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On the Photochemical Hydrogen Shifts in Arylcycloheptatrienes*[1]

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Photochemically-induced hydrogen shifts in 7-(*p*-chlorophenyl), 7-phenyl, 7-(*p*-methoxyphenyl) and 7-*p*-tolylcycloheptatrienes (Ia—d) were studied. The possibility of hydrogen 1,7 and 1,3 shifts in these compounds was examined on both experimental and theoretical grounds. It was concluded that the hydrogen 1,7 shift is the only suprafacial hydrogen shift possible in the excited cycloheptatriene system. In this study all the isomers of *p*-chlorophenylcycloheptatriene were separated by applying the Diels-Alder reaction to the photo-reaction mixture; the method of preparing each of those isomers will also be described.

The specific hydrogen shifts in substituted cycloheptatrienes have been one of the most interesting topics in photochemistry.[1-5] In 1965 Woodward and Hoffmann[6] successfully interpreted the specific mode of the hydrogen shift in the conjugated allyl system on the basis of molecular orbital symmetry considerations; they implied that the suprafacial hydrogen 1,3 and 1,7 shifts are permitted photochemically in the cycloheptatriene. ter Borg and Kloosterziel,[3] in 1965, reported the unexpected formation of 2-phenylcycloheptatriene (IIIb) from 7-phenylcycloheptatriene (Ib) upon irradiation with a high-pressure mercury lamp. They explained this transformation as a consequence of successive hydrogen 1,7 shifts *via* 1-phenylcycloheptatriene (IIb). However, Murray and Kaplan[5] have recently suggested this to be a possible case of a symmetry-allowed suprafacial hydrogen 1,3 shift.

We now wish to report on our studies of photo-hydrogen shifts in 7-arylcycloheptatrienes (Ia—Id); these studies have led us to the conclusion that the 1,3 shift is not a favorable mode of the hydrogen shift, while the hydrogen 1,7 shift is the only probable mode in the 7-substituted cycloheptatrienes when a Xenon or mercury lamp is used as the light source.

Results

Upon the irradiation of an ethereal solution of 7-(*p*-substituted-phenyl)cycloheptatriene (Ia—Id) in a quartz vessel with 150 W Xenon lamp, Ia and Ib afforded the isomers IIIa and IIIb, while Ic and Id yielded IIc and IId respectively. The formation of IIc from Ic, and that of IId from Id, can be interpreted in terms of the photo-hydrogen 1,7 shift. Such a type of photoisomerization reaction has been found to occur commonly in 7-methoxy, 7-ethoxy,[4] and 7-deuterio-cycloheptatrienes.[2] However, interpretation of the formation of IIIa from Ia, and that of IIIb from Ib, seems to be more complicated.

Two possible mechanisms can be assumed for the formation of IIIa from Ia and/or IIIb from Ib: (1) the hydrogen migrates from C_7 to C_2 in one step by the suprafacial hydrogen 1,3 shift; or (2) the hydrogen migrates from C_7 to C_1, and then from C_1 to C_2 by pepeating the suprafacial hydrogen 1,7 shift. ter Borg and Kloosterziel[3] have proposed the second mechanism, while Murray and Kaplan[5] suggested the first mechanism for the formation of IIIb from Ib.

In order to elucidate this point we investigated the photochemical isomerization of 7-(*p*-chlorophenyl)cycloheptatriene (Ia) and of 7-phenylcycloheptatriene (Ib) in detail. As 7-(*p*-chlorophenyl)-cycloheptatriene was easier to work with, we studied the photoisomerization reaction of this compound first.

The isomer IIIa formed from Ia on the photolysis was separated as a pure form by applying the Diels-Alder reaction. When a benzene solution of the reaction mixture of the photolysis of Ia was heated with maleic anhydride, only Ia afforded the Diels-Alder adduct (V). An unreacted oil was purified by vacuum distillation to give IIIa. The structure

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*[1] Organic Photochemistry. XIII. This is also Photochemical Hydrogen Shift in the Cycloheptatriene System. Part I.

1) W. von E. Doering and P. P. Gasper, *J. Amer. Chem. Soc.*, **85**, 3042 (1963).

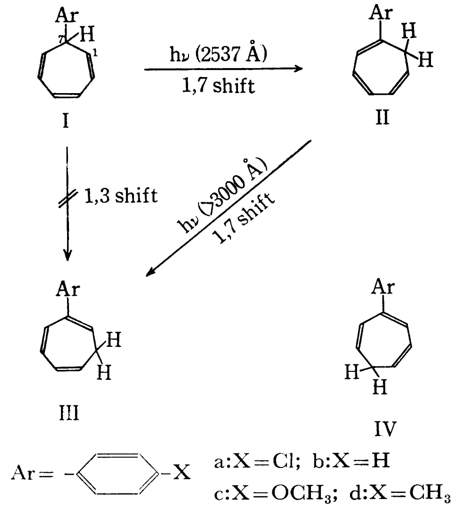
2) W. R. Roth, *Angew. Chem.*, **25**, 921 (1963).

3) A. P. ter Borg and H. Kloosterziel, *Rec. Trav. Chim., Pays-Bas*, **84**, 241 (1965).

4) G. W. Borden, O. L. Chapman, R. Swindell and T. Tezuka, *J. Amer. Chem. Soc.*, **89**, 2979 (1967).

5) R. W. Murray and M. Kaplan, *ibid.*, **88**, 3527 (1966).

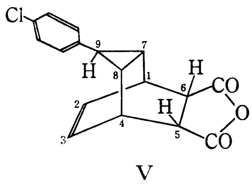
6) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965).



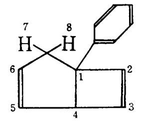
a:X=Cl; b:X=H
c:X=OCH$_3$; d:X=CH$_3$

of IIIa was established on the basis of the following physical properties: mass spectrum, m/e 202 (M); ultraviolet spectrum, $^{\mathrm{MeOH}}_{\max}$ (log ε), 247 (3.61) with tailing up to 310 mμ; infrared spectrum (oil), 3030, 2841, 1495, 1006, 820, 747, 707 cm^{-1}; NMR spectrum (in CDCl$_3$), 7.65 ($2\times H_7$; triplet, $J_{1,7}=7.0$ Hz), 4.40 (H$_1$; triplet), 4.47 (H$_6$; broad quartet), 3.75 (H$_5$; multiplet), 3.20 (H$_3$ and H$_4$; multiplet), 2.7 τ (aromatic protons) (Fig. 2). The isomer IIIa could be differentiated from the other isomers, IIa and IVa, by a comparison of their physical properties. IIa; ultraviolet spectrum, $\lambda^{\mathrm{MeOH}}_{\max}$ (log ε), 303 (3.88), 242 (4.24) mμ; infrared spectrum (oil), 3040, 2849, 1490, 1009, 826, 736, 719 cm^{-1}; NMR spectrum (in CDCl$_3$), 7.35 ($2\times H_7$; doublet, $J_{6,7}=$ 7.1 Hz), 4.60 (H$_6$) around 3.60 τ (H$_2$, H$_3$, H$_4$ and H$_5$; complex multiplet) (Fig. 3). IVa; ultraviolet spectrum, $\lambda^{\mathrm{MeOH}}_{\max}$ (log ε), 285 (3.96), 241 (4.17) mμ; infrared spectrum (oil), 3030, 2833, 1493, 1092, 1014, 824, 744 cm^{-1}; NMR spectrum (in benzene), 7.85 ($2\times H_7$; triplet, $J_{1,7}=7.0$ Hz), 4.75 (H$_1$; doublet of triplet, $J_{1,2}=9.1$ Hz), 4.65 (H$_6$; doublet of triplet, $J_{5,6}=9.1$ Hz), 3.75 (H$_2$; doublet, $J_{1,2}=9.1$ Hz), 3.85 (H$_5$; quartet), 3.29 τ (H$_4$; doublet, $J_{4,5}=4.6$ Hz) (Fig. 4).[*2]

The isomer IVa was obtained by heating Ia at 150°C, as has been described in literatures,7) while IIa was obtained by the irradiation of Ia for a short period of time with a 6 W low pressure mercury lamp (*vide infra*), followed by the application of the Diels-Alder reaction as described in the case of the isolation of IIIa.



V



VI

If the first mechanism (1) is correct, there are no intermediate products to be trapped. On the other hand, if the second mechanism (2) is correct, the isomer IIa must be trapped as an intermediate when appropriate photolysis conditions are used. In addition, the isomer IIIa must be formed from IIa at a rate faster than that of the formation of IIa from Ia, or of IIIa from Ia. With these facts in mind the photolysis of Ia and IIa was monitored under several sets of conditions.

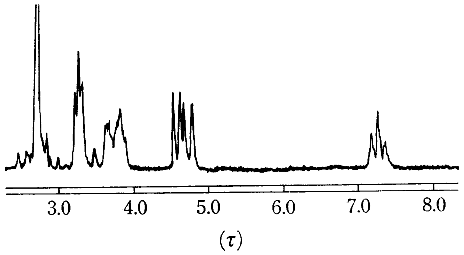


Fig. 1. NMR spectrum of 7-(p-chlorophenyl)cycloheptatriene (Ia) in CDCl$_3$.

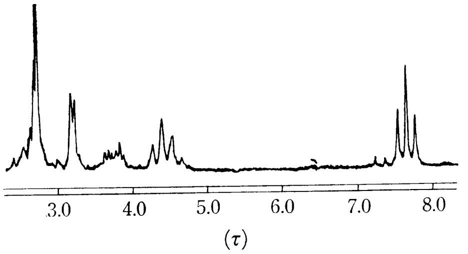


Fig. 2. NMR spectrum of 2-(p-chlorophenyl)cycloheptatriene (IIIa) in CDCl$_3$.

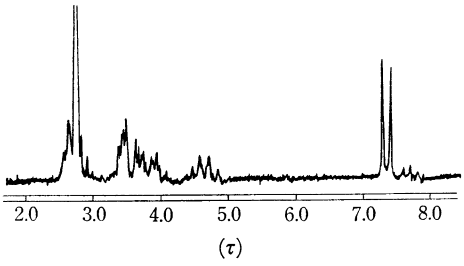


Fig. 3. NMR sepctrum of 1-(p-chlorophenyl)cycloheptatriene (IIa) in CDCl$_3$.

[*2] A triplet due to the H$_7$ and H$_{7'}$ appeared at 7.69 τ in CDCl$_3$.

7) a) G. Buchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **84**, 3104 (1962); b) A. P. ter Borg, H. Kloosterziel and N. van Meurs, *Proc. Chem. Soc.*, **1962**, 359; c) A. P. ter Borg, H. Kloosterziel and N. van Meurs, *Rec. Trav. Chem., Pays-Bas*, **82**, 717, 741, 1189 (1963); d) E, Weth and A. S. Dreiding, *Proc. Chem. Soc.*, **1964**, 59; e) A. P. ter Borg and H. Kloosterziel, *Rec. Trav. Chim., Pays-Bas*, **84**, 245 (1965); f) T. Nozoe and K. Takahashi, This Bulletin, **38**, 665 (1965).

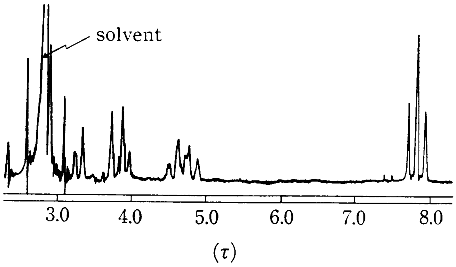


Fig. 4. NMR spectrum of 3-(*p*-chlorophenyl)cycloheptatriene (IVa) in benzene.

In order to trap the intermediate IIa, the Xenon lamp was replaced by a 6 W low-presure mercury lamp with very weak emission bands around 3000 Å, where the intermediate (IIa) has an absorption maximum. Under this condition the formation of IIIa was suppressed, and the only product identified by NMR spectroscopy during the first period of irradiation was the isomer IIa. For further confirmation of the isomer, the product (IIa) was separated from the reaction mixture by applying the Diels-Alder reaction and its structure was established by means of spectral data (*vide supra*). On prolonged irradiation, however, the gradual formation of IIIa was observed at consumption of IIa. The relative ratio of the formations of Ia, IIa, and IIIa under this irradiation condition, which was estimated from the methine or methylene signal in the NMR spectra, was plotted *vs.* the irradiation time (Fig. 5). The plot indicates that the isomer IIIa was apparently produced after the formation of IIa; *i. e.*, IIa must be the precursor of the isomer IIIa. This was supported by the fact that when Ia was irradiated with filtered 2537 Å light, IIa was produced selectively and the formation of IIIa was suppressed. In addition, the irradiation of IIa with a Xenon lamp gave the isomer IIIa at a rate approximately ten times as fast as that of the formation of IIIa from Ia.

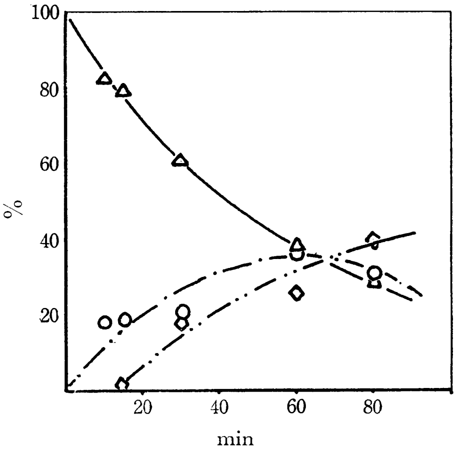


Fig. 5. Relative yields of Ia (△), IIa (○) and IIIa (◇) *vs.* time.

These evidences support the second mechanism (2), and the formation of IIIa from Ia can be interpreted in terms of successive hydrogen 1,7 shift. By absorbing light around 2500 Å, Ia isomerizes to IIa, and this is, in turn, rapidly converted into IIIa upon the further absorption of light above 3000 Å by the hydrogen 1,7 shift. Therefore, the fact that the isomer IIa was not identified by NMR spectroscopy in the case of the irradiation of Ia with a Xenon lamp can be explained as a consequence of the rapid transformation of IIa to IIIa.

A similar trend of photoisomerization was observed in the case of 7-phenylcycloheptatriene (Ib). The only isomer identified by NMR spectoscopy was IIIb when Ib was irradiated with a Xenon lamp. On the other hand, the irradiation of Ib with a 6 W low-pressure mercury lamp afforded IIb after a short period of irradiation. On prolonged irradiation, however, the isomer IIIb and the bicyclic compound,3) for which the structure (VI) is tentatively assigned from the NMR analysis were formed.

Plots of the relative ratio of Ib, IIb, and IIIb *vs.* the irradiation time indicated that the isomer IIIb was formed from IIb, which was itself produced from Ib by the hydrogen 1,7 shift. The bicyclic compound (VI) may arise from the isomer IIa.4) This may be supported by the fact that the VI was formed after the formation of IIa, which was identified by means of gas chromatographic analysis.

The irradiation of IIb with a Xenon lamp gave IIIb very rapidly. The formation of IIIb from Ib *via* IIb is sensitive to the light source used. Thus, when filtered 2537 Å light was used the formation of IIIb from IIb was suppressed; even after the irradiation of Ib for more than ten hours, the isomer IIIb was not detected; the only isomer detected by NMR spectrum was IIb.

Therefore, it may be concluded that the 1,7 shift is the only mode of hydrogen shift occurring on the photolysis of Ia—Id. This is in accord with the conclusion reached by ter Borg and Kloosterziel3) regarding the photolysis of Ib, but it is inconsistent with Murry and Kaplan's suggestion5) that IIIb may be formed from Ib by the hydrogen 1,3 shift.

It may be noted that in both cases, the isomers III and IV were relatively stable to Xenon light and did not afford the other isomers during several hours irradiation.3,14) This may be due to the electronic effect of the aryl group on the excited triene system, but the details of this effect are not clear at present.

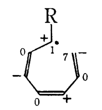
Discussion

Woodward and Hoffmann's selection rule has predicted that the symmetry-allowed suprafacial hydrogen 1,3 and 1,7 shifts would occur photochemically while the 1,5 shift would occur thermally, in the cycloheptatriene.[6] The process of the thermal 1,5 hydrogen shift has been established in many cycloheptatriene derivatives.[5,7,8] However, there are some problems as to the photochemical hydrogen shifts in the cycloheptatriene series. One of the problems is that only the hydrogen 1,7 shift has been identified experimentally, though the possibility of the occurrence of the hydrogen 1,3 shift has been suggested theoretically[6,12] for the photochemical isomerization of the cycloheptatrienes.

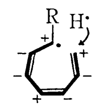
Perhaps the photochemically induced suprafacial hydrogen 1,3 shift has not occurred in the cycloheptatriene for either of following two reasons: (1) geometrical, (2) the molecular orbital symmetry relationship. Geometrically, however, the suprafacial hydrogen 1,3 shift is possible, since the distance between C_7 and C_2, through which the hydrogen 1,3 shift could occur, is approximately 2.8 Å.[9] This distance is comparable with that between C_7 and C_3, through which the hydrogen 1,5 shift occurs. In fact, a base-catalyzed hydrogen 1,3 migration has been observed in 7-cyanocycloheptatriene.[10] Therefore, it is necessary to reexamine whether or not the photo-hydrogen 1,3 shift is really a symmetry-allowed mode in the excited cycloheptatriene.

Woodward and Hoffmann's selection rule[6] for the sigmatropic rearrangement of the order $[1,j]$ is based on the molecular orbital symmetry relation of the terminal carbon atoms C_1 and C_j, in the conjugated allyl radical system containing j π-electrons. It has been stated[6] that a reverse symmetry relation exists between the highest occupied and the first excited molecular orbital at C_j. This relation always holds when C_j is located in the terminal position in the j π-electron system, but it does not hold when C_j is in a half-way position of the π-electron system containing more than j electrons. This may be seen, for example, in the heptatrienyl radical system, which is a model system taken by Woodward and Hoffmann for explaining the specific hydrogen shifts in the cycloheptatriene. The reverse relation between the highest occupied (VII) and the first excited molecular orbitals (VIII) of the heptatrienyl radical exists at the terminal position, C_7, while this relation does not exist at the C_3 position. This implies that the suprafacial hydrogen 1,3 shift is not a symmetry-allowed mode, while the 1,7 shift is the only symmetry-allowed mode of the suprafacial hydrogen shift when the excited heptatrienyl radical system (VIII) is produced by excitation in the cycloheptatriene. Jones also pointed out this point in the photochemical methyl migration of 7,7′,3-trimethylcycloheptatriene.[11]

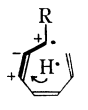
The suprafacial hydrogen 1,3 shift, however, may schematically become a symmetry-allowed mode if an excited propenyl radical (IX) or an excited pentadienyl radical (X) is produced in the cycloheptatriene molecule. Here, such an excited radical exists as an independent part in the molecule. Practically, however, the introduction of such a limited excited radical system in the cycloheptatriene molecule may be difficult, since the excitation of the triene chromophore occurs preferentially in the cycloheptatriene molecule when 2537 Å light is absorbed and, as a concequence the excited heptatrienyl radical system (VIII) is produced in the molecule.



VII



VIII



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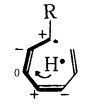
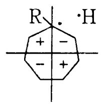
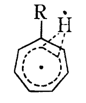


X



XI



XII

In general, the selection rule for the photochemical hydrogen shift must be used in terms of the excited radical system, but not in terms of the length of the conjugation in the ground state molecule. Such hydrogen shifts in terms of several excited radical systems can be deduced on the basis of the symmetry relation of the Hückel molecular orbital of the acyclic model.[6] Several such are presented in Table 1. Here, the length of the conjugation of double bonds in a ground state molecule is not a decisive factor, but the nature of a specific excited radical system introduced in this

TABLE 1

Excited radical system	Type of permissive suprafacial hydrogen shift	
Propenyl	1,3	
Pentadienyl	1,3	
Heptatrienyl	1,7	
Nonatetraenyl	1,5	1,7

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8) The occurrence of the thermal hydrogen 1,5 shift in Ia, Ic, and Id at 120—150°C, giving IVa, IVc, and IVd respectively, was confirmed by the present work.

9) This is the distance of the ground-state molecule as estimated by the Dreiding model. In the excited state the distance may be somewhat different from what it is in the ground state. However, in a rigid system such as cycloheptatriene the geometrical difference between the two states may be small.

10) a) K. Yamamoto, Master's Thesis, Tohoku University, 1966. b) K. Takahashi, H. Yamamoto and T. Nozoe, This Bulletin, **43**, 200 (1970).

11) L. B. Jones and V. K. Jones, *J. Amer. Chem. Soc.*, **89**, 1880 (1967).

molecule by excitation is important in determining the mode of the photochemical hydrogen shift. Whether or not such a specific excited radical system can be produced in the conjugated allyl depends on the irradiation conditions (the wave length of light used) and the geometrical conditions (the inhibition of the full conjugation of the double bonds in the molecule).

Recently, Anastassiou[12] has proposed a cyclic model (XI) for predicting the specific mode of the hydrogen shifts in the cycloheptatriene. According to Anastassiou's selection rule, all of the hydrogen 1,3 and 1,5 and 1,7 shifts can occur photochemically in the cycloheptatriene. However, this selection rule is not consistent with the observation that the photochemical hydrogen 1,3 and 1,5 shifts have not been found in the cycloheptatriene series.

It is instructive to reconsider the model system of the transition state of the hydrogen shift in the cyclic conjugated allyl system. Anastassiou has mentioned that the acyclic model employed in the derivation of Woodward and Hoffmann's selection rule is incapable of allowing for the necessary cyclic π-interaction introduced by the developing *p*-orbital at the migration origin of the cyclic system. In this we agree with Anastassiou's comments. However, it seems that Anastassiou's cyclic model does not consider the interaction between a migrating hydrogen and a remnant conjugated system. On the basis of a theoretical consideration including the above discussion, we would like to propose, for the hydrogen shift in the cyclic allyl system, new model system in which the interaction of the migrating hydrogen and the cyclic π-interaction is taken into consideration. For example, according to this treatment the transition state of the hydrogen 1,7 shift in the cycloheptatrienes is represented as XII, where a three-member part including a hydrogen atom, interacts with a dienyl radical system. With this model several modes of the hydrogen shift in the cyclic allyl system can be interpreted. A detailed interpretation and application will not be made in this report, but will appear elsewhere.

It is interesting to consider the substituent effect upon the relative rate of the formation of the bicyclic compound from 1-substituted cycloheptatriene. It has been reported that 1-methoxy- and 1-ethoxycycloheptatrienes isomerize very rapidly to 1-methoxy- and 1-ethoxy-bicyclo[3.2.0]hepta-3,6-dienes upon irradiation by light above 3000 Å.[4] In these cases, the formation of 2-methoxy- and 2-ethoxycycloheptatriene by the hydrogen 1,7 shift has not been observed.[4] On the contrary, the photolysis of 1-phenyl-, 1-(*p*-chlorophenyl)-, and 1-deuterio-cycloheptatrienes[3] afforded preferentially 2-phenyl-, 2-(*p*-chlorophenyl)-, and 2-deuterio-cycloheptatrienes respectively, instead of the bicyclic compounds. It may be noted that the substituent at the C_1 position of the cycloheptatrienes potentially affects the rate of the bond formation between C_1 and C_4 as well as the rate of the hydrogen shift. These substituent effects may be electronic in nature; electron-donating substituents facilitate the bond formation at C_1 and C_4, while electron-attracting substituents tend to retard it. However, a detailed interpretation of the mechanism of the substituent effect on the excited state must await further study.[14]

Experimental

Preparation of 7-(*p*-Chlorophenyl)cycloheptatriene (Ia). To a solution of *p*-chlorophenylmagnesium bromide which had been prepared from *p*-bromochlorobenzene (16.89 g) and magnesium (2.14 g) in absolute ether (50 m*l*), there was added a solution of 7-ethoxycycloheptatriene (10.0 g) in absolute ether (50 m*l*) at 0°C; the mixture was then stirred continuously for several hours. The reaction mixture was then treated with 2N hydrochloric acid and extracted with ether. The resultant oil was distilled to give a colorless oil, bp, 107°C/0.2 mmHg (9 g), which crystallized on standing at 0°C; after recrystallization from petroleum ether it gave colorless needles, mp 41—42°C. Ultraviolet spectrum, $\lambda_{\max}^{\text{cyclohexane}}$ (log ε), 265 mμ (3.52); infrared spectrum (KBr), 3012, 2857, 1492, 1026, 826, 754, 709 cm^{-1}; mass spectrum (*m*/*e*), 202 (M); the NMR spectrum is shown in Fig. 1.

Found: C, 77.18; H, 5.48%. Calcd for $C_{13}H_{11}Cl$: C, 77.10; H, 5.48%.

The Formation of 1-(*p*-Chlorophenyl)cycloheptatriene (IIa) from Ia by Irradiation with a Low-pressure Mercury Lamp. a) A solution of 7-(*p*-chlorophenyl)cycloheptatriene (Ia) (1.5 g) in absolute ether (180 m*l*) was irradiated with an internal 6 W low-pressure mercury lamp for 15 min under a nitrogen stream; 15% of Ia was thus converted to IIa, which was estimated by means of the doublet signal due to methylene protons of IIa at 7.35 τ in NMR spectroscopy. The oily reaction mixture was heated with maleic anhydride (500 mg) in absolute benzene (10 m*l*) for 1 hr. The evaporation of the solvent afforded an Diels-Alder adduct of Ia as white crystals; mp, 186.5°C (V) (300 mg). Infrared spectrum (KBr), 3039, 2985, 1869, 1824, 1785, 1226, 1089, 918, 792, 755 cm^{-1}; NMR spectrum (in $CDCl_3$), 2.95 (aromatic protons; quartet), 3.96 (H_2 and H_3; sextet), 6.38 (H_1 and H_4; multiplet), 6.76 (H_5 and H_6; triplet, $J_{1,5}=J_{4,5}=2.5$ Hz), 8.36 (H_9; triplet, $J_{8,9}=J_{7,9}=3.2$ Hz), 8.60 τ (H_7 and H_8; $J_{1,7}=J_{4,8}=5.0$ Hz).

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[12] A. G. Anastassiou, *Chem. Commun.*, **1968**, 15.

[13] a) Concerning the substituent effects, Professor ter Borg has found that the substituents which facilitate the valence-isomerization reaction end to retard the hydrogen-migration reaction in 1-substituted cycloheptatrienes. The authors wish here to thank Professor ter Borg for his communication on this point prior to publication. b) A. P. ter Borg, E. Razenberg and H. Kloosterziel, *Chem. Commun.*, **23**, 1210 (1967).

[14] For example, the photochemical 1,7 migration of the phenyl group in competition with the hydrogen 1,7 shift in 7-phenylcycloheptatriene has recently been reported. *Cf.* K-W Shen, W. E McEwen and A. P. Wolf, *Tetrahedron Lett.*, **1969**, 827.

Found: C, 68.11; H, 4.42%. Calcd for $C_{17}H_{13}O_3Cl$: C, 67.89; H, 4.36%.

The filtrate was purified by alumina chromatograpy, followed by vacuum distillation, to give a colorless oil (IIa); bp, 120—125°C/0.5 mmHg (80 mg).

Found: C, 77.24; H, 5.43%. Calcd for $C_{13}H_{11}Cl$; C, 77.10; H, 5.48%.

b) The photolysis of Ia under the same conditions was monitored, and the amounts of isomers formed was estimated by NMR spectroscopy. The relative ratio of the isomers *vs.* the time was estimated by the integration of the triplet at 7.31 (for Ia), the doublet at 7.33 (for IIa), and the triplet at 7.69 τ (for IIIa), in the NMR spectrum. The results are shown in Fig. 5.

The Formation of 2-(*p*-Chlorophenyl)cycloheptatriene (IIIa) from Ia by Irradiation with a Xenon Lamp. a) A solution of 7-(*p*-chlorophenyl)cycloheptatriene (Ia) (954 mg) in absolute ether (180 m*l*) in a quartz vessel was irradiated with a Xenon lamp (Toshiba XD-150) for 16 hr under a nitrogen stream. The reaction was followed by the appearance of the triplet signal due to IIIa at 7.69 τ in the NMR spectroscopy. The reaction mixture was treated with maleic anhydride (300 mg) as has been described in the case of IIa. The filtrate was purified by alumina chromatography, and subsequent vacuum distillation afforded a colorless oil, bp, 130—135°C/0.2 mmHg (246 mg), which on standing at −60°C afforded colorless needles; mp, 41—42°C (IIIa).

Found: C, 77.44; H, 5.45%. Calcd for $C_{13}H_{11}Cl$; C, 77.10; H, 5.48%.

b) A solution of Ia (20 mg) in absolute ether (5 m*l*), saturated with nitrogen, was irradiated in a sealed quartz vessel with a Xenon lamp for a few hours. The reaction mixture was analyzed by means of NMR spectroscopy, which indicated that the only isomer produced during the irradiation was IIIa. Within 90 min the Ia was converted to IIIa in 50% yield.

Irradiation of 1-(*p*-Chlorophenyl)cycloheptatriene (IIa) with a Xenon Lamp. A solution of 1-(*p*-chlorophenyl)cycloheptatriene (IIa) (20 mg) in absolute ether (5 m*l*) saturated with nitrogen was irradiated in a sealed quartz vessel with a Xenon lamp. The reaction was followed by NMR spectroscopy. The amounts of the isomers IIIa and IIa was estimated from the integrated signals at 7.69 (triplet for IIIa) and 7.35 τ (doublet for IIa) in the NMR spectrum. Within 90 min the IIa was converted into IIIa in 43% yield.

Irradiation of Ia with a 2537 Å Light. A solution of Ia (20 mg) in absolute ether (5 m*l*) saturated with nitrogen was irradiated in a sealed quartz vessel with a 2537 Å light. The reaction was followed by NMR spectroscopy. Within 6 hr the Ia was converted into IIa in 17% yield. No formation of IIIa was detected even after 14 hr of irradiation.

Irradiation of IIa with a High-pressure Mercury Lamp through a Pyrex Filter. A solution of IIa (20 mg) in absolute ether (5 m*l*) saturated with nitrogen was irradiated in a sealed quartz vessel with high pressure mercury lamp through Pyrex filter. The reaction was followed by NMR spectroscopy. Within 25 min the IIa was canverted to IIIa in a 70% yield.

Preparation of 3-(*p*-Chlorophenyl)cycloheptatriene (IVa). 7-(*p*-Chlorophenyl)cycloheptatriene (Ia) (757 mg) was heated at 150—155°C for 90 min. The crude oil was distilled to give a colorless oil, bp 120—125°C/0.5 mmHg (650 mg), which was identified by NMR spectroscopy as a mixture composed of 98% of IVa and 2% of IIa.

Found: C, 77.49; H, 6.05%. Calcd for $C_{13}H_{11}Cl$: C, 77.10; H, 5.48%.

Irradiation of 3-(*p*-Chlorophenyl)cycloheptatriene (IVa) with a Xenon Lamp. A solution of 3-(*p*-chlorophenyl)cycloheptatriene (IVa) (20 mg) in absolute ether (5 m*l*) saturated with nitrogen, was irradiated in a sealed quartz vessel with a Xenon lamp for several hours. The reaction was followed by NMR spectroscopy. No change around the methylene proton region in the NMR spectrum was observed even after 6 hr of irradiation.

Irradiation of 2-(*p*-Chlorophenyl)cycloheptatriene (IIIa) with a Xenon Lamp. A solution of 2-(*p*-chlorophenyl)cycloheptatriene (IIIa) (20 mg) in absolute ether (5 m*l*) saturated with nitrogen, was irradiated in a sealed quartz vessel with a Xenon lamp for 12 hr. No change around the methylene proton region in the NMR spectrum was observed during the time of irradiation.

Preparation of 7-Phenylcycloheptatriene (Ib). To a solution of phenylmagnesium bromide which had been prepared from bromobenzene (41.6 g) and magnesium (6.44 g) in absolute ether (129 m*l*), there was added a solution of 7-ethoxycycloheptatriene (30 g) in absolute ether (100 m*l*) at 0°C; the mixture was then continuously stirred for several hours. The reaction mixture was then treated with a 2N ammonium chloride solution and extracted with ether. The crude oil was distilled to give a pale yellow oil, bp 99—103°C/0.9 mmHg (23 g). This oil crystallized on standing at 0°C; recrystallization from petroleum ether gave colorless needles, mp, 32°C (Ib). The structure of Ib was identified by means of the following physical properties.[15,16] Ultraviolet spectrum, λ_{max}^{MeOH} 262 mμ (logε 3.53); infrared spectrum (KBr), 2994, 1592, 1493, 746, 704 cm^{-1}; mass spectrum (*m*/*e*), 202 (M).

Irradiation of 7-Phenylcycloheptatriene (Ib) with a Low-pressure Mercury Lamp. a) A solution of 7-phenylcycloheptatriene (Ib) (1.5 g) in absolute ether (180 m*l*) was irradiated with a 6 W low pressure mercury lamp under a nitrogen stream for 30 hr. The reaction products were then separated by means of gas chromatography (Silicon Grease), 1-phenylcycloheptatriene (IIb) (300 mg) and bicyclic product (VI) (35 mg) were thus obtained. The structure of these products was suggested on the basis of the NMR spectrum.

IIb: Infrared spectrum (oil), 3031, 2941, 1600, 1477, 1449, 759, 711, 698 cm^{-1}; NMR spectrum (in $CDCl_3$), 7.34 (H_7 and H_7; doublet, $J_{6,7}=J_{1,7}=7.1$ Hz) 4.72 (H_6; multiplet, $J_{5,6}=9.2$ Hz), 3.60 τ (H_2 and H_5, multiplet).

Bicyclic compound (VI): NMR spectrum*[3] (in $CDCl_3$), 6.87 (H_4), 6.18 (H_7; doublet with small coupling), 6.42 (H_8; doublet with small coupling), 4.35 (H_5; doublet with small coupling, $J_{5,6}=5$ Hz), 4.02 (H_6; doublet

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15) a) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **76**, 3203 (1954); b) A. P. ter Borg and H. Kloosterziel, *Rec. Trav. Chem., Pays-Bas*, **82**, 741 (1963).

16) H. Horino, Master's Thesis, Tohoku University (1962).

*3 An assignment is only tentative.

with small coupling), 3.79 (H_3; quartet, $J_{3,4}=1.4$ Hz), 3.61 (H_2; doublet, $J_{2,3}=3.0$ Hz), around 3.0 τ (aromatic).

b) A solution of 7-phenylcycloheptatriene (Ib) (20 mg) in absolute ether (5 m*l*) saturated with nitrogen was irradiated in a sealed quartz vessel with a low-pressure mercury lamp. The relative ratio of the isomers, (IIb) and (IIIb), was estimated by the integration of the doublet signals at 7.34 and 7.70 τ (in $CDCl_3$) respectively.

Irr. time (min)	% of IIIb	% of IIb	% of Ib
15	0	25	75
35	33	33	33
60	15	53	30

Irradiation of 7-Phenylcycloheptatriene (Ib) with a Xenon Lamp. A solution of 7-phenylcycloheptatriene (Ib) (20 mg) in absolute ether (5 m*l*) saturated with nitrogen was irradiated in a sealed quartz vessel with a Xenon lamp. The reaction was followed by NMR spectroscopy. The only product identified by means of the NMR spectrum was IIIb, which showed a triplet at 7.70 τ (in $CDCl_3$) during several hours irradiation.

Irradiation of 1-Phenylcycloheptatriene (IIb). A solution of 1-phenylcycloheptatriene (IIb) (20 mg) in absolute ether (5 m*l*) saturated with nitrogen was irradiated in a sealed quartz vessel with a Xenon lamp. The reaction was followed by means of NMR spectrum at intervals. The results are as follows.

Irr. time (min)	% of IIb	% of IIIb
5	90	10
10	82	18
30	60	40
60	42	53
90	47	47

Preparation of 7-(*p*-Methoxyphenyl)cycloheptatriene (Ic). To a Grignard solution of *p*-methoxyphenylmagnesium bromide which had been prepared from *p*-bromoanisole (8.25 g) and magnesium (1.07 g) in absolute ether (50 m*l*) was added 7-ethoxycycloheptatriene (5 g) in absolute ether (30 m*l*) at 0°C; the mixture was continuously stirred for 5 hr. The reaction mixture was treated as has been described in the case of Ib. The oily product was distilled to give a yellow oil, bp, 114—115°C/0.3 mmHg (5.6 g), which crystallized on standing at −60°C to give, after recrystallization from petroleum ether, colorless needles, mp, 28°C.

Found: C, 84.58; H, 7.35%. Calcd for $C_{13}H_{14}O$; C, 84.81; H, 7.12%.

Mass spectrum (*m*/*e*), 198 (M); ultraviolet spectrum, $\lambda_{\max}^{\text{cyclohexane}}$ (log ε), 270 mμ (3.70); infrared spectrum (oil) 3002, 2994, 1605, 1508, 1250, 1176, 1034, 830, 747, 707 cm^{-1}; NMR spectrum (in $CDCl_3$), 7.34 (H_7 and H_7; triplet, $J_{1,7}=J_{6,7}=6.0$ Hz), 6.30 (OCH_3; singlet), 4.65 (H_1 and H_6; quartet, $J_{5,6}=J_{1,2}=9.1$ Hz), 3.82 (H_2 and H_5; multiplet), 3.32 (H_3 and H_4; multiplet), 2.96 τ (aromatic; quartet).

Irradiation of 7-(*p*-Methoxyphenyl)cycloheptatriene (Ic) with a Xenon Lamp. A solution of 7-(*p*-methoxyphenyl)cycloheptatriene (Ic) (20 mg) in absolute ether (5 m*l*), saturated with nitrogen, was irradiated in a sealed quartz vessel with a Xenon lamp for several hours. The reaction was followed by NMR spectroscopy. The only product identified by means of the NMR spectrum was IIc, which showed a doublet peak at 7.37 τ (in $CDCl_3$).

Preparation of 7-*p*-Tolylcycloheptatriene (Id). To a Grignard solution which had been prepared from *p*-bromotoluene (7.64 g) and magnesium (1.0 g) in absolute ether (20 m*l*) was added 7-ethoxycycloheptatriene (5 g) in absolute ether (20 m*l*) at 0°C; the mixture was then stirred continuously for several hours. The reaction mixture was treated as had been described in the case of Ib. The resultant oil was distilled to give a yellow oil, bp 85—89°C/0.5 mmHg (4 g), which crystallized on standing at −60°C to give, after recrystallization from petroleum ether, yellow needles, mp, 31°C.

Found: C, 91.98; H, 7.68%. Calcd for $C_{14}H_{14}$; C, 92.26; H, 7.74%.

Mass spectrum (*m*/*e*), 182 (M); ultraviolet spectrum, $\lambda_{\max}^{\text{cyclohexane}}$ 265 mμ (logε 3.569); infrared spectrum, (KBr) 3040, 1603, 1520, 1391, 814, 746, 704 cm^{-1}; NMR spectrum (in $CDCl_3$) 7.70 (CH_3; singlet), 7.33 (H_7 and H_7; triplet, $J_{1,7}=J_{6,7}=5.5$ Hz), 4.66 (H_1 and H_6; quartet, $J_{5,6}=J_{1,2}=6.0$ Hz), 3.82 (H_2 and H_5; multiplet), 3.34 (H_3 and H_4; multiplet) and 2.89 τ (aromatic; multiplet).

Irradiation of 7-*p*-Tolylcycloheptatriene (Id) with a Xenon Lamp. A solution of 7-*p*-tolylcycloheptatriene (Id) in absolute ether (5 m*l*), saturated with nitrogen, was irradiated in a sealed quartz vessel with a Xenon lamp for several hours. The only product identified by NMR spectroscopy was IId, which showed a doublet peak at 7.40 τ (in $CDCl_3$).