for the three methine hydrogen atoms (Q_H), the nitrogen atom (Q_N), and the methylene group (Q_{CH_2}) are $A_H = 2[65(2)], 5[29(1)]$, $A_N = 2[61(2)]$, and $A_{CH_2} = 6[79(2)]$ gauss, respectively. In computing the methylene coupling we have taken the spin density to be proportional to the square of the sum of the coefficients of the H orbital at each carbon atom, *i.e.*, of the form $Q(C_1 + C_2)^2$ rather than $Q(C_1^2 + C_2^2)$.[8] These couplings would lead to a spectrum with a width of 40 gauss which is far in excess of the experimental spectrum. Furthermore, in order to fit the total number of lines observed, further hyperfine interactions with peripheral methylene groups would have to be invoked, which would make the situation worse.

It is clear on the basis of this discussion that much further experimental work on a range of substituted porphin structures must be carried out before definitive analysis can be attempted. It is also clear that simple Hückel spin density calculations are not sufficiently accurate for meaningful theoretical predictions to be made of the nature of these porphyrin reduction products.

We note in conclusion that Mauzerall and Feher[10] have obtained a transient paramagnetic radical by irradiation of porphin–phlorin mixtures in glycerine solution. This is probably the neutral phlorin radical PH. The identification of intermediates of this type is essential for an understanding of porphin oxidation–reduction reactions, and for an understanding of the electron spin resonance signals observed in photosynthetic materials.[11]

(10) D. Mauzerall and G. Feher, *Biochim. Biophys. Acta*, **79**, 430 (1964).

(11) B. Commoner, J. Townsend, and G. E. Pake, *Nature*, **174**, 4432 (1954).

Photochemical Conversion of 7-Methoxycycloheptatriene to 1-Methoxybicyclo[3.2.0]hepta-3,6-diene[1]

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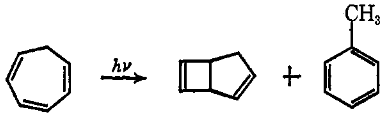
Contribution from the Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010. *Received February 7, 1967*

Abstract: The photochemical conversion of 7-methoxycycloheptatriene to 1-methoxybicyclo[3.2.0]hepta-3,6-diene is shown to involve initial photoisomerization to 1-methoxycycloheptatriene followed by photochemical valence isomerization to the bicyclic product. Irradiation of 1-methoxycycloheptatriene gives 7-methoxycycloheptatriene and the bicyclic valence tautomer. The sigmatropic reactions of order [1,7] involved in the interconversion of 7-methoxycycloheptatriene and 1-methoxycycloheptatriene are shown to arise from singlet states. The 1,7-hydrogen shift by which 1-methoxycycloheptatriene is converted to 7-methoxycycloheptatriene is remarkably specific. No 2-methoxycycloheptatriene could be detected. The photochemical valence tautomerization of 1-methoxycycloheptatriene to 1-methoxybicyclo[3.2.0]hepta-3,6-diene is shown to arise from a singlet state of the triene.

Photoisomerization of cycloheptadienes, cycloheptatrienes, and tropolones to unsaturated derivatives of bicyclo[3.2.0]heptane is one of the most generally applicable photochemical reactions.[3] Irradiation of cycloheptatriene gives both toluene and bicyclo[3.2.0]hepta-2,6-diene.[3,4] Toluene is the major product in the vapor phase[4] and the bicyclic valence tautomer in solution.[5] Irradiation of certain substituted cycloheptatrienes gives isomeric cycloheptatrienes by 1,7-hydrogen shifts.[6–8] Thermal isomerization of cycloheptatrienes gives rise to 1,5-hydrogen shifts which lead to isomeric cycloheptatrienes when substituents are present.[9] More complex thermal isomerizations are observed with 7,7-disubstituted cycloheptatrienes.[10]



We now wish to report a photoisomerization reaction which is anomalous both in solution and in the vapor phase with respect to the behavior of cycloheptatriene. Irradiation of 7-methoxycycloheptatriene or 7-ethoxycycloheptatriene in ether solution gives in each case the 1-alkoxybicyclo[3.2.0]hepta-3,6-diene. Yields in excess of 90% have been obtained, and vpc and nmr analysis of the crude reaction mixture shows that the reactions are essentially quantitative.

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(1) A preliminary report of portions of this research has been published: O. L. Chapman and G. W. Borden, *Proc. Chem. Soc.*, 221 (1963). Portions of this work were abstracted from the thesis of G. W. Borden, Iowa State University, 1963. Photochemical Transformations. XIX.

(2) (a) Predoctoral Fellow, National Institutes of Health, 1961–1963; (b) Postdoctoral Fellow, National Institutes of Health, 1965–1966.

(3) For a review see O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963).

(4) R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 3432 (1962).

(5) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

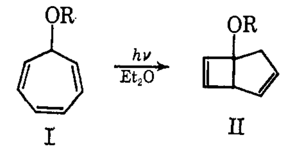
(6) W. von E. Doering and P. P. Gaspar, *J. Am. Chem. Soc.*, **85**, 3043 (1963).

(7) W. R. Roth, *Angew. Chem.*, **75**, 921 (1963).

(8) A. P. ter Boorg and H. Kloosterziel, *Rec. Trav. Chim.*, **84**, 241 (1965).

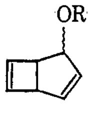
(9) (a) G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **84**, 3104 (1962); (b) A. P. ter Boorg, H. Kloosterziel, and N. van Meurs, *Proc. Chem. Soc.*, 359 (1962); (c) A. P. ter Boorg, H. Kloosterziel, and N. van Meurs, *Rec. Trav. Chim.*, **82**, 717, 741, 1189, (1963); (d) E. Weth and A. S. Dreiding, *Proc. Chem. Soc.*, 59 (1964); (e) A. P. ter Boorg and H. Kloosterziel, *Rec. Trav. Chim.*, **84**, 245 (1965); (f) H. J. Dauben, private communication.

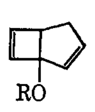
(10) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **87**, 2751, 2752 (1965); **88**, 2494 (1966).



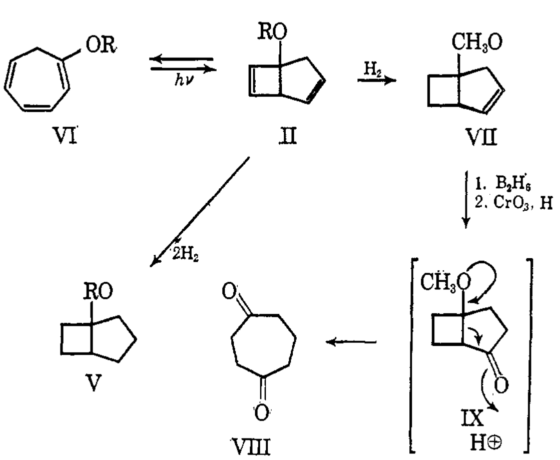
a, R=CH_3
b, R=C_2H_5

The ultraviolet spectra of the photoproducts show no maxima above 220 mμ, which suggests bridging of the ring. The nmr spectra of the photoproducts IIa and b show in each case four olefinic protons, three protons on saturated carbon, and methoxyl (IIa) or ethoxyl (IIb) protons. The presence of the cyclobutene double bond could be detected by the characteristic coupling constant (IIa, 2.9 cps)[11] and field position (IIa, τ 3.80; IIb, τ 3.77). The first indication that the photoproducts were not the simple valence tautomers IIIa and b was the absence of a resonance characteristic of the >CHOR group in the nmr spectra of the tetrahydro derivatives of the photoproducts. This must mean that the alkoxyl functions are at the bridgehead in the tetrahydro derivatives Va and b and consequently that the photoproducts are either IIa and b or IVa and b. A decision in favor of the 1-alkoxybicyclo[3.2.0]hepta-3,6-diene structures (IIa and b) was possible on the basis of the thermal transformations of the photoproducts. When IIa and b were dropped through a pyrolysis column preheated to 340–350° the sole products were 1-methoxycycloheptatriene (VIa) and 1-ethoxycycloheptatriene (VIb) respectively. A control experiment showed that the 7-alkoxycycloheptatrienes (Ia and b) were converted only partially to the 1-alkoxycycloheptatrienes (VIa and b) under identical conditions.[12] Irradiation of the 1-alkoxycycloheptatrienes gave the valence tautomers IIa and b. Confirmation of the assigned structures was obtained by the sequence of reactions described below. In the reduction of the photoproducts it had been noted that the two double bonds were reduced at different rates. Addition of 1 equiv of hydrogen gave the dihydro derivative VII in which the cyclobutene double bond had been selectively reduced. The nmr spectrum of VII showed a multiplet at τ 4.30 due to the cyclopentene protons. The characteristic absorption of the cyclobutene protons (τ 3.80) was no longer present. Hydroboration followed by chromic acid oxidation[13] gave 1,4-cycloheptanedione (VIII). Hydroboration and oxidation of VII could give rise to two possible ketones IX and X. No evidence for the presence of X was obtained. Tetrahydrophoto-γ-tropolone methyl ether (IX) is known to be transformed rapidly to 1,4-cycloheptanedione in acid solution.[14] The alternate structure IVa for the photoproduct cannot account for the formation of VIII since the oxygen functions after partial reduction, hydroboration, and oxidation of IV must be either 1,2 or 1,3 with respect to each other rather than 1,4 as required by the formation of VIII.

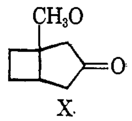

III


IV

a, R=CH_3
b, R=C_2H_5



a, R=CH_3
b, R=C_2H_5


X

Irradiation of 7-methoxycycloheptatriene at low pressure in the vapor phase gave a mixture which consisted of 7-methoxycycloheptatriene (14%), 1-methoxycycloheptatriene (38%), and 1-methoxybicyclo[3.2.0]hepta-3,6-diene (48%). This was the first indication that 1-methoxycycloheptatriene might be an isolable intermediate in the formation of IIa and suggested that the reaction in solution should be monitored carefully.

The photochemical transformation of 7-methoxycycloheptatriene was monitored by ultraviolet and nmr spectroscopy and by vapor phase chromatography.[15] The ultraviolet spectra of the solution during irradiation show disappearance of the 255-mμ maximum of 7-methoxycycloheptatriene and appearance and decay of a maximum at about 280 mμ. Both vapor phase chromatography and nmr spectra show the formation and destruction of an intermediate (Figures 1 and 2). Isolation of the intermediate and comparison of spectra identified it as 1-methoxycycloheptatriene (VIa). Careful monitoring of the photochemical rearrangement of 7-methoxycycloheptatriene (Ia) in the early phase of the reaction showed that 1-methoxycycloheptatriene (VIa) was the sole primary product since the concentration *vs.* time plot for this substance extrapolated to zero at zero time (Figure 3).

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[11] O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963); P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2016 (1963); G. V. Smith and H. Kriloff, *ibid.*, **85**, 2017 (1963).

[12] The thermal isomerization of 7-methoxycycloheptatriene has been studied in detail.[9d,f] The first product from 7-methoxycycloheptatriene is 3-methoxycycloheptatriene and the second is 1-methoxycycloheptatriene. More extensive rearrangement would have been observed at the temperatures used except for the very short residence time in the pyrolysis column.

[13] H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2951 (1961).

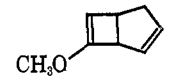
[14] O. L. Chapman and D. J. Pasto, *ibid.*, **82**, 3642 (1960).

[15] Under the conditions of the analysis, 7-methoxycycloheptatriene isomerized to 3-methoxycycloheptatriene. Both 1-methoxycycloheptatriene and 1-methoxybicyclo[3.2.0]hepta-3,6-diene were stable to the conditions.

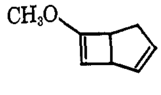
Similar extrapolation for 1-methoxybicyclo[3.2.0]hepta-3,6-diene (IIa) did not pass through the origin (Figure 3). The bicyclic product (IIa) thus is a secondary product formed only after 1-methoxycycloheptatriene is formed. It should be noted that the bicyclic photoproduct is formed very early in the reaction when a relatively small fraction of the light is being absorbed by VIa. The photoisomerization of VIa to IIa thus must be a reasonably efficient process (see Figures 4 and 5 for nmr spectra of VIa and IIa, respectively).

No evidence for any intermediate beside 1-methoxycycloheptatriene was obtained. A sequence of two 1,5-hydrogen transfer processes (known to occur thermally)[9d,f] could convert 7-methoxycycloheptatriene to 1-methoxycycloheptatriene. If this were the case, 3-methoxycycloheptatriene would be an intermediate between 7-methoxycycloheptatriene and 1-methoxycycloheptatriene. With this in mind, 3-methoxycycloheptatriene was irradiated. The reaction mixture was very complex in contrast to the clean reactions of 7-methoxycycloheptatriene and 1-methoxycycloheptatriene. The crude product was separated into two fractions. The first fraction was shown to contain at least three bicyclic compounds. One was separated and identified as 1-methoxybicyclo[3.2.0]hepta-3,6-diene. The other two bicyclic compounds were not separated. Hydrolysis of the mixture gave rise to infrared carbonyl absorptions characteristic of five-membered and four-membered ring ketones suggesting the presence of enol ethers. Reduction of the mixture gave, after work-up, bicyclo[3.2.0]heptan-6-one (XI) identified by comparison of its infrared spectrum with that of an authentic sample.[16] The formation of XI shows that XII and/or XIII is present in the mixture. The second fraction consisted of a mixture of methoxycycloheptatrienes.[17] The nature of the photoproducts from 3-methoxycycloheptatriene makes it very clear that it is not an intermediate in the photochemical rearrangements of 7-methoxycycloheptatriene.

XI



XII



XIII

Irradiation of 1-methoxycycloheptatriene for short periods of time gave 1-methoxybicyclo[3.2.0]hepta-3,6-diene (IIa) and 7-methoxycycloheptatriene (Ia). Longer irradiation gave only the bicyclic valence tautomer IIa. A photostationary state is thus established between 7-methoxycycloheptatriene and 1-methoxycycloheptatriene which is displaced by conversion of 1-methoxycycloheptatriene to 1-methoxybicyclo[3.2.0]hepta-3,6-diene. Two points of substantial interest arise when one considers the reactions involved. First, why is it that the 1,7-hydrogen shift in VI is so specific, *i.e.*, why is no 2-methoxycycloheptatriene formed? Second, why is isomerization to the bicyclic valence tautomer so much more efficient when a methoxyl group is present in the 1 position?[18] The specificity of the 1,7-hydrogen shift in VIa is even more dramatic when considered in the light of the lack of specificity in the reactions of 3-methoxycycloheptatriene and other substituted cycloheptatrienes.[6-8]

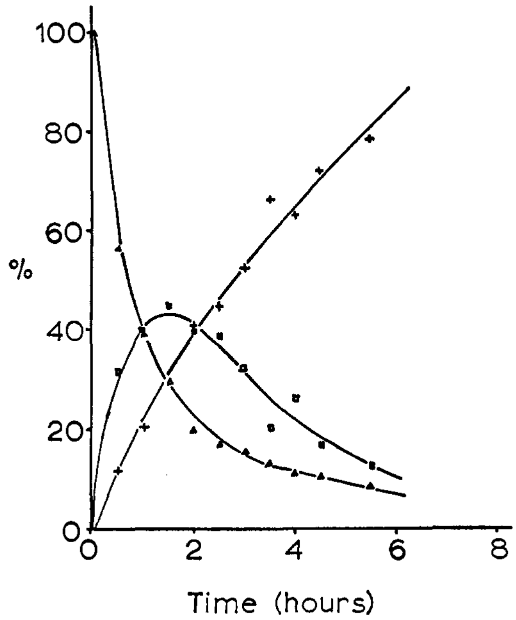
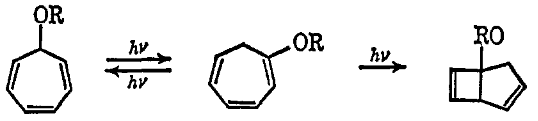


Figure 1. Plot of per cent 7-methoxycycloheptatriene (Ia, Δ), 1-methoxycycloheptatriene (VIa, □), and 1-methoxybicyclo[3.2.0]hepta-3,6-diene (IIa, +) *vs.* time of irradiation.



I VI II

a, R=CH_3
b, R=C_2H_5

The multiplicities of the states responsible for the reversible 1,7-hydrogen shifts and the photoisomerization to the bicyclic system are of some interest. The photoisomerization of 7-methoxycycloheptatriene to 1-methoxycycloheptatriene was not sensitized by acetophenone ($E_t \sim 74$ kcal/mole)[19] and was not quenched by oxygen. The photosensitization experiments with 7-methoxycycloheptatriene were very clean because the absorption of 7-methoxycycloheptatriene above 3400 A is negligible. The filter system used had zero transmission below 3400 A and 65% transmission at 3600 A. All of the light was absorbed by the sensitizer, and no reaction could be detected by vpc analysis. Acetophenone ($E_t \sim 74$ kcal/mole) should have a sufficiently high triplet energy to transfer energy to the triene. The triplet energy of cycloheptatrienes is not known but should lie between that of simple olefins (ethylene, 82 kcal/mole)[20] and planar trienes (*trans*-1,3,5-hexa-

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(16) The mode of formation of XI is not completely clear. It might involve reductive cleavage of the ether or more likely hydrolysis of a dihydro derivative of XII or XIII in work-up. The authentic sample of XI was prepared by D. L. Garin, Ph.D. Thesis, Iowa State University, 1964.

(17) It can be argued that the mixture of methoxycycloheptatrienes is an artifact resulting from the work-up procedure. The mixture of bicyclic compounds, however, must have been formed in a photochemical process and clearly shows that the photochemical transformations of 3-methoxycycloheptatriene are less specific than those of 7-methoxycycloheptatriene and 1-methoxycycloheptatriene.

(18) Photoisomerization of cycloheptatriene[5] in solution requires several days' irradiation while photoisomerization of 1-methoxycycloheptatriene under comparable conditions requires only a few hours' irradiation.

(19) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

(20) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

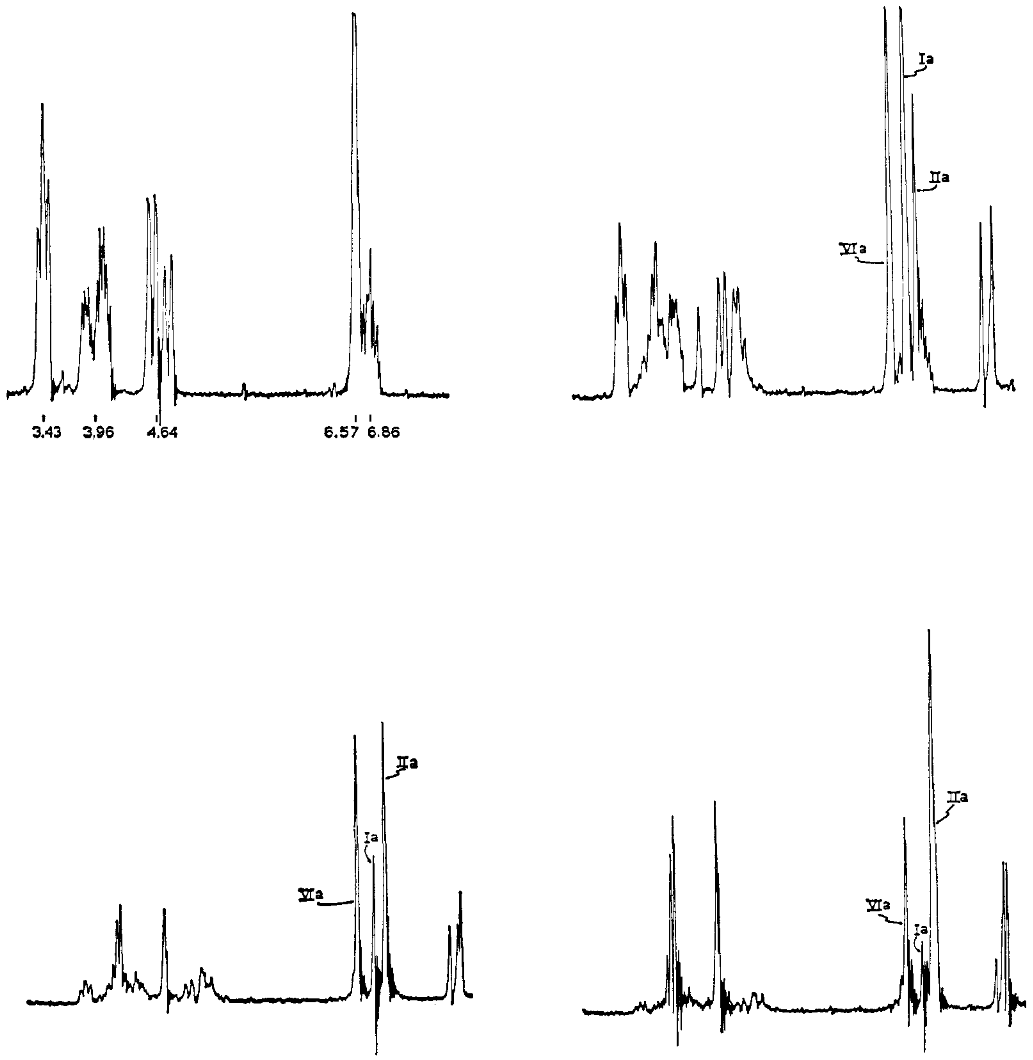

Figure 2. Upper left, 7-methoxycycloheptatriene (Ia) before irradiation. Resonance positions are given on the τ scale relative to internal tetramethylsilane. Upper right, sample after irradiation for 30 min. Lower left, sample after irradiation for 120 min. Lower right, sample after irradiation for 270 min.

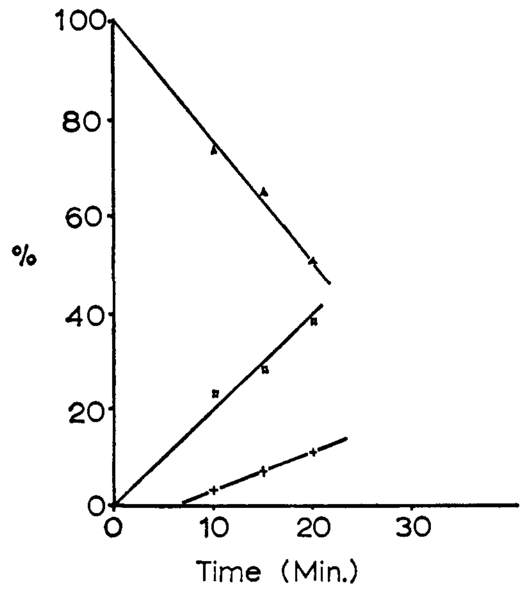

Figure 3. Plot of per cent 7-methoxycycloheptatriene (Ia, Δ), 1-methoxycycloheptatriene (VIa, $\square$), and 1-methoxybicyclo[3.2.0]-hepta-3,6-diene (IIa, $+$) *vs.* time for the first 20 min of irradiation (vpc analysis).

triene, 47 kcal/mole)[20] and is probably somewhat closer to the latter.[21] Neither the conversion of 1-methoxycycloheptatriene to 7-methoxycycloheptatriene nor the conversion to 1-methoxybicyclo[3.2.0]hepta-3,6-diene was affected significantly by oxygen. No evidence for photosensitization of either process by acetophenone was obtained. The photosensitization experiments were somewhat more complicated in this case because 1-methoxycycloheptatriene (λ_{max} 290 mμ) has significant absorption above 3400 A (ϵ_{3600} 4.1) and because it gives two products. The results, however, make it clear that reaction is much slower when most of the light is absorbed by sensitizer. When enough sensitizer is present to absorb >88% of the incident light, reaction is too slow to be detected in the usual irradiation period (1 hr).

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(21) The nonplanar ground state of cycloheptatrienes makes it difficult to extrapolate the available results. Furthermore, it is clear that ring size affects triplet energy (1,3-cyclopentadiene, E_t = 58.4; 1,3-cyclohexadiene, E_t = 53.5 kcal/mole).[20] If 7-methoxycycloheptatriene is assumed to have a singlet (S_1)-triplet (T_1) gap of the same energy as *trans*-1,3,5-hexatriene (59.8 kcal/mole)[20] and the maximum (2550 A) of the $S_0 \rightarrow S_1$ absorption band is used as a measure of the $S_0 \rightarrow S_1$ transition energy, the result is an estimated triplet energy of about 52 kcal/mole, which is in a reasonable range.

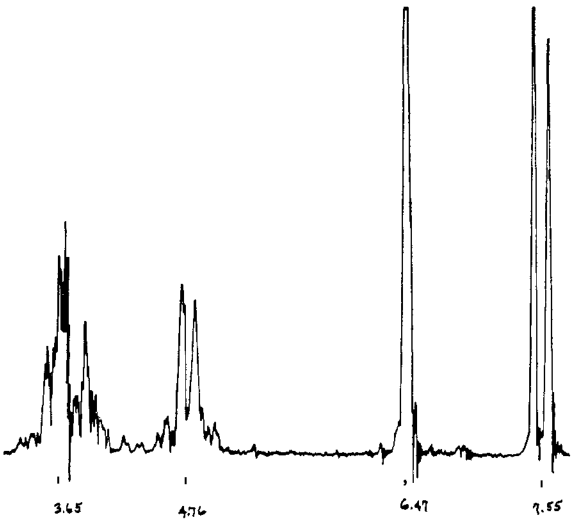


Figure 4. Nuclear magnetic resonance spectrum of 1-methoxycycloheptatriene (VIa). Calibration is on the τ scale relative to internal tetramethylsilane.

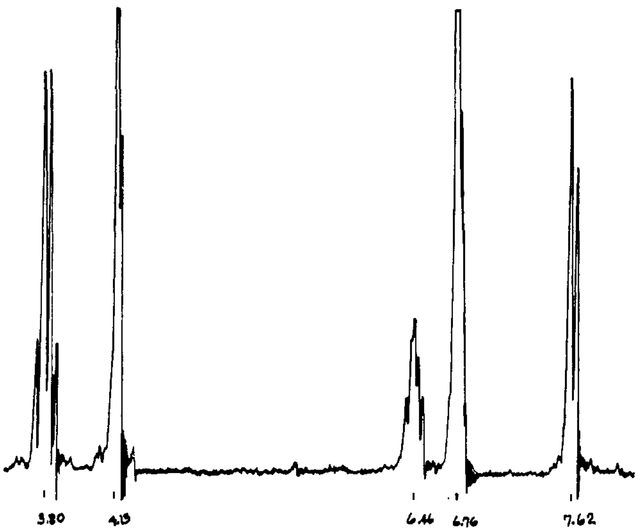
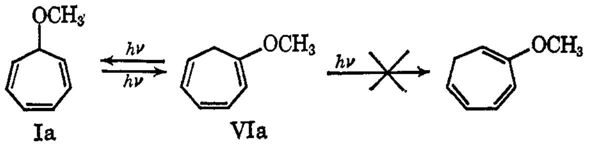


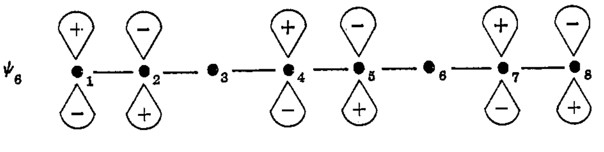
Figure 5. Nuclear magnetic resonance spectrum of 1-methoxybicyclo[3.2.0]hepta-3,6-diene (IIa). Calibration is on the τ scale relative to internal tetramethylsilane.

It seems reasonable to conclude that the reversible photochemical 1,7-hydrogen shift between 7-methoxycycloheptatriene and 1-methoxycycloheptatriene involves a singlet state regardless of which compound initially absorbs the light. This conclusion is in accord with the recognized inefficiency of intersystem crossing of most conjugated olefins.[20] There remains a question of whether the reaction occurs *via* an electronic excited state or a vibrationally excited ground state. The fact that thermal isomerization gives products derived from 1,5-hydrogen atom shifts does not preclude reaction *via* a vibrationally excited ground state. No experimental distinction between the two possibilities is available, although it seems reasonable that vibrational deactivation would be extremely rapid in solution. Orbital symmetry arguments also suggest that the interconversion of I and VI occurs *via* electronic excited states.[22] We conclude that the photochemical interconversion of 7-methoxycycloheptatriene and 1-methoxycycloheptatriene probably proceeds *via* the lowest singlet excited state of the triene in each case.

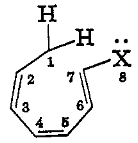
The specificity of the photochemical interconversion of 7-methoxycycloheptatriene and 1-methoxycycloheptatriene is of special interest. Orbital symmetry arguments suggest that photochemical, suprafacial, sigmatropic reactions of order [1,7] are allowed in cycloheptatrienes.[22] This suggestion is consistent with experimental observation.[6–8] A single sigmatropic shift of order [1,7] is possible for 7-methoxycycloheptatriene and leads to 1-methoxycycloheptatriene. Two related sigmatropic shifts are possible for 1-methoxycycloheptatriene which should lead to 7-methoxycycloheptatriene and 2-methoxycycloheptatriene. Experimentally, only the sigmatropic shift leading to 7-methoxycycloheptatriene is observed. Orbital symmetry arguments apply only to processes in which the transition state has some element of symmetry. Previously developed orbital symmetry arguments for hydrogen transfer reactions have been applied only to transfers between the terminals of systems of the type $>CH(C{=}C)_m$.[22] In these cases the symmetry of the highest occupied molecular orbital is the controlling factor. The transition state for the conversion of VIa to Ia is asymmetric, and simple orbital symmetry arguments cannot be applied. It is interesting to note, however, that the highest occupied molecular orbital (ψ_6, XIV) for the electronically excited nine-electron, eight-atom π system[23] is such that suprafacial hydrogen transfer from position 1 to position 7 with continuous overlap is feasible,[24] while suprafacial transfer from position 1 to position 2 with continuous overlap is not feasible.



Ia VIa



XIV



Photochemical valence isomerization of conjugated dienes to cyclobutenes involves singlet excited states in certain cases and triplet excited states in others. Srinivasan has shown that a singlet excited state is the reactive species in the valence isomerization of cycloheptatriene and has provided other examples of valence

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(22) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 2511 (1965).

(23) The ether oxygen atom with two electrons is included in the basic π system.

(24) In general, for systems in which two or more sigmatropic reactions of order $[1,j]$ are possible, the reaction with the highest value of j is favored. This may be a consequence of the greater degree of conjugation in the transition state for the process with the highest value of j.[22]

tautomerization *via* singlet excited states.[4,25] Schenck and co-workers[26] have noted photosensitization of the valence tautomerization of *cis,cis*-1,3-cyclooctadiene, and Dauben and co-workers[27] have demonstrated photosensitization of the valence tautomerization of 1,1-bicyclohexenyl and have provided additional examples which proceeed *via* singlet excited states. Liu[28] has shown that the photosensitized isomerization of *cis,cis*-1,3-cyclooctadiene first gives *cis,trans*-1,3-cyclooctadiene which undergoes thermal cyclization to bicyclo[4.2.0]oct-7-ene in the manner described by Fonken and co-workers.[29] Liu[28] has suggested that a similar sequence of reactions may occur in 1,1′-bicyclohexenyl.

In the photoisomerization of 1-methoxycycloheptatriene to 1-methoxybicyclo[3.2.0]hepta-3,6-diene it is clear that the reaction is not quenched by oxygen. Addition of acetophenone to the solution slows the reaction because of light absorption by the sensitizer. No photosensitization is observed. It thus seems likely that the triplet excited state is not involved in formation of the valence tautomer IIa. This again poses the problem of electronic *vs.* vibrational excitation. Formation of 1-methoxybicyclo[3.2.0]hepta-3,6-diene is favored in solution but not in the vapor phase. This observation strongly suggests that the reaction proceeds through an electronic excited state rather than a vibrationally excited ground state. Molecular orbital arguments also suggest that an electronic excited state is the species responsible for valence isomerization.[30]

Experimental Section

Analytical Techniques. Nuclear magnetic resonance spectra were recorded at 60 Mc on either a Varian Associates A-60 analytical nmr spectrometer or upon a Varian Associates HR-60 nmr spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 21 double-beam infrared spectrophotometer. Ultraviolet spectra were recorded on a Beckman DK-2A ratio recording spectrophotometer. Gas chromatographic analyses were performed on an F & M Model 500 programmed temperature gas chromatograph or a Perkin-Elmer vapor fractometer using helium as a carrier gas at flow rates from 40 to 100 cc/min. Individual columns and conditions of chromatography are described as they appear in the Experimental Section.

Solvents. Benzene (Matheson Coleman and Bell) was purified just prior to use by the method of Fieser.[31] Ethyl ether (Mallinckrodt) was distilled from phosphorus pentoxide and stored over sodium wire. Oxygen was removed by bubbling nitrogen gas through these solvents for 1 hr just prior to use.

Filter Solution. The filter solution used in this work was prepared by dissolving 0.600 g of 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate[32] and 25 g of potassium hydrogen phthalate in 1 l. of water. This solution (1 ml), diluted to 10 ml with water, gave 65% transmission of light at 3660 A and no transmission below 3400 A (1-cm path).

Preparation of 7-Methoxycycloheptatriene (I). Tropilidine chloride prepared by the method of Kursanon[33] was used to prepare 7-methoxycycloheptatriene according to the procedure of Doering and Knox.[35]

Preparation of 3-Methoxycycloheptatriene. This material was was prepared in 76% yield by the method of Weth and Dreiding,[9d] bp 74–75° (25 mm).

Preparation of 1-Methoxycycloheptatriene (VIa). This material was prepared in 63% yield from 7-methoxycycloheptatriene according to the method of Weth and Dreiding,[9d] bp 77–80° (30 mm).

Irradiation of 7-Methoxycycloheptatriene. A solution of 8.0 g (0.065 mole) of 7-methoxycycloheptatriene in 2.0 l. of anhydrous, oxygen-free ether was irradiated with a quartz-jacketed Hanovia immersion lamp (Type A) for 8 hr. After evaporation of the solvent, the residue was distilled through a short column to give 9.4 g (92%) of 1-methoxybicyclo[3.2.0]hepta-3,6-diene [bp 39° (20 mm)]. This was the highest yield obtained. Yields varied substantially (25–92%) and seemed to depend on the amount of polymerization during distillation. Vapor phase chromatography (using internal standards) and nmr analysis of the crude product showed an essentially quantitative yield of 1-methoxybicyclo-[3.2.0]hepta-3,6-diene.

Anal. Calcd for $C_8H_{10}O$: C 78.65; H, 8.25, Found C, 78.83; H, 8.36.

1-Ethoxybicyclo[3.2.0]hepta-3,6-diene. A solution of 7-ethoxycycloheptatriene (10 g) in absolute ether (2 ml) was irradiated 8 hr with a Hanovia immersion lamp (Type A) encased in a quartz immersion well. Distillation of the ethereal solution through a short Vigreux column gave 1-ethoxybicyclo[3.2.0]hepta-3,6-diene (9.1 g, 91%), bp 47° (21 mm).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.53; H, 8.83.

Pyrolysis of 1-Ethoxybicyclo[3.2.0]hepta-3,6-diene. 1-Ethoxybicyclo[3.2.0]hepta-3,6-diene (2.0 g) was dropped into a preheated (340°) vertically mounted pyrolysis column packed with Pyrex helices and swept through with a stream of dry nitrogen. The exit from the pyrolysis column was connected to a trap immersed in a Dry Ice–acetone bath. The infrared, ultraviolet, and nmr spectra of the material collected in the trap were identical with those of an authentic sample of 1-ethoxycycloheptatriene.

A control experiment in which 7-ethoxycycloheptatriene was put through the same pyrolysis column at 340° gave only 30% 1-ethoxycycloheptatriene. At 410° complete conversion to 1-ethoxycycloheptatriene was achieved. The product in this case was isolated in 71% yield.

Pyrolysis of 1-Methoxybicyclo[3.2.0]hepta-3,6-diene. 1-Methoxybicyclo[3.2.0]hepta-3,6-diene was pyrolyzed in the manner described above with the column preheated at 352°. The product was identified by comparison of spectra with an authentic sample of 1-methoxycycloheptatriene.

In a control experiment pyrolysis of 7-methoxycycloheptatriene at 350° in the same column gave less than 40% conversion to 1-methoxycycloheptatriene. At 420° conversion was complete and 1-methoxycycloheptatriene was isolated in 74% yield.

1-Ethoxybicyclo[3.2.0]heptane. Platinum oxide (20 mg) in carbon tetrachloride (3 ml) was prereduced, and 1-ethoxybicyclo-[3.2.0]hepta-3,6-diene (73 mg) was added. The solution absorbed 2.08 equiv of hydrogen. After filtration, the product was isolated by preparative-scale vapor phase chromatography on a $^3/_8$ in. × 6 ft Ucon LB 550X on Chromosorb P (1:5) column. The nmr spectrum of the product showed only protons on saturated carbon.

Anal. Calcd for $C_9H_{16}O$: C, 77.14; H, 11.43. Found: C, 76.86; H, 11.14.

1-Methoxybicyclo[3.2.0]heptane. Platinum oxide (20 mg) in carbon tetrachloride (3 ml) was prereduced. 1-Methoxybicyclo-[3.2.0]hepta-3,6-diene (97 mg) was added. The solution absorbed 2.05 equiv of hydrogen. The product was separated by preparative-scale vpc as described above. The nmr spectrum of the prod-

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(33) This preparation was first reported by D. N. Kursanon and M. E. Volpin, *Dokl. Akad. Nauk SSSR*, **113**, 339 (1957). Since that time, other workers[34] have suggested that, while this preparation yielded a compound whose chemical properties were essentially the same as tropilidine chloride, in actual fact a chlorophosphorus complex was formed with cycloheptatriene.

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(35) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

uct showed only protons on saturated carbon and the methoxyl protons.

Anal. Calcd for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 76.02; H, 11.16.

Vapor-Phase Irradiation of 7-Methoxycycloheptatriene. The apparatus used consisted of a vacuum line containing two cold traps connected by a coil made from a 12-ft length of 10 mm (o.d.) quartz tubing. The coil was 4 in. high and 3 in. in diameter. A Hanovia lamp (Type A) was mounted in the center of the coil. 7-Methoxycycloheptatriene (1.2 g) was introduced into one trap and cooled in Dry Ice–acetone. The system was then evacuated to 0.05 mm. The Dry Ice–acetone bath was then moved to the other trap and the 7-methoxycycloheptatriene slowly distilled through the coil to the other trap. This distillation was repeated twice, and the condensed liquid was recovered. Vpc analysis showed 7-methoxycycloheptatriene (14%), 1-methoxycycloheptatriene (38%), and 1-methoxybicyclo[3.2.0]hepta-3,6-diene (48%).

1-Methoxybicyclo[3.2.0]hept-3-ene. A solution of 1-methoxybicyclo[3.2.0]hepta-3,6-diene (2.74 g) in carbon tetrachloride containing 10% platinum on charcoal (50 mg) was permitted to absorb 1 equiv of hydrogen. Vpc analysis of the product showed one major component (95%). The nmr spectrum of the product showed only traces of residual absorption due to the cyclobutene protons but showed a strong resonance at τ 4.30 for the cyclopentene protons. The product proved to be rather sensitive and was used in the next step without further purification.

Conversion of 1-Methoxybicyclo[3.2.0]hept-3-ene to 1,4-Cycloheptanedione. A mixture of sodium borohydride (0.55 g) and anhydrous zinc chloride (0.1 g) in anhydrous ether (20 ml) was stirred for 1.4 hr under a nitrogen atmosphere. A solution of 1-methoxybicyclo[3.2.0]hept-3-ene (6.2 g) in anhydrous ether (15 ml) was added.[36] Boron trifluoride etherate (2.2 g) in anhydrous ether (5 ml) was added dropwise during 1 hr. After stirring for 2 hr, excess hydride was destroyed with water (2 ml). A solution of sodium dichromate (12.5 g) in sulfuric acid (4 ml of concentrated, diluted to 25 ml with water) was added over a 15-min period. After heating under reflux for 2 hr, the upper layer was separated, and the lower (aqueous) layer was extracted twice with ether (10 ml). The combined ether solutions were dried over magnesium sulfate and carefully concentrated to 20 ml. Treatment of a 5-ml portion of this solution with 2,4-dinitrophenylhydrazine in ethanolic acid gave, after recrystallization from nitrobenzene–ethanol, orange crystals, mp 242–243°. These crystals were identified as 1,4-cycloheptanedione bis(2,4-dinitrophenylhydrazone) by mixture melting point with an authentic sample and comparison of infrared spectra. Analysis of the remainder of the ether solution by vpc showed only ether and 1,4-cycloheptanedione. Vpc analysis using an internal standard (*n*-butyl ether) gave an estimated yield of 1,4-cycloheptanedione of 21% (based 1-methoxybicyclo[3.2.0]hepta-3,6-diene).

Irradiation of 3-Methoxycycloheptatriene. A solution of 3-methoxycycloheptatriene (8.5 g) in ether (2 l.) was irradiated for 21 hr with a Hanovia mercury lamp (Type A) in a quartz immersion well. Evaporation of the ether and distillation gave an oil (4.74 g) and tar (~4 g). The oil was separated into two fractions by preparative-scale vpc (F silicone column), A (1.23 g) and B (680 mg). Analysis (vpc) of fraction A showed the presence of three components. Careful separation of fraction A (1 g) by preparative-scale vpc (diisodecyl phthalate column) gave 1-methoxybicyclo[3.2.0]hepta-3,6-diene (50 mg) and a mixture of two other bicyclic compounds (530 mg). Reduction of the mixture of bicyclic compounds (530 mg) in ethyl acetate (2.5 ml) containing 5% Pd–C, filtration, and removal of the solvent gave a colorless oil (500 mg). Vpc analysis of the oil showed the presence of at least three compounds. Separation of the oil by preparative-scale vpc (Ucon LB 550X column) gave fractions A-1 (50 mg), A-2 (18 mg), and A-3 (17 mg). Fraction A-1 showed only saturated protons (including $CH_3OCH<$ absorption). A-2 also showed OCH_3 absorption. A-3 was identified as bicyclo[3.2.0]heptan-6-one by comparison of its infrared spectrum with that of an authentic sample.[16] The ultraviolet absorption of fraction B suggested that it was a mixture of isomeric methoxycycloheptatrienes. This was confirmed by the nmr spectrum of the mixture. Comparison of the nmr spectrum of the mixture with the spectra of authentic samples of the isomeric methoxycycloheptatrienes suggested the presence of 1-, 2-, and 3-methoxycycloheptatrienes.

A portion of A (230 mg) in ethanol (0.5 ml) and 1 *N* sulfuric acid (0.5 ml) was heated on a steam bath for 30 min. Extraction, drying, and removal of the solvent gave an oil which showed infrared absorption at 5.62, 5.78 (sh), 5.87, and 6.04 μ.

Monitored Irradiations of 7-Methoxycycloheptatriene. A. A solution of 7-methoxycycloheptatriene (8.0 g) in oxygen-free ether (1.75 l.) was irradiated with a Hanovia mercury lamp (Type A) in a quartz immersion well. Samples (50 ml) were withdrawn every 30 min and analyzed by ultraviolet, vpc, and nmr methods. The ultraviolet analysis showed steady decrease of the 255-mμ maximum of 7-methoxycycloheptatriene, buildup of a broad maximum at 280 mμ, and decay of the 280-mμ maximum. Vpc analysis (F silicone, 80°) gave the plots shown in Figure 1 which show the formation and destruction of an intermediate. The nmr analysis showed steady decrease in the OCH_3 signal (τ 6.63) of 7-methoxycycloheptatriene, rapid formation of a new OCH_3 signal (τ 6.47) at lower field and a CH_2 signal (τ 7.55, doublet, J_{app} = 7.4 cps)[37] due to 1-methoxycycloheptatriene, and slower formation of a OCH_3 signal (τ 6.76) and CH_2 signal (τ 7.62) due to 1-methoxybicyclo[3.2.0]hepta-3,6-diene. As the reaction progressed, the signals characteristic of 7-methoxycycloheptatriene disappeared first, then the signals characteristic of the intermediate (1-methoxycycloheptatriene) disappeared, leaving only signals due to 1-methoxybicyclo[3.2.0]hepta-3,6-diene.

B. A solution of 7-methoxycycloheptatriene (8.0 g) in ether (1.75 l.) was irradiated as described above. Samples were withdrawn every 5 min and analyzed by vpc. The results obtained are plotted in Figure 2. It is clear that 1-methoxybicyclo[3.2.0]hepta-3,6-diene is not formed until a significant amount of the intermediate (1-methoxycycloheptatriene) is formed. The bicyclic product thus is not a primary photoproduct of 7-methoxycycloheptatriene.

C. A solution of 7-methoxycycloheptatriene (8.0 g) in ether (1.75 l.) was irradiated as described above for 2 hr. Evaporation of the ether gave the crude mixture of photoproducts. The crude product showed three components (vpc). Separation of 1 g of the mixture by preparative-scale vpc gave 1-methoxybicyclo[3.2.0]hepta-3,6-diene (190 mg), 1-methoxycycloheptatriene (100 mg), and 3-methoxycycloheptatriene (thermal rearrangement product of 7-methoxycycloheptatriene, 120 mg). The products were identified by comparison of spectra with those of authentic samples.

Irradiation of 1-Methoxycycloheptatriene. A solution of 1.4 g (0.012 mole) of 1-methoxycycloheptatriene in 2 l. of anhydrous ether was irradiated for 9 hr with a quartz-jacketed Hanovia immersion lamp (Type A). The solution was concentrated on a rotary evaporator and distilled, giving 1-methoxybicyclo[3.2.0]hepta-3,6-diene (0.6 g 43%) identified by comparison of nuclear magnetic resonance and infrared spectra with that of a sample prepared by the irradiation of 7-methoxycycloheptatriene. No attempt to maximize the yield was made.

Short-Term Irradiation of 1-Methoxycycloheptatriene. A solution of 1-methoxycycloheptatriene (500 mg) in oxygen-free benzene (250 ml) was irradiated for 1 hr using a Pyrex-jacketed Hanovia immersion lamp (Type A). The solvent was distilled off, and the nmr spectrum of the crude reaction mixture was taken. Three peaks in the methoxy region were observed and identified as being due to 7-methoxycycloheptatriene, 1-methoxycycloheptatriene, and 1-methoxybicyclo[3.2.0]hepta-3,6-diene. Integration of these three peaks showed that the 7-methoxy compound composed approximately 20% of the total product mixture. Formation of 7-methoxycycloheptatriene could also be followed by the appearance of its characteristic ultraviolet absorption at 255 mμ.

Irradiation of 7-Methoxycycloheptatriene in the Presence and Absence of Oxygen. A solution of 1.0 g (0.0082 mole) of 7-methoxycycloheptatriene in 240 ml of oxygen-free benzene was irradiated with a Pyrex-jacketed Hanovia immersion lamp (Type A) for 3 hr. The solvent was evaporated from a 50-ml aliquot, and the nmr spectrum of the residue was taken. The amount of reaction was estimated by comparing the integral ratios of the peaks due to the methoxy groups of I, II, and III. This integration gave the values Ia (38%), VIa (17%), and IIa (45%).

The experiment was repeated using oxygen-saturated benzene and bubbling oxygen through the mixture during the reaction. The nmr spectrum of the crude product showed Ia (22%), VIa (14%), and IIa (64%). Errors in the integration are relatively large (±10%), but it is clear that continuous saturation of the solution with oxygen does not quench the reaction.

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(36) The procedure used was adapted from that of Brown and Garg.[13]

(37) The apparent splitting probably is not a true coupling constant.

Irradiation of 1-Methoxycycloheptatriene in the Presence and Absence of Oxygen. A solution of 1-methoxycycloheptatriene (500 mg) in oxygen-free benzene (250 ml) was irradiated with a Pyrex-jacketed Hanovia immersion lamp (Type A) for 1 hr. A 50-ml aliquot of this solution was taken, and the solvent was removed. Examination of the residual oil by nmr showed Ia (21%), VIa (55%), and IIa (24%).

The same scale experiment was repeated using oxygen-saturated benzene (oxygen was bubbled through the solution throughout the period of irradiation). After 1-hr irradiation, nmr analysis showed Ia (19%), VIa (59%), and IIa (22%).

Irradiation of 7-Methoxycycloheptatriene in the Presence and Absence of Acetophenone. A solution of 100 mg (0.0082 mole) of 7-methoxycycloheptatriene in 5 ml of oxygen-free benzene was prepared. This solution (1 ml) was placed in each of two Pyrex nmr tubes. To one of the tubes 30 mg of acetophenone was added, then both were sealed. The tubes were irradiated with a Pyrex-jacketed Hanovia immersion lamp (Type A) through a 2-mm-thick layer of filter solution (described above). At appropriate intervals the tubes were removed, and the nmr spectra were run. After 12-hr irradiation no significant reaction had occurred in either tube.

Irradiation of 1-Methoxycycloheptatriene in the Presence and Absence of Sensitizers. These irradiations were carried out using nmr tubes as described above. However, in this case, after 1-hr irradiation *ca.* 50% of the 1-methoxycycloheptatriene had rearranged to a mixture of 7-methoxycycloheptatriene and 1-methoxybicyclo[3.2.0]hepta-3,6-diene. Addition of 1 molar equiv of acetophenone definitely slowed down the rearrangement while a 10 molar equiv excess of acetophenone effectively halted the rearrangement as did 1 equiv of benzophenone. At the concentrations used (0.16 *M* in substrate and sensitizer) 1-methoxycycloheptatriene (ϵ_{3600} 4.1) had a slightly higher absorbance (0.65 at 3600 A) than acetophenone [ϵ_{3600} 3.1; A (0.16 M) = 0.49]. Using 0.16 *M* 1-methoxycycloheptatriene and 1.6 *M* acetophenone, the respective absorbances were 0.65 and 4.90. In this case >88% of the incident light is absorbed by the acetophenone. No reaction could be detected after 1-hr irradiation. Benzene absorption is not a problem (ϵ_{3400} 4.44×10^{-4}; $\epsilon_{3600} \approx 0$).

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The Mechanism of Isotopic Exchange between Arylmercuric Compounds and Elemental Mercury[1a]

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Abstract: The mechanism of the facile isotope exchange between arylmercuric compounds in solution and metallic mercury was examined. All reasonable mechanisms except a true isotopic exchange at the surface of the liquid are eliminated. The reaction rate is not significantly limited by mass transport in either phase. The reaction shows a real but small solvent dependence which is not correlated with the solubility of the substrate or any common solvent parameter. This and the value of $\Delta S^{\neq}$ favor a rate-determining chemisorbtion step. The efficiency of substrate collisions with the metal is much higher than that of collisions with the Hg^0 atoms in solution for bringing about exchange, suggesting a rate-determining electron transfer. Reactivity seems to be in the order RHgI > RHgBr > RHgCl > RHgOAc >> RHgR. An over-all mechanism is proposed.

Several years ago Reutov and Ostapchuk[2] reported that the isotope exchange shown in eq 1, rather surprisingly, proceeded under mild conditions in a variety of solvents. Halogen atoms, aryl groups, and

$$R_1HgR_2 + {}^{203}Hg^0 \rightleftharpoons R_1{}^{203}HgR_2 + Hg^0 \qquad (1)$$

certain special alkyl groups can be used as R_1 and R_2.[2-5] The original report has been confirmed and extended in a series of papers by Reutov and his co-workers,[3] and by Pollard and Westwood.[4,5] The most important findings of these workers have been that the reaction could be carried out under conditions where its rate was not transport controlled, and that it was totally unaccompanied by chemical changes. In the case that R_1 or R_2 is optically active there is not even a loss of optical activity accompanying the exchange.[3] From these observations, and others, a mechanism involving a four-center transition state was deduced.

The present paper describes the exchange between *p*-methoxyphenylmercurials, RHgX, and elemental mercury. In contrast with previous work the rate of encounter of the substrate with the surface can be estimated. The surface area and conditions were more closely controllable than those of previous investigators. A much wider range of substrate concentrations was conveniently studied by labeling the organomercurial rather than the elemental mercury. The effect of solvent on reactivity and the solubility of the substrate in the same solvents were extensively studied. The effect of varying X, through the halogens and acetate, was studied. An upper limit was placed on the rate of the analogous reaction in homogeneous solution. The findings that the exchange is interfacial, largely unlimited by mass transport, and unaccompanied by chemical reactions were confirmed. Surface encounters are at least several orders of magnitude more effective than encounters with mercury atoms in solution for producing exchange. This finding, com-

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(2) O. A. Reutov and G. M. Ostapchuk, *Dokl. Akad. Nauk SSSR*, **117**, 826 (1957).

(3) O. A. Reutov, *Angew. Chem.*, **72**, 198 (1960); other papers by Reutov and his co-workers are referred to here.

(4) D. R. Pollard and J. V. Westwood, *J. Am. Chem. Soc.*, **87**, 2809 (1965).

(5) D. R. Pollard and J. V. Westwood, *ibid.*, **88**, 1404 (1966).