highly reactive intermediate of its iron tricarbonyl complex, which cannot be isolated.[28]

Registry No.—**1**, 71-43-2; **2**, 91-20-3; **3**, 120-12-7; **4**, 85-01-8; **5**, 218-01-9; **6**, 217-59-4; **7**, 198-55-0; **8**, 191-07-1; **9**, 129-00-0; **10**, 100-42-5; **11**, 92-52-4; **12**, 275-51-4; **13**, 250-25-9; **14**, 257-24-9; **15**, 497-20-1; **16**, 539-79-7; **17**, 91-12-3; **18**, 531-45-3; **19**, 1120-53-2; **20**, 629-20-9.

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[28] Note Added in Proof.—After this note was submitted for publication, we noticed two important papers by B. A. Hess and L. J. Shaad [*ibid.*, **93**, 305, 2413 (1971)] describing a similar approach. We found general agreement between our results and theirs. A discussion about these two approaches is given in our paper on monocyclic conjugated molecules, submitted for publication in *Croat. Chem. Acta.*

The Photolysis of 1-Phenylcyclohexene in Methanol[1]

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The photolysis of 1-phenylcyclohexene in methanol, with or without triplet sensitizer, yields the ionic addition product, 1-methoxy-1-phenylcyclohexane.[2] This reaction was found to be susceptible to acid catalysis.[2] No other adducts or reduction products have previously been reported for this reaction. Recent reports of hydrogen atom abstraction reactions for electronically excited olefins[3] prompted us to reexamine the photolysis of 1-phenylcyclohexene in methanol.

The photolysis of degassed solutions of 1-phenylcyclohexene (I) (0.2 *M*) in methanol for 96 hr at 2537 or 3000 Å afforded four major products: phenylcyclohexane (II), 13%, 1-methoxy-1-phenylcyclohexane (III), 26%, 1-hydroxymethyl-1-phenylcyclohexane (IV), 7%, and a dimer of 1-phenylcyclohexene of undetermined structure (V), 46%. Yields are based on reacted 1-phenylcyclohexene. Quantum yield for disappearance of I at 3000 Å was 0.12. The reaction products were separated by column chromatography (Al_2O_3) and the characterized products gave ir spectra which were identical with those of authentic samples. It is noted that in previous studies[2a,b] the radiation exposures were considerably less than in the present study and that irradiation of a methanol solution of 1-phenylcyclohexene (E_T = 62 kcal/mol[4]) containing 3-methoxyacetophenone (E_T = 72.5 kcal/mol[5]) at 3500 Å gave the first three products (II, III, IV) in the above ratios and only trace amounts of dimer. 1-Phenylcyclohexene was unreactive at 3500 Å in the absence of sensitizer. A solution of 3-methoxyacetophenone in methanol and a similar solution containing 1-phenylcyclohexene were photolyzed simultaneously at 3500 Å. The quantum yield for disappearance of 3-methoxyacetophenone in the first solution was significantly lower than the quantum yield for disappearance of 1-phenylcyclohexene, thereby indicating the occurrence of triplet energy transfer rather than hydrogen atom transfer "chemical sensitization." 1,3-Cyclohexadiene (E_T = 52.5 kcal/mol[6]) quenched the photochemical formation of II, III, and IV, but not V, on irradiation at 3000 Å. These data are consistent with the following mechanism.

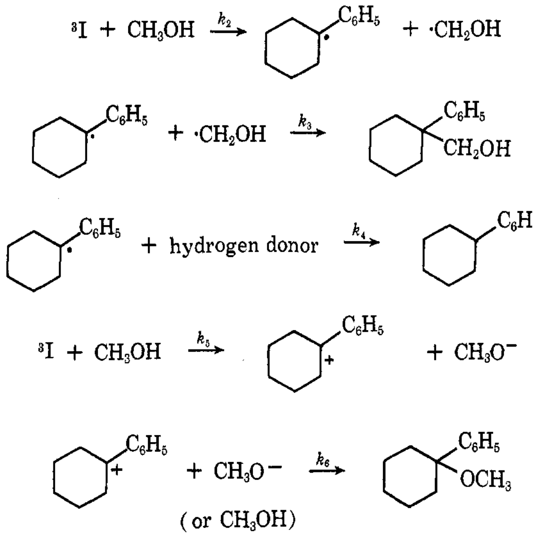
$$\mathrm{I} \xrightarrow{h\nu} {}^1\mathrm{I}$$

$${}^1\mathrm{I} + \mathrm{I} \xrightarrow{k_1} \mathrm{V}$$

$${}^1\mathrm{I} \xrightarrow{k_d} \mathrm{I}$$

$${}^1\mathrm{I} \xrightarrow{k_{\mathrm{ics}}} {}^3\mathrm{I}$$

$${}^3\mathrm{I} \xrightarrow{k_D} \mathrm{I}$$



In the above mechanism we have assumed that phenylcyclohexane is formed *via* a hydrogen abstraction process, although there is evidence for photoreduction of some olefins.[7] We have also treated the formation of products from free radical and carbonium ion as irreversible. Although we have represented hydrogen abstraction and protonation as involving ^{3}I directly, we do not preclude prior decay of the triplet to ground state trans molecule.

Stern–Volmer quenching studies of 1-phenylcyclohexene were performed in degassed acetonitrile solu-

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tions containing varying concentrations of methanol and 1,3-cyclohexadiene. Relative quantum yields for formation for products II, III, and IV were determined by glpc. Stern–Volmer plots (eq 1) were

$$\Phi_0/\Phi = 1 + k_q\tau[Q] \qquad (1)$$

linear. k_q and τ represent quenching rate constant and triplet lifetime, respectively. Values for $k_q\tau$ and τ are given in Table I, in which k_q is assumed to be 1.1×10^{10} sec^{-1}.[8]

TABLE I

QUENCHING OF THE REACTION OF 1-PHENYLCYCLOHEXENE WITH METHANOL BY 1,3-CYCLOHEXADIENE IN ACETONITRILE

[Methanol], 10^{-2} *M*	$k_q\tau$, M^{-1}	τ, 10^{-8} sec
8.3	655	5.95
12.5	484	4.40
16.7	394	3.58
20.8	329	2.99

Rate constants for unimolecular triplet decay (k_D) and the sum of bimolecular rate constants for hydrogen atom and proton abstraction ($k_2 + k_5$) were obtained from the plot of $1/\tau$ *vs.* [methanol] according to eq 2

$$1/\tau = k_D + (k_2 + k_5)[\text{methanol}] \qquad (2)$$

and were found to be 0.60×10^7 and 1.31×10^8 M^{-1} sec^{-1}, respectively. From the product ratios, $k_2 = 1.07 \times 10^8$ M^{-1} sec^{-1} and $k_5 = 0.23 \times 10^8$ M^{-1} sec^{-1}. These values are subject to the assumptions previously stated.

Experimental Section

Materials.—1-Phenylcyclohexene, phenylcyclohexane, and 3-methoxyacetophenone were purchased from the Aldrich Chemical Co. Cyclohexadiene was obtained from Matheson Coleman and Bell. 1-Hydroxymethyl-1-phenylcyclohexane was prepared according to the method of Wilt and Roberts.[9] 1-Methoxy-1-phenylcyclohexane was prepared as follows: A solution of 1-phenylcyclohexanol (8.6 g, 0.05 mol) and concentrated sulfuric acid (3 drops) in 50 ml of methanol was stirred at room temperature for 15 hr. The solution was then poured into a separatory funnel containing 150 ml of ether and 100 ml of a saturated sodium chloride solution. The ether layer was separated, washed with a 5% sodium bicarbonate solution, and dried over anhydrous sodium sulfate. Removal of the ether yielded a liquid which upon distillation gave 1-methoxy-1-phenylcyclohexane (7.5 g, 82%), bp 91–92° (0.6 mm). *Anal.* Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.15; H, 9.67.

Photolysis of 1-Phenylcyclohexene.—A degassed solution of 3 g of 1-phenylcyclohexene in 100 ml of methanol in a quartz vessel was irradiated for 96 hr in a Rayonet photochemical reactor containing lamps having peak emission at 3500 Å. Four major products were isolated by column chromatography (Al_2O_3): phenylcyclohexane (13%), 1-methoxy-1-phenylcyclohexane (26%), 1-hydroxymethyl-1-phenylcyclohexane (7%), and the dimer of 1-phenylcyclohexene (46%). The first three products were identified by comparison of ir spectra with those of authentic samples. The fourth product exhibited a mass spectral parent peak of 316 corresponding to a dimer of 1-phenylcyclohexene. It had the following spectral properties: ir (thin film) 3020, 2900, 1450, 920, 735, 700 cm^{-1}; nmr (60 MH_2, CCl_4) τ 8.5 (m, 16 H), 7.15 (m, 2 H), 2.75 (m, 10 H).

Kinetic Study.—All quantitative measurements were made on a rotating assembly with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L-450-W). Samples in 12-mm Pyrex vessels were placed in holders approximately 6 cm from the immersion well. The light was filtered by a 1-mm Corex jacket fitted over the light source. Samples in 12-mm Pyrex test tubes were degassed to 10^{-3} mm in three freeze–thaw sequences. After the last thawing, an atmosphere of helium was placed over the solutions. The solutions were irradiated to about 15% completion at a constant temperature of 25.7°. Excess solvent was removed under reduced pressure. The extent of reaction was measured by glpc, 3% SE-30 column, using 1-dodecane as an internal reference. Both the loss of 1-phenylcyclohexene and the production of products was measured, the first method being easier to monitor.

In a typical run, 1 ml of 0.05 *M* 1-phenylcyclohexene in acetonitrile was added to each of the reaction vessels. To each vessel was also added 1 ml of a 0.5 *M* methanol in acetonitrile solution and a variable amount of a 0.3 *M* 1,3-cyclohexadiene in acetonitrile solution. Reaction vessels were then brought to equal volume by the addition of the appropriate amount of acetonitrile.

Attempted Sensitization of the Reaction of 1-Phenylcyclohexene in Methanol.—A solution of 1-phenylcyclohexene (0.80 g, 0.005 mol) in methanol (50 ml) was divided into two portions. To one portion was added 3-methoxy acetophenone (1.5 g, 0.01 mol). Both solutions were degassed, placed under a helium atmosphere, and irradiated at 3500 Å. After 96 hr, the sensitized solution had reacted to about 30% completion while the unsensitized solution had failed to react.

Registry No.—I, 771-98-2; I dimer, 32239-45-5; III, 32249-58-4; methanol, 67-56-1.

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The Clemmensen Reduction of 2-Acetonaphthone

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The Clemmensen reduction of ketones has been reviewed[2] and mechanisms[2b,c,3] accounting for major products have been proposed. We have used the Clemmensen reaction to reduce the carbonyl group of 2-acetonaphthone (**1**) and have observed the hydrocarbon products **3**, **4**, and **5**, formation of which requires reduction of the naphthalene nucleus (Scheme I). The maximum combined yield (16%) of these hydrocarbons was realized when boiling toluene and mossy zinc amalgam were used (Table I). Other combinations of reagents studied and the yields of the resulting volatile hydrocarbons as well as nonsteam-volatile products are reported in Table I.

The conventional Clemmensen reduction[2a] (procedures D and E) of **1** gave low yields (30–40%) of **2** and mainly condensation products which include **7**, **8**, and **9**. In addition, since distillation of the condensation products resulted in some pot residue, polymerization products may be present.

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