THE JOURNAL OF Organic Chemistry®

VOLUME 41, NUMBER 18 SEPTEMBER 3, 1976

Synthesis and Chemistry of Some Polychlorinated Oxetanes

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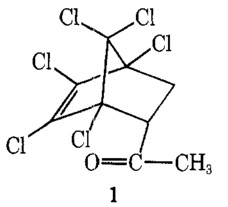
Received April 20, 1976

Three new polychlorooxetanes have been prepared by photocyclizations of the halogenated acylnorbornenes **1**, **2a**, and **2b**. The oxetanes were unusually stable toward acidic reagents, but **4a** was shown to undergo a deep-seated rearrangement on treatment with sulfuric acid. The major product of this reaction was shown by x-ray crystallography to be the nortricyclanone derivative **5** which is believed to have been formed via intramolecular participation of a methoxyl group concurrent with ring opening of the oxetane ring. Some aspects of bond shortening effects in cyclopropyl ketones are discussed, and it is concluded that hybridization effects could be sufficient to explain the data.

Studies of the synthesis and chemistry of polyhalogenated ring systems have generated a wealth of useful synthetic intermediates and numerous mechanistically interesting transformations. For example, many novel ring systems have been synthesized by a general route which involves photocyclization of a polyhalonorbornene followed by a ring contraction reaction of the Favorskii type. Ring systems which have been prepared by this sequence include the following: secocubane,[1] homocubane,[2] cubane,[3] and norcubane.[4] Other ring systems, e.g., bishomocubane[5] and "bird-cage" systems,[6] have been prepared directly by intramolecular photocycloaddition reactions of polyhalogenated ring systems. The chemistry of these molecules is frequently characterized by deep-seated molecular rearrangements as a consequence of strain relief and the electronic influence of the halogen atoms on the reaction intermediates.[1,5,7,8,9] These results and our interest in the chemistry of polycyclic oxetanes[10,11] stimulated an investigation of the photochemistry of the polychloroacylnorbornenes **1**, **2a**, and **2b**.



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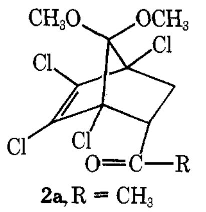
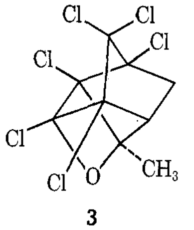


2a, R = CH$_3$
b, R = H

These molecules are of photochemical interest in that they offer an opportunity to evaluate the steric and electronic effects of chlorine on the efficiency of intramolecular oxetane formation. In simpler acylnorbornenes, steric inhibition does not appear to play a role,[10] but the increased interactions caused by the four proximate chlorine atoms could be deleterious. In addition, the presence of chlorine on the double bond would be expected to raise the ionization potential of the π system[12] and thereby lower the rate of exciplex formation between that function and the excited carbonyl group.[13,14] Consequently, lowered quantum efficiency and/or side reactions might ensue.

Syntheses. The adducts **1** and **2** were prepared by Diels–Alder reactions according to literature procedures,[7,15] and it is believed that the carbonyl functions are largely or exclusively endo oriented on the basis of NMR data and chemical yield data (vide infra). Irradiations of **1**, **2a**, and **2b** in benzene gave isomeric products whose spectral parameters[16] were consistent with oxetane structures **3**, **4a**, and **4b**, respectively. On a qualitative basis it was observed that irradiation times were much longer than those required for the nonhalogenated analogues.



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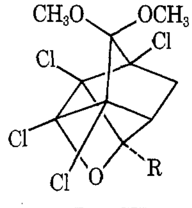


4a, R = CH$_3$
b, R = H

Chemistry of Oxetanes 3 and 4a. Oxetane **3** showed a remarkable stability toward acid-catalyzed rearrangements in contrast to nonchlorinated analogues. The material was recovered unchanged after treatment with perchloric acid in methanol (42 h, reflux), boron trifluoride etherate (72 h, reflux), and concentrated sulfuric acid (0 °C, 1 h). Treatment of **3** with aluminum chloride for 20 h in refluxing benzene resulted in formation of the original ketone **1** in 43% yield. Since the nonchlorinated analogue undergoes acid-catalyzed cleavage at the carbon bearing the methyl substituent,[14] the geminal chlorine atom may actually facilitate the ring opening. The major effect of the chlorine atoms could be to reduce the

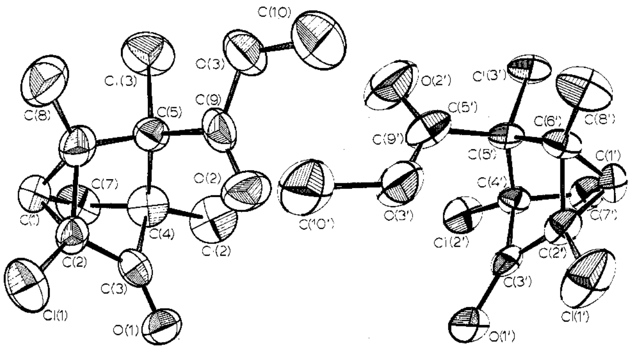


Figure 1. (+)- and (−)-methyl 2,4,5-trichloro-6-methyltricyclo[2.2.1.$0^{2,6}$]heptan-3-one-*syn*-5-carboxylate; 50% probability thermal ellipsoids are shown.

Table I. Selected Bond Lengths[a] of Nortricyclene Derivatives

Bond	Nortricyclene[b]	4-Chloronortricyclene[c]	5[d]
C(1)–C(2)	1.50	1.510	1.52
C(2)–C(6)	1.50	1.510	1.54
C(1)–C(6)	1.50	1.510	1.52
C(1)–C(7)	1.54	1.535	1.50
C(2)–C(3)	1.54	1.535	1.48
C(5)–C(6)	1.54	1.535	1.52
C(3)–C(4)	1.54	1.537	1.55
C(4)–C(5)	1.54	1.537	1.54
C(4)–C(7)	1.54	1.537	1.53

[a] Angstroms. [b] Reference 17. [c] Reference 18, standard deviations range from 0.0078 to 0.0025. [d] Average of the values of the enantiomers.

basicity of the oxygen atom and, hence, the overall reaction rate.

Similarly, oxetane **4a** was shown to be stable toward perchloric acid in methanol (3 days, reflux), $FeCl_3$ (19 h, 80 °C), and sulfuric acid in methanol (3 days, reflux). A rapid reaction was observed upon treatment of **4a** with concentrated sulfuric acid (0 °C, 15 min) from which a crystalline product was isolated in 58% yield. The elemental analysis of this material revealed that it had been formed from **4a** with the loss of the elements of CH_3Cl. The following functionality was identified from an analysis of various spectroscopic data: carbonyl (5.55, 5.65, and 5.75 μ); CH_3O (δ 3.9); and CH_3C (δ 1.6, s). No evidence for unsaturation could be adduced from the spectral data, but the presence of tetrasubstituted double bonds could not be excluded.

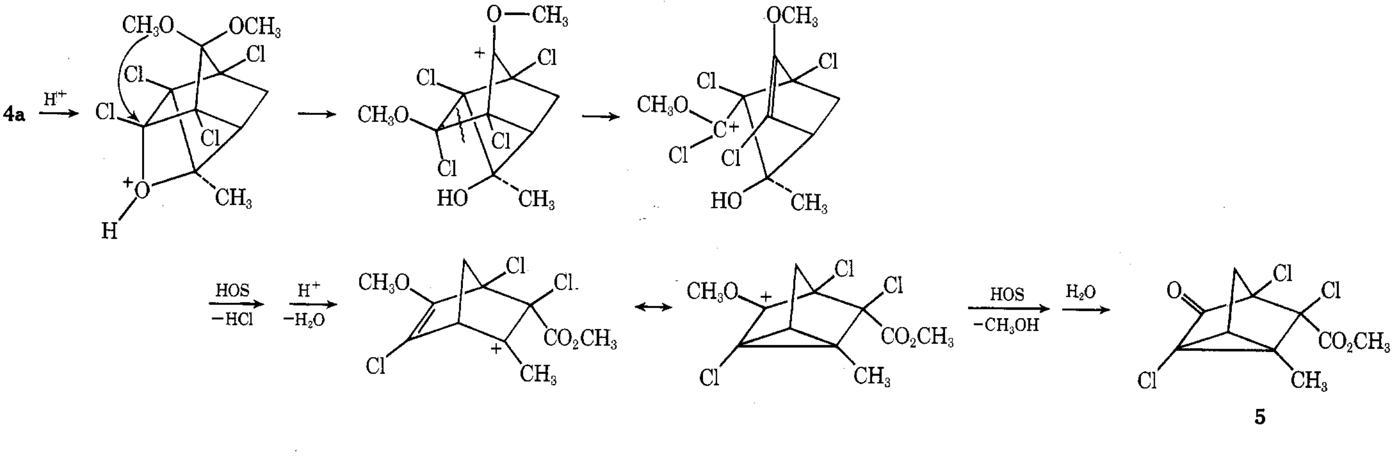
In view of the larger number of possible structures, it was decided to resolve the structure of this product by use of x-ray crystallographic techniques. The results of this determination are shown in the ORTEP plot (Figure 1). The relative orientations of the two enantiomers in the asymmetric unit has been altered slightly from that in the crystal to allow for easier visualization. It is noteworthy that the conformations of the carbomethoxy groupings are nonidentical in the two enantiomers shown. Since the unit cell is centrosymmetric, this asymmetry is balanced by the presence of a mirror image pair elsewhere in the cell.

The structural parameters obtained for this system correspond closely with those obtained for nortricyclene[17] and 4-chloronortricyclene[18] (Table I) with the exception of the C(2)–C(3) bond length. This bond is unusually short, a result which may be a manifestation of conjugation between the orbitals of the cyclopropyl ring and those of the carbonyl π systems.[19] It is generally agreed that this kind of interaction is maximized when the cyclopropyl ring is bisected by the plane which contains the carbonyl group and the adjacent carbon of the ring.[19] This concept is supported by numerous studies on the effect of structure on the absorption spectra of cyclopropyl ketones.[19,20] In addition, other x-ray crystallographic studies on cyclopropyl ketones[21,22] (with one exception[22c]) show a similar bond shortening although a clear correlation between the carbonyl torsion angle and the ultraviolet spectral shift was not found.[22a]

A complete analysis of bond shortening phenomena must also take into account changes attributable to variations in carbon hybridization.[18,23] The effect of the chlorine atoms on carbon hybridization is believed to be negligible (<0.005 Å) by analogy with published results on 1,4-dichloronorbornane.[18] On the other hand, bonds attached to the cyclopropyl ring are known to possess a large fraction of s character in comparison with sp^3 bonds, and a hybridization index of 2 has received theoretical and experimental support.[23–25] Since the C(2)–C(3) bond, an essentially sp^2–sp^2 linkage, could be shortened by as much as 0.05 Å by hybridization effects alone,[26] the importance of "conjugative" bond shortening becomes equivocal. The problem is clearly complex owing to the many interrelated factors, and we conclude that the existing data are not conclusive in this regard.

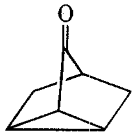
The formation of **5** from **4a** poses a mechanistic dilemma. The exceptionally mild conditions needed for this transformation are in strong contrast to the much more vigorous conditions needed to hydrolyze similar ketals in polychlorinated systems[1,5,7] and to the inertness of the hexachlorooxetane **3** to more vigorous conditions. Thus, it would appear that synergism is required, and we outline a possible mechanism for this rearrangement in Scheme I which involves participation by the methoxyl group in the ring opening of the pro-

Scheme I



tonated oxetane. This kind of assistance by methoxyl groups is well documented in the norbornyl system for which the geometrical relationships are similar.[27]

Since some of the spectroscopic properties of ketone **5** are of more than routine interest, they are discussed briefly here. The ultraviolet spectrum, for example, showed an unusually short wavelength maximum at 265 nm (ϵ 40) which is attributed to the n,π^* transition. The blue shift of this transition relative to that observed for nortricyclanone (**6**) [λ_{max} (EtOH) 285 nm (ϵ 20)][28] is attributable to the effect of the two vicinal carbon–chlorine bonds. This situation is closely analogous to that found in α-chlorocyclohexanones in which equatorially substituted chlorine atoms shift the carbonyl absorption maximum to shorter wavelengths by ~7 nm.[29] The presence of these chlorine atoms is felt in the infrared spectrum also. Whereas nortricyclanone shows maxima for the carbonyl stretching mode at 5.66 and 5.70 μ,[30] ketone **5** shows three maxima at 5.55 (s), 5.65 (m), and 5.75 μ (m). The α-chloro ester grouping accounts for at least one of the longer wavelength bands, and the band at the shortest wavelength is assigned to the ketonic function. The magnitude of the effect of the two chlorine atoms may be estimated from the behavior of compounds **7** (5.64 μ) and **8** (5.51 μ) for which a shift of −0.13 μ is found.[31,32] The calculated values for **5** are 5.53 and 5.57 μ in good agreement with the observed spectrum.



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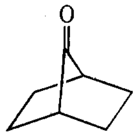

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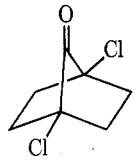

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Photochemistry. Since the absorption spectrum of the hexachloro ketone **1** was virtually identical with that of the nonchlorinated analogue *endo*-5-acetylnorbornene (**9**), it is concluded that there are no significant ground state interactions between the chromophores.[10] In addition, it was found that there was no significant fluorescence emission from **1** under conditions which produced easily measurable emission from 2-hexanone ($\Phi_f = 0.00039$).[33,34] From these data, it may be estimated that the lifetime of the singlet state of ketone **1** is no greater than 10^{-11} s.[35] This limit is of the same order of magnitude as that estimated for **9**, and it is presumed that exciplex formation between the carbonyl singlet and the double bond defines the singlet state lifetime in both cases.[10,13] In this context, it is interesting to note that the quantum yield for formation of oxetane **3** (0.026) is ca. six times lower than that measured for the nonchlorinated analogue. This result may be a manifestation of severe steric crowding in the formation of oxetane **3** or a reflection of more efficient decay of the chlorinated exciplex. It should also be noted that the lowered quantum yield observed here is in accord with predictions based on the expected ionization potential of the double bond.[36]

Summary and Conclusions

The generality of the intramolecular oxetane synthesis has been extended by these studies of polychlorinated bicyclic carbonyl systems. The potentially deleterious steric and electronic effects of the chlorine atoms were manifest in a sixfold lowered quantum yield of oxetane formation, but not in the formation of side products. Oxetane **4a** underwent a novel rearrangement under conditions of mild acid catalysis and it was concluded that methoxyl participation with migration was an important aspect of the transformation. The product of this reaction (**5**) is the first example of a nortricyclanone system to be examined by x-ray crystallography. The data revealed that the bond between the carbonyl group and the cyclopropane ring was unusually short (1.48 Å), and it was concluded that hybridization changes could be responsible for this effect.

Experimental Section

Elemental analyses were performed at Robertson Laboratory, Florham Park, N.J. Infrared spectra were determined as Nujol mulls or KBr pellets on a Perkin-Elmer Model 137 spectrometer. Nuclear magnetic resonance data were obtained on Varian Model T-60, CFT-20, and JEOL-100 spectrometers in chloroform with tetramethylsilane as an internal standard. Gas chromatographic data was recorded on an Aerograph Model A-90-P chromatograph. The following columns were employed: 3% SE-30 (5 ft × 0.25 in.) on Chromosorb G and 5% SF-96 (5 ft × 0.25 in.) on Chromosorb P. Mass spectra were determined at 70 eV on a Hitachi RMU 7 mass spectrometer. Melting points were determined on a Mel-Temp apparatus. X-ray diffraction data were collected on a Nonius CAD-3 automated diffractometer. Fluorescence measurements were taken on a Perkin-Elmer MPF-2 spectrometer.

Starting Materials. 1,4,5,6,7,7-Hexachloro-5-norbornen-2-yl methyl ketone (1) was prepared by the procedure of Prill[15] and had mp 70–71 °C (lit. mp 70 °C). The ^{1}H NMR spectrum (100 MHz) showed a single sharp peak at δ 2.40 (CH_3), a quartet centered at 3.76, and complex absorption between 2.50 and 2.80; λ_{max} (C_6H_6) 287 nm (ϵ 27); λ_{max} (CH_3CN) 283 nm (ϵ 16).

1,4,5,6-Tetrachloro-7,7-dimethoxy-5-norbornen-2-yl methyl ketone (2a) was prepared by the procedure of McBee et al.[7] and had mp 85–86 °C (lit. mp 86–87 °C). The ^{1}H NMR spectrum (100 MHz) showed two methoxyl peaks at δ 3.58 and 3.66, and acetyl peaks at 2.34 and 2.38 (rel area ca. 3.5:1); λ_{max} (C_6H_6) 288 nm (ϵ 27).

1,4,5,6-Tetrachloro-7,7-dimethoxy-5-norbornene-2-carboxaldehyde (2b) was prepared according to ref 7, and had bp 148 °C (3 mm) [lit.[7] bp 155–156 °C (5 mm)]. The ^{1}H NMR spectrum showed two methoxyl peaks at δ 3.53 and 3.59, and complex absorptions centered at δ 9.8 indicative of a mixture of epimers.

Photolyses. Preparative scale irradiations were carried out in a 1.1-l. immersion apparatus equipped with a Hanovia 450-W lamp. Nitrogen gas was passed through the solutions throughout the irradiation period. Spectral grade benzene was used as solvent, and the photolyses were run for 7–8 days (polymer was removed from the immersion well as necessary).

1,2,5,6,9,9-Hexachloro-3-methyl-4-oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane (3). Irradiation of 10 g of **1** in 1.1 l. of benzene (Vycor filter) in the presence of 1.5 g of piperylene for 200 h sufficed to consume >90% of the ketone (GC, SE-30). The volatiles were removed by evaporation and the residue chromatographed on silica (hexane–benzene eluents) to yield 5.5 g (55%) of oxetane **3:** mp 175–176 °C; ^{1}H NMR δ 1.6 (s, CH_3), 3.3 (m, 2 H), 2.1 (d, J = 12 Hz, 1 H).

Anal. Calcd for $C_9H_6OCl_6$: C, 31.53; H, 1.76; Cl, 62.04. Found: C, 31.82; H, 2.03; Cl, 61.80.

1,2,5,6-Tetrachloro-3-methyl-9,9-dimethoxy-4-oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane (4a). Similarly, 10.1 g of **2a** was irradiated for 7 days using a Vycor filter. Evaporation of the benzene gave a solid which was washed with hexane and crystallized from petroleum ether: yield 6.30 g (63%); mp 160–161 °C; ^{1}H NMR δ 3.6, 3.58 (s, CH_3O), 1.50 (s, CH_3), 2.8 (m, 2 H), 1.85 (d, J = 12 Hz).

Anal. Calcd for $C_{11}H_{12}O_3Cl_4$: C, 39.55; H, 3.68; Cl, 42.23. Found: C, 39.59; H, 3.68; Cl, 42.23.

1,2,5,6-Tetrachloro-9,9-dimethoxy-4-oxatetracyclo[4.2.1.0^{2,5}.0^{3,7}]nonane (4b). Aldehyde **2b** (5 g) was irradiated for 7 days using a Corex filter. Removal of the benzene and chromatography of the residue on alumina gave 1.22 g (24%) of oxetane **4b:** mp 161–162 °C; ^{1}H NMR δ 4.60 (d, J = 2 Hz, 2 H), 3.50, 3.48 (s, CH_3O, 6 H), 1.8–3.0 (m, 3 H).

Anal. Calcd for $C_{10}H_{10}O_3Cl_4$: C, 37.53; H, 3.15; Cl, 44.31. Found: C, 37.58; H, 3.28; Cl, 44.11.

Methyl 2,4,5-Trichloro-6-methyltricyclo[2.2.1.0^{2,6}]heptan-3-one-*syn*-5-carboxylate (5). A mixture of 10 ml of concentrated sulfuric acid and 0.5 g of oxetane **4a** was stirred at 0 °C for 15 min. The solution was poured onto ice and the organic product was extracted into ether. The extracts were washed with saturated sodium bicarbonate solution, brine, and water. The dried extracts were evaporated to give 0.29 g (58%) of a solid which was sublimed at 60 °C (0.5 mm): mp 66°; ^{1}H NMR δ 3.9 (s, OCH_3), 1.55 (s, CH_3), 2.4–3.1 (m, 3 H); ^{13}C NMR (rel intensity) 9.54 (CH_3, 60), 33.87 (94), 39.55 (98), 44.00 (28), 49.31 (12), 54.19 (58), 71.83 (18), 165.94 (CO_2R, 7), 191.58 (C=O, 7); ir 5.55 (s), 5.65, 5.75 μ (m); λ_{max} ($CHCl_3$) 265 nm (ϵ 40).

Anal. Calcd for $C_{10}H_9O_3Cl_3$: C, 42.36; H, 3.20; Cl, 37.51. Found: C, 42.26; H, 3.29; Cl, 37.23.

Treatment of oxetane **3** with concentrated sulfuric acid for 1 h at 0 °C yielded only unreacted starting material.

Treatment of 3 with $AlCl_3$. A mixture of 1.1 g of aluminum chloride and a solution of 1.78 g of **3** in 50 ml of dry benzene was heated at reflux for 20 h. The reaction mixture was poured onto an HCl–ice mixture. The organic phase was washed with water and sodium bicarbonate solution, dried, and evaporated to give 0.78 g (43%) of ketone **1** as shown by comparative infrared spectra.

Quantum Yield Determination. Three sample tubes (Pyrex, 100 × 13 mm) each containing 0.251 M **1** and 0.0098 M tetradecane (internal standard) in 2.0 ml of purified benzene[10] were degassed by the freeze–thaw method and sealed under vacuum (0.05 Torr). Three solutions were irradiated on a merry-go-round apparatus for 31 h with a 450-W Hanovia lamp. The output of the lamp was filtered through 1.9 cm of an aqueous solution of potassium chromate (0.00127 M) and potassium carbonate (0.0543 M). The entire apparatus was immersed in a water bath which was kept at 25 ± 4 °C. The averaged percent conversion of the ketone **1** to the oxetane **3** was 5.5 ± 0.05 as determined by quantitative GC analysis. The corresponding nonchlorinated ketone (0.251 M) served as the actinometer for calculation for the quantum yield. Four separate tubes were sequentially irradiated over the same time period. Using a value of 0.14 for the quantum yield of oxetane formation for this compound, a value of 0.026 ± 0.02 was calculated for oxetane formation from **1**.

Collection and Reduction of X-Ray Data. A crystal approximately 0.34 × 0.43 × 0.69 mm was obtained from an ether–decane solution and mounted in a sealed glass capillary along the *a* axis. Weissenberg photographs revealed a monoclinic space group with systematic absences of $h0l$, $l = 2n + 1$; and $0k0$, $k = 2n + 1$. The centrosymmetric space group $P2_1/c$ is the only one consistent with these extinctions.

Unit cell constants were determined at 22 ± 1 °C from a least-squares fit of 15 medium intensity reflections centered on an Enraf-Nonius CAD-3 computer controlled diffractometer. The unit cell dimensions were $a = 9.066\ (4)$, $b = 10.863\ (6)$, $c = 24.63\ (2)$ Å, $\beta = 92.35\ (4)°$, and $V = 2424\ (2)$ Å^3. A density of 1.58 (1) g/cm^3 was determined by the density gradient method using a carbon tetrachloride–tetrabromoethane mixture; this compared well with the value of 1.55 g/cm^3 calculated for eight molecules per unit cell.

Data were collected with the Enraf-Nonius diffractometer using graphite monochromated Mo Kα radiation detected with a pulse height analyzer set to admit approximately 95% of the Kα peak. A θ–2θ scan was used to collect a unique data set in the range $2° < \theta < 30°$. Background measurements were made at beginning and end of each scan with the total time for background counting equal to the scan time. Reflections with 2θ less than 4° were shielded by the beam stop and were not recorded. The scan range s was a function of θ chosen according to $s = 1.00 + 0.5 \tan \theta$. Each reflection was scanned before being recorded, and zirconium foil attenuators were automatically inserted if the intensity of the diffracted beam exceeded 6000 counts/s. A circular aperture, 1.3 mm in diameter, was placed 4.4 cm from the crystal. The scan rate was ⅙° per second, and each reflection was scanned repeatedly to a maximum of four scans, or until 5000 total counts were obtained. Intensities were placed on a common scale by dividing by the number of scans and multiplying by the appropriate filter factor. The intensity of a standard reflection, measured at 50 reflection intervals, showed a deviation of ±3%. A total of 3841 reflections was collected and corrected for Lorentz and polarization effects. The data were also scaled using the standard reflection to bring all reflections to a common scale. The linear absorption coefficient for Mo Kα radiation was 7.55 cm^{-1}, while maximum and minimum absorption factors for the data collected were calculated to be 1.37 and 1.28, respectively. Because of this small variation in A^*, absorption corrections were not applied. Standard deviations were assigned to F^2 values according to $\sigma(F^2) = (1/Lp)\ [N_t + (0.02N_n)^2]^{1/2}$, where N_t is the total count (scan plus background); N_n is the net count (scan minus background), and 0.02 is the estimated instrument error. Of the 3841 measured reflections, 1733 with F^2 greater than 3σ were used in the refinement.

Solution and Refinement.[37] The phases of 348 reflections with $|E| \geqslant 1.50$ were determined by use of the tangent formula. Of the 16 solutions generated by the MULTAN program for four starting reflections (in addition to those defining the origin), one with an absolute figure of merit of 0.97 and a residual of 46.2[38] was used as the basis for a Fourier synthesis. The 6 chlorine atoms and 18 lighter atoms, weighted as carbon, were located from this map. A structure factor calculation based on these 24 atoms gave $R_F = \Sigma||F_o| - |F_c||\Sigma|F_o| = 0.34$. An electron density map prepared using the phases generated by these 24 atoms revealed the remaining eight nonhydrogen atoms and discriminated between oxygen and carbon atoms.

Refinement was based on F. Scattering factors for Cl, O, and C atoms were taken from the compilations of Cromer and Waber,[39] and all atoms were treated as neutral species. Both real and imaginary parts of the anomalous dispersion correction were applied to chlorine.[40] The weighting scheme was chosen by an analysis of variance[41] to make $|\Delta F|/\sigma$ independent of $|F_o|$. A best fit plot led to the following assignments for $\sigma(F_o)$.

$$\sigma(F_o) = 0.33 + 0.12|F_o| \text{ for } |F_o| \leqslant 15.0$$

$$\sigma(F_o) = 4.59 - 0.16|F_o| \text{ for } 15.01 < |F_o| \leqslant 22.0$$

$$\sigma(F_o) = -0.20 + 0.05|F_o| \text{ for } |F_o| > 22.0$$

Positional parameters for the six ring hydrogen atoms were calculated using known distances (C–H = 1.08 Å) and tetrahedral angles, and were included for subsequent refinement with the overall temperature factor obtained using Wilson's method. Two cycles of refinement with anisotropic temperature factors for all nonhydrogen atoms gave values of 0.081 for R_F and 0.103 for $R_{wF} = [\Sigma w(F_o - F_c)^2/\Sigma wF_o{}^2]^{1/2}$.

A difference Fourier at this point revealed the positions of at least one hydrogen atom on each methyl group. These positions were used to calculate the remaining methyl hydrogen positions. Methyl hydrogen atoms were assigned the isotropic temperature factor obtained from the Wilson plot plus 1.0. Two final cycles of refinement varying all parameters except hydrogen temperature factors gave final values of 0.062 and 0.077 for R_F and R_{wF}, respectively. A final difference map showed no significant features and a general background of 0.3 electron/Å^3. Final atomic parameters and their estimated standard deviations are shown in Table II. Selected bond distances and angles are given in Tables III and IV, respectively (see paragraph at end of paper regarding supplementary material).

Acknowledgments. We are indebted to the Rutgers University Research Council and the Rutgers Computing Center for support. We are also grateful to Byron Burros and Dorothy Denney for ^{13}C NMR data, and to D. Mastropaolo for assistance with the crystallographic studies. Finally, we are especially grateful to P. Hudrlik for numerous discussions concerning the mechanism of the arrangement.

Registry No.—**1**, 15584-73-3; **2a**, 59473-95-9; **2b**, 59473-96-0; **3**, 59473-97-1; **4a**, 59473-98-2; **4b**, 59473-99-3; **5**, 59474-00-9.

Supplementary Material Available. Tables of final atomic parameters, selected bond distances, and selected bond angles for compound **5** (4 pages). Ordering information is given on any current masthead page.

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Photochemical Cyclization of 4-Methallyl-4-methylcyclopentenone. 220-MHz Nuclear Magnetic Resonance Spectra of Tricyclo[3.3.0.0^{2,7}]octanes

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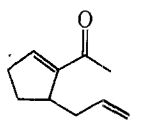
Received February 24, 1976

Preparation of 4-methallyl-4-methylcyclopentenone (**4**) from hydroxy ketone **5** is described. Irradiation of **4** leads to [2 + 2] cycloaddition and formation of tricyclic ketone **10** in high yield. NMR spectra (220 MHz) of ketones **10–13** are recorded and interpreted in a consistent fashion.

Irradiation of 1-acetyl-5-allylcyclopentene (**1**) leads to [2 + 2] cycloaddition between the two olefinic double bonds with formation of tricyclic ketone **2**.[1] Other representatives of this tricyclo[3.3.0.0^{2,7}]octane ring system have been long known through intramolecular photocycloaddition of vinylcyclohexenes.[2-5] However, the cyclization of **1** was the first example of formation of this skeleton from an allylcyclopentene, and this result suggests that similar cyclization might occur photochemically in suitable 4-allylcyclopentenones (**3**), as illustrated in eq 1. The position of the carbonyl group on the ring double bond is reversed on passing from **1** to **3**, but the available evidence indicates that this change should not influence the mode of cyclization.[3,5] As others have noted before,[5] regiospecificity in intramolecular photocycloaddition of 1,5-hexadienes to yield bicyclo[2.1.1]hexanes (and not bicyclo[2.2.0]hexanes) is quite general, and apparently it is insensitive to the nature and position of substituents on the reacting double bonds. The only aberrant example of which we are aware has been described as being "structurally inhibited" from reaction in the usual fashion.[6] In this report we describe the intramolecular cycloaddition of an allylcyclopentenone according to eq 1, along with the 220-MHz ^1H NMR spectra of several tricyclo[3.3.0.0^{2,7}]octanes that were determined in the course of securing the structure of the photoproduct.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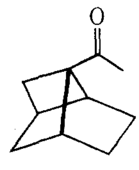
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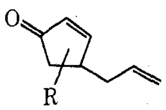
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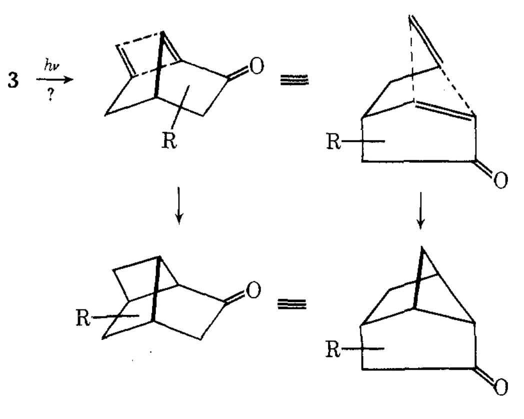

(1)

A convenient substrate for this work was 4-methallyl-4-methylcyclopent-2-enone (**4**), since it could be prepared from the related hydroxy ketone **5**, which was already on hand for another investigation.[7] The hydroxyl group of **5** was converted to the corresponding tosylate **6**, which yielded bromide **7** on reaction with sodium bromide in acetone. Treatment of **7** with bromine in ethylene glycol, according to the procedure of Garbisch,[8] then gave the dibromo ketal **8**. A double dehydrohalogenation took place when **8** was exposed to potassium *tert*-butoxide in dimethyl sulfoxide, furnishing the diene ketal **9**. Use of the primary bromide **7** rather than the corresponding tosylate **6** was desirable in this sequence in order to minimize competing ether formation during treatment with alkoxide;[9] for the same reason we employed *tert*-butoxide as base rather than methoxide, which was originally suggested.[8] In the event