

Similar irradiation of benzonitrile (51.5 g.) and ethyl vinyl ether (36 g.) for 44 hr. yielded 0.5 g. of 8-ethoxybicyclo[4.2.0]-

octa-2,4-diene-1-carbonitrile, b.p. 55–57° (0.05 mm.); ultraviolet spectrum, λ_{max}^{EtOH} 277 mμ (ϵ 3660, λ_{min} 234 mμ (ϵ 2360); $\nu_{max}^{CS_2}$ 2220 and 1600 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48. Found: C, 75.61; H, 7.46.

Photochemical Addition of Benzonitrile to 3-Hexyne.— Benzonitrile (35.9 g., 0.35 mole) and redistilled 3-hexyne (28 g., 0.34 mole) were added to an irradiation vessel, and 400 ml. of anhydrous methanol was distilled into the reaction vessel under a slightly positive pressure of nitrogen. A thin layer of polymer forming around the heated section of the lamp had to be removed twice a day. This was most easily done by immersing the lamp, first in concd. sulfuric acid, and then in concd. ammonium hydroxide. After 3 weeks irradiation, excess acetylene and solvent were removed at 50° (80 mm.), and unreacted benzonitrile was distilled from the dark orange residue through a spinning-band column at a bath temperature of 60–70° (1.5 mm.); recovery, 20 g. (56%). The thick residue (7.1 g.) was chromatographed over 200 g. of Florisil.[31] Elution with pentane–benzene (40:60) gave a product which was distilled through a micro spinning-band column at 62–72° (0.07–0.40 mm.); yield 2.43 g. (8%) of a light yellow, pleasant smelling oil which was homogeneous to vapor phase chromatography on a silicone oil column; λ_{max}^{EtOH} 214 mμ (ϵ 21,500); ν_{max}^{liquid} 3000(m), 2900(s), 2205(m), 1620(w), 1450(s), 1370(m), 870(s), 830, 790, 760 (all m) and 725(vs) cm.$^{-1}$; n.m.r., see text.

Anal. Calcd. for $C_{13}H_{15}N$: C, 84.24; H, 8.16; N, 7.56. Found: C, 84.04; H, 8.15; N, 7.86.

Similarly, irradiation of benzonitrile and 5-decyne gave the corresponding adduct, λ_{max}^{EtOH} 216 mμ (ϵ 20,800).

Anal. Calcd. for $C_{17}H_{23}N$: C, 84.59; H, 9.60; N, 5.80. Found: C, 84.43; H, 9.56; N, 5.98.

Irradiation of 5-decyne or 2-butyne in excess benzonitrile without solvent yielded less than 100 mg. of adduct in 7 days.

Irradiation of 7,8,8-Trimethylbicyclo[4.2.0]octa-2,4-diene-1-carbonitrile.—Photoadduct 6 (497 mg.) in methanol (10 ml.) was irradiated in a quartz container cooled in a running waterbath. The ultraviolet spectrum of an aliquot of this solution after 4 hr. 15 min. irradiation showed the three high intensity peaks characteristic of benzonitrile at 222, 225 and 231 mμ; conversion was 42%. After 22-hr. irradiation the ultraviolet spectrum was a composite of the spectra of benzonitrile and tetraene 13. From the intensity of absorption at 320 mμ, conversion to the tetraene was calculated to be 8% and to benzonitrile 90%. There was no further change after a total of 52 hr. Vapor phase chromatographic analyses of the solution established the presence of both benzonitrile and 2-methyl-2-butene and the apparent absence of photoadduct; the tetraene was not eluted because of its ready polymerization. By comparison with standard solutions, the conversion to benzonitrile and olefin was calculated to be greater than 90%. The n.m.r. spectrum of the crude residue left after evaporation of solvent showed that there was a small amount (1–2%) of photoadduct remaining; this amount would have escaped detection on the v.p.c. A control solution of the photoadduct which was kept in the dark for the same length of time had an unchanged ultraviolet spectrum and v.p.c. showed the presence of starting material only.

Condensation of 7,8,8-Trimethylbicyclo[4.2.0]octa-2,4-diene-1-carbonitrile (6) with Dimethyl Acetylenedicarboxylate.— Photoadduct 6 (2.00 g., 11.6 mmoles) and dimethyl acetylenedicarboxylate (2.80 g., 20 mmoles) were dissolved in 20 ml. of benzene and 50 mg. of catechol was added. The reaction mixture was flushed with nitrogen and heated in an oil-bath for 50 hr. at 65°, followed by further heating at gentle reflux during 48 hr., under a positive pressure of nitrogen. The solvent was removed *in vacuo* and when no crystals deposited after 16 hr. at −20°, the mixture was dissolved in 6 ml. of pentane–benzene (1:1) and chromatographed on 150 g. of silica gel. Benzene eluted 719 mg. (36%) of starting material and ether–benzene (1:50) eluted 1.50 g. (54%) of acetylenic ester. Further elution with 5–20% ether in benzene yielded 2.44 g. (66% conversion) of crude adduct in the form of a thick oil. Cooling a concentrated ether solution of the product in Dry Ice–acetone caused immediate crystallization. Ether was found to be the best solvent for recrystallization and a total of 1.19 g. (32% conversion, 50% yield) of pure adduct was obtained, m.p. 121.5–123°; λ_{sh}^{EtOH} 215 mμ (ϵ 4500); $\nu_{max}^{CCl_4}$ 2940(m), 2220(w), 1740(s), 1640(w), 1605(w), 1435(m), 1280(s) cm.$^{-1}$; n.m.r., see Fig. 2.

Anal. Calcd. for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71. Found: C, 68.77; H, 6.69.

Pyrolysis of the Diels–Alder Adduct 8.—The adduct 8 (1.03 g., 3.50 mmoles) was placed in a 10-ml. side-arm flask fitted with a receiver, containing 1 ml. of methanol cooled to −20°.

The pressure was reduced to 50 mm. and the flask immersed in an oil-bath at 165°. The adduct melted and pyrolyzed to give a clear, colorless distillate which was hydrogenated immediately in 3 ml. of methanol over 63 mg. of 7% Pd–SrCO₃.[14] Hydrogen absorption (38 ml., 1.6 mmoles) was complete in 78 minutes. The solution was filtered, the catalyst washed with 1 ml. of methanol, and the solvent removed at atmospheric pressure. The residue was distilled at 50 mm. to give 72 mg. of nitrile 12. Nuclear magnetic resonance and infrared spectra of this material and that obtained below possessed the same bands, differing in intensity. Both products showed only one peak on several v.p.c. columns, but the n.m.r. spectra indicated clearly that a mixture of epimers was present.

Hydrogenation of 2,2-Dimethyl-3-methylenecyclobutanecarbonitrile.[15,16]—Nitrile 11 (2.39 g., 19.7 mmoles), in 10 ml. of methanol, was reduced over 153 mg. of Pd–SrCO₃. After 2.5 hours, hydrogen absorption ceased and a total of 480 ml. of hydrogen had been absorbed (calcd., 480 ml. at 24°). The solution was filtered through cotton, washed with 2 × 5 ml. of methanol, and the solvent removed through a spinning-band column in order to minimize loss of the volatile product which was subsequently distilled through a micro spinning band column; b.p. 70–80° (55 mm.), yield 1.97 g. (81%); ultraviolet spectrum: ϵ at 210 mμ is 14 compared to 205 for 11; infrared spectrum: 2240 cm.$^{-1}$ (sharp).

Anal. Calcd. for $C_8H_{13}N$: C, 78.00; H, 10.64; N, 11.37. Found: C, 78.21; H, 10.51; N, 11.70.

Identification of Dimethyl Phthalate.—The residue in the flask from the above pyrolysis of the Diels–Alder adduct had an infrared spectrum nearly identical with that of dimethyl phthalate. A portion (115 mg.) in ethanol was added to a solution of potassium hydroxide in aqueous ethanol and refluxed 4 hours. The solution was acidified and evaporated to dryness *in vacuo*. Sublimation (bath 200°, 760 mm.) gave 60 mg. (67%) of phthalic anhydride, m.p. and mixture m.p. 130–131°.

1-Methylacetamido-7,8,8-trimethylbicyclo[4.2.0]octane (7).— A solution of 7,8,8-trimethylbicyclo[4.2.0]octa-2,4-diene-1-carbonitrile (6) (790 mg.) in acetic anhydride was hydrogenated at room temperature and atmospheric pressure in the presence of 100 mg. of Adams' catalyst. Uptake of hydrogen beyond one mole-equivalent was slow and the reaction was continued for 72 hours with addition of fresh catalyst. The solution was filtered and excess anhydride destroyed by stirring with water. The acid was neutralized with solid potassium hydroxide and the product extracted with ether. After the ether solution was washed with 5% hydrochloric acid and water, the solvent was evaporated to give 830 mg. of a white sticky solid. Crystallization from petroleum ether–benzene gave colorless rods, m.p. 139–140°. The infrared spectrum (10% in CHCl₃) shows bands characteristic of monosubstituted amides at 3340, 1650 and 1510 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{25}NO$: C, 75.28; H, 11.28; N, 6.27. Found: C, 75.69; H, 11.54; N, 6.16.

Pyrolysis of the Photoadduct 6.—The photoadduct (1.00 g.) was dissolved in 10 ml. of benzene containing a few crystals of catechol, placed in a bomb tube which was flushed with nitrogen, evacuated and sealed. The tube was heated to 128° for 38 hr., cooled to freeze the solvent, and opened. Benzene was distilled off at atmospheric pressure and the residue was distilled. A volatile material (250 mg.), b.p. 60–80° (bath temperature) (0.2 mm.) was obtained and ultraviolet and n.m.r. spectra indicated that it was a mixture of benzonitrile (15%) and starting material (85%). Raising the bath temperature to 110–120° caused distillation of 350 mg. of a clear oil. A n.m.r. spectrum indicated a mixture of the tetraene 13 (70%) and starting material (30%). It showed all peaks of the starting material and in addition five sharp peaks at 7.83, 8.03, 8.08, 8.13 and 8.25 τ. The sample partially crystallized in a refrigerator and the crystals were washed with pentane and dried under vacuum. A sample which had been stored at room temperature for a few hours was found to be insoluble in ethanol, but a fresh sample had λ_{sh}^{EtOH} 295 mμ (ϵ 38,000), λ_{max} 307 mμ(ϵ 45,000), λ_{max} 322 mμ (ϵ 1000); ν_{max}^{liquid}: 3050(s), 2950(s), 2240(m), 1640(w), 1610(m), 1570(m), 1440(s), 1375(s), 1000 (vs), 960(s), 720(vs), 690(s) cm.$^{-1}$. The compound melted below room temperature and did not give satisfactory analytical values.

Hydrogenation of 2,3-Diethylcycloöctatetraene-1-carbonitrile (18).—The photoadduct (832 mg., 4.50 mmoles) in 1 ml. of methanol was shaken with a small amount of Pd–SrCO₃ catalyst for 3 hr. before reduction. The methanol solution was centrifuged and the catalyst washed with two 1-ml. portions of solvent. The two methanol solutions were combined and added (with the aid of a syringe) to a hydrogenation flask containing methanol (5 ml.) and Pd–SrCO₃ catalyst (52 mg.). Hydrogen absorption began immediately and proceeded with no break in the curve until 2.03 equivalents had been absorbed, at which point the reaction stopped. The solution was centrifuged and decanted from the catalyst which was washed with two 10-ml.

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(31) Florisil has very low affinity for low molecular weight materials but retains the colored and polymeric products from irradiations. The products usually come through in the first two or three fractions of eluent

portions of methanol. The methanol solutions were poured into 40 ml. of water and the aqueous suspension was extracted with five 10-ml. portions of pentane. After drying over calcium chloride, the solvent was evaporated to give 768 mg. (90%) of crude material which was distilled, b.p. 70° (0.05 mm.), λ_{max}^{EtOH} (of the mixture) 222 and 250 mμ (ϵ 8600 and 3500). Analysis by v.p.c. showed that the product was a 3:1 mixture of two compounds, one a tetrahydro and the other a hexahydro derivative, as indicated by mass spectral parent peaks at m/e 189 and 191, respectively. Samples of the two components were collected from v.p.c., and the major, faster eluting component was obtained pure; λ_{max}^{EtOH} 226 and 250 mμ (ϵ 8080 and 5060); ν_{max}^{liquid} 2900(vs), 2210(m, sharp), 1650(w), 1620(m), 1420(vs), 920(m), 865(s) cm.$^{-1}$; n.m.r.: symmetrical triplet centered at 4.40 τ, J = 7.3 c.p.s.

Anal. Calcd. for $C_{13}H_{19}N$: C, 82.47; H, 10.12; N, 7.40. Found: C, 82.90; H, 9.79; N, 7.01.

The minor component was contaminated with about 25% of the other; λ_{max}^{EtOH} 224 mμ (ϵ 7440), ϵ at 250 mμ of 1340. No further work was done with this material.

Ozonolysis of 2,3-Diethylcycloöcta-1,3-diene-1-carbonitrile (20).—A sample of the pure tetrahydro derivative described above (130 mg., 0.69 mmole) was dissolved in 5 ml. of chloroform and ozone passed through the solution at −25° to −30° for 15 minutes. At the end of this time the solution had become bright green in color. The solvent was removed below 30° to leave a yellow-green oil to which was added 5 ml. of water and 1.5 ml. of 3% hydrogen peroxide (1.3 mmoles). The mixture was heated for 30 minutes on the steam-bath, during which

time most of the oil dissolved. Another 0.5 ml. of 3% hydrogen peroxide was added and the mixture left at room temperature for 45 min. Aqueous ammonium hydroxide (1 ml. of 10% solution) was then added and 20 microliters of this solution was placed on a paper chromatogram along with a comparison sample of propionic acid in ammonia. The developing system was made up by adding 1 ml. of concd. ammonium hydroxide to 100 ml. of denatured ethanol; the spray reagent was 0.05% bromphenol blue in water acidified with citric acid.[32] Three spots appeared on the chromatogram of the unknown with R_f values of 0.40 (propionic acid), 0.31 (formic acid) and 0.072. The aqueous solution was made strongly basic with sodium hydroxide and extracted with three 10-ml. portions of ether. The ether solution was dried (Na_2SO_4) and evaporated to yield 21 mg. of a clear oil (ν_{max}^{liquid} 3450, 2950, 2220, 1745, 1710(sh), 1450 and 1370 cm.$^{-1}$) which was discarded. The aqueous solution was acidified (HCl) and extracted continuously with ether for 22 hours. Drying and careful evaporation left a sharp-smelling oil which crystallized partially in a refrigerator. Two recrystallizations from 0.2 ml. of concd. nitric acid gave a compound, m.p. 152–154.4°, pure and mixed with authentic adipic acid. The infrared spectrum of the unknown (KBr) was superimposable on that of recrystallized adipic acid.

(32) E. P. Kennedy and H. A. Barker, *Anal. Chem.*, **23**, 1033 (1951).

Kinetics and Mechanism of the Spontaneous Decompositions of Some Peroxoacids, Hydrogen Peroxide and *t*-Butyl Hydroperoxide

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The kinetics of the decompositions of peroxoacetic acid, peroxochloroacetic acid, peroxomonophosphoric acid, hydrogen peroxide and *t*-butyl hydroperoxide have been measured in aqueous alkaline media. EDTA was added to suppress homogeneous catalysis presumably by trace metal ions. The decompositions of the peroxoacids studied were second order with respect to the peroxoacid concentrations. The dependence of rate on pH indicated that the rate of decomposition is maximum at 50% dissociation of the peroxoacids. Peroxochloroacetic acid undergoes spontaneous decomposition about 100 times as fast as does peroxoacetic acid, although the former peroxoacid oxidizes nitrosobenzene only 30 times as rapidly as does the latter peroxoacid.

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The analysis of the products of decomposition of $CH_3CO^{18}-O^{18}-H$ showed that 83% of the heavy oxygen isotope appeared as $O^{18}-O^{18}$. A reinvestigation of the aqueous alkaline decomposition of hydrogen peroxide showed that this decomposition is almost immeasurably slow when the base is purified and EDTA added to the reaction solution. Under these conditions the rate of decomposition is about one-hundredth that attributed to spontaneous decomposition alone in the literature. Mechanistic implications of these data are discussed.

Introduction

The results of a kinetic study of the aqueous decomposition of Caro acid were reported in a previous paper.[1] Both the catalytic and spontaneous paths were observed for decomposition, which was shown to be homogeneous. The catalytic path was eliminated by addition of EDTA and the spontaneous decomposition found to be second order with respect to Caro acid concentrations. The dependence of rate on pH indicated that the rate law is: rate = $k_2[SO_5^{-2}][HSO_5^{-}]$. These results were interpreted in terms of a nucleophilic attack by the dinegative anion of Caro acid upon the peroxidic oxygen of its mononegative ion.

The decomposition of H_2O_2 is known to be catalyzed heterogeneously by the surface of the container[2] and homogeneously by many transition and heavy metal ions even at very low concentrations. Despite numerous kinetic studies[3,4] it seems certain that the true rate of the spontaneous decomposition of H_2O_2 has never been measured. Duke and Haas[3] were able to eliminate

successfully heterogeneous catalysis, but a reinvestigation of their system has now revealed that homogeneous catalysis must have contributed significantly to the rate attributed to spontaneous decomposition alone.

A recent study[5] of the uncatalyzed decomposition of variously substituted peroxobenzoic acids in aqueous solutions has shown that the reaction is governed by the second-order kinetic law with maximum rates at 50% dissociation of the peroxoacids; the behavior is thus analogous to that reported for Caro acid.[1]

This paper presents data on the kinetics of the decompositions of peroxoacetic acid, peroxochloroacetic acid, peroxomonophosphoric acid, *t*-butyl hydroperoxide and hydrogen peroxide. Mechanistic implications of these studies are discussed.

Results

The kinetics were measured by following the rate of disappearance of the peroxo compound iodometrically in each case. The compounds studied were of the type

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ROOH, where R is H, *t*-butyl, CH_3C-, $ClCH_2C-$ or

(1) D. L. Ball and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1125 (1956).

(2) L. Erdy and I. Inczedy, *Acta Chim. Acad. Sci. Hung.*, **7**, 93 (1955).

(3) F. R. Duke and T. W. Haas, *J. Phys. Chem.*, **65**, 304 (1961).

(4) W. C. Schumb, C. N. Satterfield and R. L. Wentworth, "Hydrogen Peroxide," Reinhold Publishing Corp., New York, N. Y., 1955, Ch. 8 and references cited therein.

(5) J. F. Goodman, P. Robson and E. R. Wilson, *Trans. Faraday Soc.*, **58**, 1846 (1962).