Photosensitized Fragmentation of a Bicyclo[4.2.0]octa-2,4-diene Derivative. Preparation of the Isomeric 1,2-Diacetoxyethylenes

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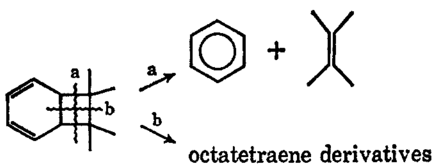
Photosensitized reactions of *trans*-7,8-diacetoxybicyclo[4.2.0]octa-2,4-diene (1) lead to the isomeric diacetoxyethylenes and benzene in good yield and to a cycloadduct dimer of 1 as a minor product. The results contrast sharply with the results of direct irradiation of 1. Both *cis* and *trans* isomers of diacetoxyethylene are formed as primary products, though 1 is known to be cleanly a *trans* compound. Mechanisms which will account for the stereochemical result are discussed; one possibility is the fragmentation of triplet 1 to benzene and triplet diacetoxyethylene, a reaction of theoretical significance.

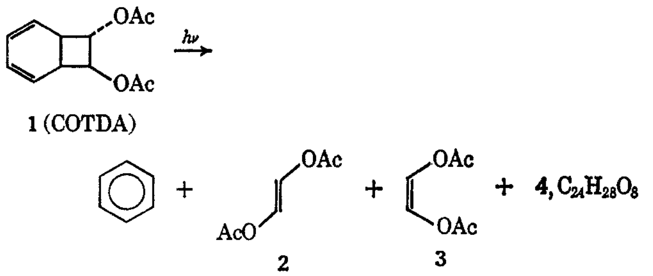
The photochemical behavior of bicyclo[4.2.0]octa-2,4-diene derivatives has been of interest to several groups.[1–3] Two general modes of reaction has been observed. Thus, the well-known bullvalene synthesis[1]



involves a type a fragmentation of a dimer of cyclooctatetraene. The benzonitrile–trimethylethylene photoadduct undergoes both types of cleavage,[2] while only type b cleavage has been reported for *trans*-7,8-diacetoxybicyclo[4.2.0]octa-2,4-diene (1).[3] We have investigated the photochemistry of 1 in the presence of photosensitizers and find, in contrast, evidence only for the type a process. This paper describes the products arising from the triplet state of 1 and discusses possible mechanisms for their formation.

Results

Irradiation of 1 in ether in the presence of benzophenone, thioxanthone, or fluorenone as photosensitizer at wavelengths longer than 3000 Å led to benzene and the isomeric 1,2-diacetoxyethylenes 2 and 3 as the major products in 50–80% yield. Since the only previous report[4] of 2 and 3 gave minimal structure evidence, a thorough spectral investigation seemed appropriate. The high-resolution mass spectrum confirms $C_6H_8O_4$ as the molecular formula. For each isomer, the nmr shows two singlets in the ratio of 6:2 in the acetyl and vinyl regions, respectively. Assignment of geometry follows from the observation of a C=C stretch in the ir of the higher melting *cis* isomer but not in the *trans*. Observations of the olefinic H–H coupling constant from the C^{13} satellite peaks (J_{H-H} = 11 Hz, *trans*; 4 Hz, *cis*.) confirms the isomer assignment[5] and eliminates vinylidene acetate as a possibility.



Concentration of the ether solution afforded a 5–10% yield of 4, mp 209–211.5° after recrystallization from toluene. The structure of this material has not been established in detail, but the molecular weight, mass spectral fragmentation pattern, and nmr show it to be a cycloadduct dimer of 1. There is ample analogy for photosensitized dimerization of cyclohexadienes.[6]

A quantitative study of the fragmentation reaction has been carried out. The reaction can be sensitized in either ether or benzene by fluorenone, thioxanthone, or benzophenone with substantially the same results. Interestingly, both 2 and 3 are primary photoproducts though the starting material 1 is exclusively *trans*. The quantum yields (at 3660 Å) for 2 and 3 add to about 0.3 at 0.02 *M* 1 (see Table I). The ratio of quantum yields ϕ_2/ϕ_3 is 1.22 ± 0.02 in ether and 1.48 ± 0.02 in benzene, invariant to sensitizer. The ratio is independent of the extent of conversion in the early stages of the reaction for all sensitizers; however, prolonged irradiation of the benzene solutions leads to changes in the *cis–trans* ratio for benzophenone and thioxanthone due to a subsequent photosensitized isomerization of the diacetoxyethylenes. This effect was not observed with fluorenone.

The reaction has been studied as a function of the concentration of 1. The sum of the quantum yields of 2 and 3, $\phi_2 + \phi_3$, diminishes markedly as the concentration of 1 increases though no change in the ratio ϕ_2/ϕ_3 is observed outside of experimental error. This observation is expected for a unimolecular fragmentation to give 2 and 3 which must compete with the bimolecular dimerization reaction. These data lead to the mechanism outlined below (eq 1–6).

$$S \xrightarrow{h\nu} S^1 \xrightarrow{\phi_{ic}} S^3 \tag{1}$$

$$S^3 + \text{COTDA} \longrightarrow S + \text{COTDA}^3 \tag{2}$$

$$\text{COTDA}^3 \xrightarrow{k_2} C_6H_6 + trans\text{-AcOCH=CHOAc} \tag{3}$$

$$\text{COTDA}^3 \xrightarrow{k_3} C_6H_6 + cis\text{-AcOCH=CHOAc} \tag{4}$$

$$\text{COTDA}^3 \xrightarrow{k_D} \text{COTDA} \tag{5}$$

$$\text{COTDA}^3 + \text{COTDA} \xrightarrow{k_{DIM}} 4 \tag{6}$$

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[1] G. Schröeder, *Chem. Ber.*, **97**, 3140 (1964).

[2] J. G. Atkinson, D. E. Ayer, G. Büchi, and E. W. Robb, *J. Amer. Chem. Soc.*, **85**, 2257 (1963).

[3] D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959).

[4] M. F. Shostakovskii, V. N. Kuznetzof, and C.-M. Yang, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk*, 710 (1962).

[5] The isomers were incorrectly assigned in ref 4.

[6] D. Valentine, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5202 (1964).

TABLE I

YIELDS OF DIACETOXYETHYLENES FROM SENSITIZED PHOTOLYSES OF COTDA (**1**)

Solvent	(**1**), *M*	Sensitizer	E_T	% **2**[a]	% **3**[a]	ϕ_2[b]	ϕ_3[b]	ϕ_2/ϕ_3
Ether	0.055	Fluorenone	53	32	26	0.13	0.10	1.22 ± 0.02
Ether	0.022	Fluorenone	53	40	32	0.16	0.13	1.24 ± 0.02
Ether	0.012	Thioxanthone	65	44	37	0.25	0.21	1.21 ± 0.02
Benzene	0.021	Benzophenone	69	16.5	22	0.18	0.12	1.50 ± 0.05
Benzene	0.022	Fluorenone	53	43.5	30.6	0.17	0.12	1.48 ± 0.02
Benzene	0.030	Thioxanthone	65	28.8	35.7	0.18	0.125	1.47 ± 0.02

[a] Over-all yield. [b] Quantum yield at 5–15% reaction.

This mechanism leads readily to the following kinetic expression (eq 7). Here $\phi_F = \phi_2 + \phi_3$ = the total

$$\frac{\phi_{ic}}{\phi_F} = 1 + \frac{k_D}{k_F} + \frac{k_{DIM}}{k_F}\,(\text{COTDA}) \qquad (7)$$

fragmentation quantum yield, $k_F = k_2 + k_3$ = the sum of the fragmentation rate constants, and COTDA (cyclooctatetraene diacetate) stands for **1**. A fit to eq 7 is observed, with $k_D/k_F = 1.55 \pm 0.1$ and $k_{DIM}/k_F = 36\ M^{-1}$ in benzene (Figure 1).

Discussion

Multiplicity.—Compound **1** represents the first bicyclo[4.2.0]octa-2,4-diene derivative for which data are available both for direct[3] and sensitized irradiation. We have repeated the direct irradiation and, in a preliminary experiment, find no evidence for the formation of **2** or **3**. We conclude that, for **1** at least, the type a fragmentation is a triplet-state process while the type b process must be essentially exclusively a singlet-state process. This in accord with observations on cyclohexadiene itself, where ring opening to hexatriene occurs from the singlet state,[7] but the triplet-state chemistry exclusively involves dimerization.[6]

An attractive, though speculative, conclusion is that all type a processes occurring upon direct irradiation[1,2] involve intersystem crossing to the triplet. The competing conrotatory ring-opening process allowed photochemically by the Woodward–Hoffmann rules[8] would lead to the strained *trans,cis,cis*-cyclooctatriene derivative and therefore might be relatively slow in the bicyclo system. Intersystem crossing then might compete, even though it appears not to in the cyclohexadiene–hexatriene conversion.

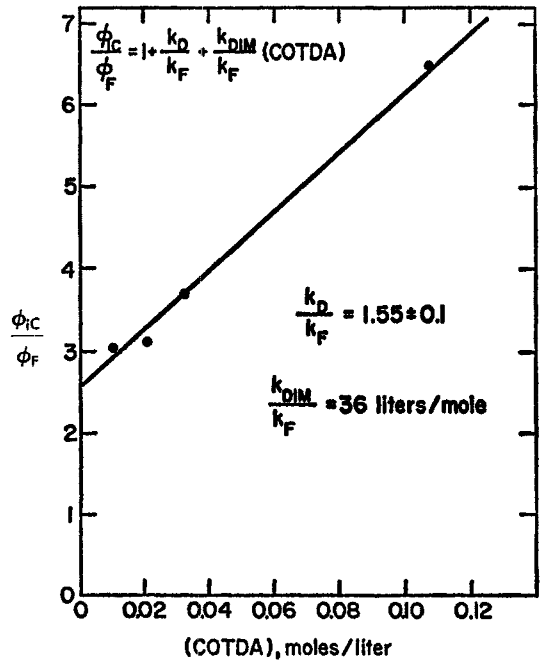

Figure 1.—Plot of the reciprocal fragmentation quantum yield for COTDA *vs.* COTDA concentration.

Kinetic Results.—Figure 1 allows determination of the ratio k_{DIM}/k_D as 23 M^{-1}. This may be compared with the results of Hammond and Vesley referred to by Lam, Valentine, and Hammond[9] who determined that, for dimerization of cyclohexadiene sensitized by benzophenone, $1/\phi = 1 + 0.028/(\text{cyclohexadiene})$. This leads to $k_{DIM}/k_D = 36\ M^{-1}$ for cyclohexadiene. Comparison of the results for **1** is gratifying. For **1**, dimerization appears to be slowed down relative to decay by a factor of two or so, quite consistent with what one would have expected on the basis of the increased steric hindrance on the one face of the cyclohexadiene ring. One may therefore conclude that the lifetime of the triplet state of **1**, k_D^{-1}, probably is close to that for cyclohexadiene. There appears to be no very efficient anomalous decay process, analogous to that suggested for ketones which may undergo the Norrish II reaction,[10] dominant in the present case.

The rate constant k_F for total type a fragmentation must be no larger than about 10^8 sec^{-1}, since k_{DIM} must be less than or equal to the rate constant for diffusion in benzene, about $5 \times 10^9\ M^{-1}$ sec^{-1}. Since the only estimate available for a dimerization reaction between a diene triplet and a ground-state diene molecule is a *maximum* value of about $5 \times 10^6\ M^{-1}$ sec^{-1} for isoprene,[11] k_F may be considerably less. One may conclude that the rate constant for fragmentation is probably somewhere in the range of 10^5–10^8 sec^{-1}: fast, but no means extremely fast for a unimolecular reaction of a triplet state.

Details of the Fragmentation.—Either a stepwise or a concerted process for the fragmentation, eq 8 and 9 will explain the data. The observation that *both* olefins are primary photoproducts demands a mechanism that can account for the loss of stereochemistry. In reaction 8, loss of stereochemistry arises from rotation about a single bond in the biradical intermediate. In reaction 9, it arises from the partitioning of the (presumably twisted) olefin triplet between decay to *trans* isomer and *cis* isomer.

Distinguishing between eq 8 and 9 is an extremely important point, since a reaction such as 9a is of considerable theoretical significance. There are no proven examples of photochemical fragmentations of

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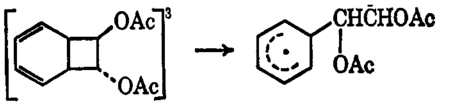
[7] R. Srinivasan, *Advan. Photochem.*, **4**, 113 (1966), and references contained therein.

[8] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

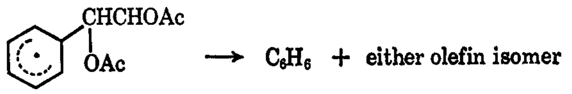
[9] E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *ibid.*, **89**, 3482 (1967).

[10] P. J. Wagner, *ibid.*, **89**, 5898 (1967).

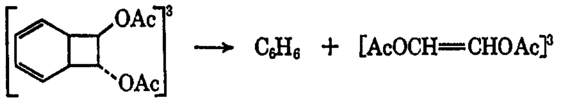
[11] R. S. H. Liu, N. J. Turro, and G. S. Hammond, *ibid.*, **87**, 3406 (1965).



(8a)



(8b)



(9a)

$$[AcOCH{=}CHOAc]^3 \longrightarrow \text{either olefin isomer} \qquad (9b)$$

large organic molecules which give electronically excited fragments. However, the reasonable supposition that chemical reactions of an initially formed molecule may lead to intermediate or product molecules containing electronic excitation is an integral part of one of the more successful schemes for rationalizing photochemical mechanisms.[12] Indeed, Zimmerman[13] has raised very similar questions in a recent communication dealing with the photorearrangement of 6,6-disubstituted bicyclo[3.1.0]hex-3-en-2-ones.

We feel that organic photochemistry needs direct evidence relating to the question of the timing of the loss of electronic excitation, if only for a few simple systems such as the present one, in view of the theoretical importance of the question. It might be noted that the present example might be particularly favorable for the occurrence of a reaction such as 9a since (1) it is a retro [2 + 2] cycloaddition which is allowed[14] to occur photochemically, (2) Woodward–Hoffmann correlation diagrams for [2 + 2] cycloadditions correlate excited-state reactants *with excited-state products*, and (3) reaction 9a should be exothermic[15] and is therefore energetically feasible.

The experimental distinction between reactions 8 and 9 rests on the determination of the decay ratio for triplet diacetoxyethylene. If reaction 9 is correct, the decay ratio should be precisely equal to the observed initial product ratio, ϕ_2/ϕ_3. Unfortunately, determination of the decay ratio by photosensitized isomerization experiments[16] has proved extraordinarily difficult. Such experiments have led to the conclusion that there must be some interaction between a benzophenone or propiophenone triplet and diacetoxyethylene which leads neither to any observable new photoproduct nor to diacetoxyethylene triplet.[17]

Further experiments in this system, and on related derivatives for which quantitative evidence pertinent to eq 9 may be more easily obtained, are in progress. We are also investigating the photosensitized isomerization of the diaxetoxyethylenes and related compounds.

Experimental Section

***trans*-7,8-Diacetoxybicyclo[4.2.0]octa-2,4-diene (1)** was prepared by the method of Cope, *et al.*[18] It was purified by recrystallization from hexane, sublimation at 10^{-3} mm and one further recrystallization from hexane; mp 60–61.8, lit.[18] 60–61°. The material was homogeneous to tlc and showed two nonequivalent acetates in the nmr spectrum, requiring that the acetates be *trans*. The chemical[18] and spectral[19] observations thus leave no doubt that the stereochemistry of 1 is correct as drawn. The uv of 1 showed one maximum, λ_{max} 269 mμ (ϵ 3900).

Other Compounds.—Sensitizers were twice recrystallized and sublimed. Mallinckrodt anhydrous ether was suitable for preparative use as received. Dodecane was used as an internal standard in all quantitative work. Commercial dodecane (Aldrich Chemical Corp.) was shaken five times with its own volume of cold concentrated sulfuric acid, five times with distilled water, dried over P_2O_5, and distilled, bp 95° (*ca.* 10 mm). Vpc analysis showed the presence of 0.2% impurity, but other experiments[17] showed that the impurity did not quench benzophenone triplets detectably.

Benzene for quantitative photochemical work was shaken with its own volume of cold concentrated sulfuric acid until the washings were almost colorless (four or five times). It was washed with distilled water, dried over P_2O_5, and distilled from P_2O_5.

Preparative-Scale Photolysis of 1.—Fluorenone (0.9 g), 1 (5.00 g), and 1 l. of ether were stirred in a standard 1-l. photochemical reaction vessel, equipped with a Pyrex immersion well, and purged with a slow stream of nitrogen. After 30 min, the reaction mixture was irradiated with a Hanovia 450-W medium-pressure mercury lamp. Results were identical for irradiation times from 2 to 40 hr.

Four such reaction mixtures were combined and concentrated to 200 ml. A solid material (4) (1.05 g) precipitated and was collected. The remainder of the material was distilled on a Teflon spinning-band distillation column to afford (1) ether, (2) a fraction, bp 26.5° (100 mm), identified by vpc retention time and infrared spectrum as predominantly benzene, and (3) three fractions of diacetoxyethylene isomers (2 and 3) totaling 8 g (62%), bp 96.5–99.5° (23 mm). The most careful distillations performed gave 50% of the total as better than 90% pure *trans*, about 15% as an approximately equimolar mixture, and the remaining 35% as better than 95% pure *cis*, which solidified in the receiver. Further purification of the two isomers could be accomplished by preparative gas chromatography on a Carbowax 20M column or, better, by several low-temperature recrystallizations from cyclohexene for the *trans* isomer 2, mp 23°, or for the *cis* isomer 3, mp 42.6–43.8°, trituration as a melt with an equal volume of hexane during solidification.

Spectral data for 2 were as follows: ir, 3080, 1770, 1440, and 1375, no absorption between 1600 and 1700 cm^{-1}; nmr (CCl_4), δ 7.33 (2 H), 2.10 (6 H), $J_{C^{13}-H}$ = 192 Hz for the vinyl protons. Fine structure to the C^{13} satellite of the vinyl protons gives J_{H-H} as 11 Hz. Spectral data for 3 were as follows: ir, 3100, 3020, 1770, 1690, 1620, 1440, 1375, and 1360 cm^{-1}; nmr (CCl_4), δ 6.7 (2 H), 2.15 (6 H), $J_{C^{13}-H}$ = 195 Hz for vinyl protons, J_{H-H} 4 Hz. The mass spectra of the two isomers were very similar, showing major fragments at 102 (M − ketene), 60, 44, 43 (base), 42 for both. Parent peaks were at 144.0416 for 2 and 144.0427 for 3 ($C_6H_8O_4$ requires 144.0422).

Compound 4 showed a weak parent peak in the mass spectrum at 444.1808 ($C_{24}H_{28}O_8$ requires 444.1784), fragments corresponding to the loss of up to four acetate or acetyl or ketene or acetic acid moieties, and major fragments at 222.0893 ($C_{12}H_{14}O_4$ requires 222.0892), 144, 102, and 43. Metastable peaks for 222 → 144 and 144 → 102 were observed. The molecular weight measured by vapor-pressure osmometry was 454. The nmr spectrum in $CDCl_3$ showed 2 H (approximate triplet) at δ 6.4, 2 H (broad singlet) at 5.7, 4 H (multiplet) at 4.6–5.1, and 20 H at 1.8–3.2, including 9 H (broad singlet) at 2.05 and 3 H at 2.1. No uv absorption attributable to a conjugated diene was observed.

Quantitative photochemical experiments were performed in 13-mm Pyrex ampoules. The tubes were necked down for sealoff

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[12] H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

[13] H. E. Zimmerman and J. O. Grunewald, *J. Amer. Chem. Soc.*, **89**, 3354 (1967).

[14] R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

[15] Assuming 20 kcal of strain for the cyclobutane ring, all π bonds as 60 kcal, all σ bonds as 80 kcal, the resonance energy of the benzene ring as 36 kcal, and the E_T values (at the potential minimum) for 1 and 2 as 54 and 60 kcal, the estimated $\Delta H°$ for reaction 9a is −9 kcal/mol.

[16] For details of this technique, see (a) G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964); (b) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965); (c) R. B. Cundall and Davies, *Proc. Roy. Soc.*, **A290**, 563 (1966).

[17] R. A. Caldwell, unpublished results.

[18] A. C. Cope, N. A. Nelson, and D. A. Smith, *J. Amer. Chem. Soc.*, **76**, 1100 (1954).

[19] R. Anet, *Tetrahedron Lett.*, 720 (1961).

under vacuum and connected through grease traps to 14/35 joints, which could then be connected to a vacuum manifold through a cow. Reaction mixtures, containing a known amount of purified dodecane, were added to the sample tube *via* a calibrated syringe, and the samples were subjected to five freeze–thaw outgassing cycles on the vacuum manifold at an ultimate pressure of about 10^{-4} mm. After sealoff, the tubes were irradiated for the desired period of time in a "merry-go-round" rotating sample stage apparatus, with a Hanovia 450-W medium-pressure mercury lamp whose output was filtered (Corning C.S. Number 7-83) to pass only the 3660-Å region.

Actinometry was carried out with potassium ferrioxalate in the standard manner.[20] Reproducibility of quadruplicate (or more) samples throughout the period of a run was ±2% in general and often ±0.5%.

Yields of **2** and **3** measured gas chromatographically relative to dodecane were corrected for differences in detector response. Analyses were performed on 0.25 in. × 6 ft Carbowax 20M columns, 5–10% on either Chromosorb P or Chromosorb W. It was shown that both isomers were stable to the analysis conditions and that **1** did not give **2** and **3** by pyrolysis during analysis.

Registry No.—**1**, 7698-06-8; **2**, 19191-10-7; **3**, 19191-11-8.

Acknowledgment.—I wish to thank Research Corporation for funds used for the purchase of a gas chromatograph, the Petroleum Research Fund for support of this work through Grants 519-G-1 and 3031-A-4, Mr. G. W. Sovocool for assistance with actinometry, and Dr. Stephen Shrader for mass spectrometric analyses and helpful discussions.

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[20] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 785.

Homogeneous Catalytic Deuteration of Olefinic Double Bonds[1]

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The specific deuteration of olefins using tris(triphenylphosphine)rhodium(I) chloride (A) as a homogeneous catalyst has been investigated. Seventeen *n*-monoolefins were deuterated and the distribution and the vicinal positions of the deuterium atoms were located by mass spectrometry. Deuterium adds specifically across the double bonds in *n*-monoolefins and the reaction proceeds to completion in a reasonable time. The mass spectral fragmentation patterns for the deuterioalkanes formed by this specific labeling technique can be used to locate the deuterium atoms and thus to determine the position of the double bond in the original olefin.

For some time, we have been interested in the location of double bonds in olefins for characterization of olefin fractions of shale-oil distillates. About one-third of Green River shale-oil middle distillate (C_{12}–C_{20}) consists of olefins. Knowledge about the type of olefins and the positions of the double bonds in the olefins would be an aid in their utilization.

Young and coworkers[2a] have demonstrated the connection between the formation of a hydride intermediate and homogeneous hydrogenation by using a new compound, tris(triphenylphosphine)rhodium(I) chloride (A). They state that the compound can be used as a catalyst for the reduction of compounds containing double or triple bonds. In a later article, Osborn and coworkers[2b] studied the properties and reactions of A and proposed a mechanism for the hydrogenation of olefins and acetylenes. Birch and Walker[3,4] used A as a homogeneous catalyst for hydrogenation and deuteration. They found that cyclohexene, methyl oleate, methyl linoleate, and ergosterol were deuterated without introduction of additional deuterium. Djerassi[5] and Bielmann[6] have used A as a homogeneous catalyst for the deuteration of steroids, and Zeeh[7] used this homogeneous catalyst to deuterate hydrindanones.

This homogeneous catalytic research is of interest because the heterogeneous, catalytic deuteration of straight-chain olefins is an unsatisfactory method for the selective introduction of deuterium.[8] Heterogeneous catalysts cause double-bond migration and/or exchange reactions between the chemisorbed olefin and the adsorbed deuterium resulting in unspecific labeling.[9,10] For example, Nguyen and Ryhage[11] reported the deuteration of methyl oleate using Adam's platinum catalyst. Their mass spectral results showed a series of molecular ion peaks whose intensities decrease with increasing mass number, due to unspecific labeling.

This paper reports the specific deuteration of 17 *n*-monoolefins using deuterium and A as a homogeneous catalyst. Mass spectrometry was used to determine the location of the deuterium in the alkanes formed.

Monoolefins are readily deuterated using deuterium and A as a homogeneous catalyst to give the corresponding dideuterioalkanes. For example, 1-tridecene was deuterated without difficulty in less than 2 hr at room temperature and slightly above atmospheric pressure. Examination of the mass spectra of the deuterated tridecane showed the addition of two deuteriums to the monoolefin with little evidence of unspecific labeling.

When a heterogeneous catalyst, such as platinum black, was used for the deuteration of 1-tridecene,

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[1] Presented at the Midwest Regional Meeting of the American Chemical Society, Manhattan, Kan., Oct 31–Nov 1, 1968.

[2] (a) J. F. Young, J. A. Osborn, J. H. Jardine, and G. Wilkinson, *Chem. Commun.*, No. 7, 131 (1965); (b) J. A. Osborn, J. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).

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[9] T. I. Taylor in "Catalysis," Vol. 5, P. H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1957, Chapter 5.

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