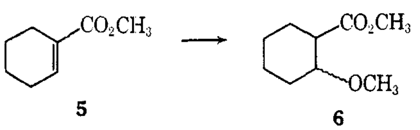
methanol to afford a 1:4 mixture of the two epimeric methanol adducts **6**.[15,16,16a]

Thus, it is apparent that there is a fundamental difference in behavior between **1** and **5** which parallels the differences previously observed between analogous cyclic and acyclic alkenes.[2] To what extent this parallel behavior indicates similar mechanistic features between the addition reactions of cycloalkenes and cycloalkenones is under further investigation.



5 **6**

Experimental Section[17]

Irradiations. A. General.—Irradiations were conducted with 150-ml methanolic solutions containing 30 mmoles of acid or ester using a Hanovia 450-w, medium-pressure mercury arc and a water-cooled Vycor immersion well. Vigorous stirring of the reaction mixture was effected by the introduction of a stream of nitrogen through a jet opening in the bottom of the outer jacket. The progress of reactions was followed by gas chromatographic analysis of aliquots removed periodically from the reaction mixture. (In the case of crotonic acid aliquots were treated with diazomethane prior to analysis.) Yields were calculated relative to an internal hydrocarbon standard. For product identification the irradiation mixtures were concentrated on an 18-in. spinning-band column, and the individual components were isolated by preparative gas chromatography and characterized as described below. None of the photochemical reactions reported occurred under identical conditions in the absence of ultraviolet light.

B. Crotonic Acid (1a) and Methyl Crotonate (1b).—From irradiation of methyl crotonate (**1b**), or of crotonic acid (**1a**) followed by treatment with diazomethane, as outlined in Table I, the following products were isolated.

Methyl isocrotonate (2b) was obtained as a colorless liquid: λ_{max} 5.78 and 6.04 μ; nmr spectrum, τ ~3.75 (m, 1, CH-3),[18] 4.25 (d, 1, J = 11 Hz, CH-2), 6.34 (s, 3, CO_2CH_3), and 7.90 (2 d, 3, J = 7 and ~1 Hz, CH_3-4). An identical sample was obtained by esterification of a commercial sample of isocrotonic acid (**2a**).

Methyl 3-butenoate (3b) was obtained as a colorless liquid: λ_{max} (CH_2Cl_2) 5.74 and 6.08 μ; nmr spectrum, τ ~4.20 (m, 1, CH-3), ~4.90 (2 m, 2, CH_2-4), 6.39 (s, 3, CO_2CH_3), and 6.98 (2 m, 2, CH_2-2).

Direct comparison with an authentic sample prepared as described below failed to reveal any detectable formation of methyl 3-methoxybutyrate (**4b**).

C. Methyl 1-Cyclohexene-1-carboxylate (5).—A 150-ml methanolic solution containing 2.97 g (21 mmoles) of ester **5**[14] and 3 ml of xylene was irradiated as described above for 8 hr. Gas chromatographic analysis at this point revealed the presence of recovered starting material (33%) accompanied by a poorly resolved mixture of **methyl *cis*- and *trans*-2-methoxycyclohexanecarboxylate (6)** (23%), which were formed in an approximately 1:4 ratio. Isolation of the mixture as described above afforded a colorless liquid: λ_{max} 5.75 and 9.15 μ; nmr spectrum, τ 6.22 (m, 1, CH-2), 6.34 (s, 3, CO_2CH_3), and 6.71 and 6.75 (2 s, 3, OCH_3).

Methyl 3-Methoxybutyrate (4b).—Treatment of 10.0 g of methyl crotonate (**1b**) with 10 ml of anhydrous methanol and several small pieces of sodium for 16 hr under reflux in an atmosphere of nitrogen followed by extraction with ether and distillation at 60–61° (1 mm) afforded 9.3 g (71% yield) of the methoxy adduct **4b**, a colorless liquid: λ_{max} 5.72 μ; nmr spectrum, τ 6.28 (m, 1, CH-3), 6.38 (s, 3, CO_2CH_3), 6.73 (s, 3, OCH_3), ~7.56 (m, 2, CH_2-2), and 8.83 (d, 3, J = 6 Hz, CH_3-4) (lit.[19] bp 149–150°).

Registry No.—**1a**, 107-93-7; **2b**, 4358-59-2; **3b**, 3724-55-8; **4b**, 3136-17-2; **6** (*cis*), 13640-65-8; **6** (*trans*), 13640-66-9.

Acknowledgment.—The authors are indebted to Dr. R. A. Damico for a generous supply of methyl 1-, 2-, and 3-cyclohexenecarboxylates.

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[15] These adducts are assumed on the basis of mechanistic reasoning to be the two 2-methoxycyclohexane carboxylates **6**, which were previously described by M. A. Febrer and J. Pascual, *Anales Real Soc. Espan. Fis. y Quim.*, **52B**, 541 (1956) (*Chem. Abstr.*, **51**, 5711 (1957)). That they are not the corresponding 1-methoxy isomers is evident by the presence of absorption equivalent to one proton at τ 6.22. The possibility that they are 3- or 4-methoxy isomers has not been rigorously precluded, but comparison with authentic specimens revealed no detectable evidence for the formation of the 2- or 3-cyclohexene isomers of **5** during the course of the irradiation. Treatment of **5** with methanolic sodium methoxide afforded a 1.5:1 mixture of two adducts exhibiting spectral behavior similar to that of the photoadducts. It is characteristic of the photochemical addition reactions of cycloalkenes to afford product ratios different from those obtained by thermodynamically controlled ground-state reactions.[2,3]

[16] It is not unlikely that the 6.5% conversion of crotonic acid (**1a**) into 3-methoxybutyric acid (**4a**) observed by Stoermer and Stockmann[10] after *3 weeks'* irradiation with a "Uviollampe" was the result of an acid-catalyzed dark reaction.

[16a] Note Added in Proof.—A similar photochemical addition of alcohols to 1-acetylcyclohexene has recently been reported by B. J. Ramey and P. D. Gardner, *J. Am. Chem. Soc.*, **89**, 3949 (1967).

[17] Infrared spectra were obtained on neat samples with a Perkin-Elmer Infracord spectrophotometer. Nuclear magnetic resonance (nmr) spectra were determined in chloroform-d_3 solution with a Varian HA-100 spectrometer, using tetramethylsilane as an internal standard. Gas chromatographic analyses were performed on an Aerograph 90-P instrument using 10 ft × 0.25 in. columns packed with 20% SE-30 or Carbowax 20 M on 60/80 mesh Chromosorb W.

[18] Indicates multiplicity (s = singlet, d = doublet, q = quartet, and m = unresolved multiplet), integration, and assignment.

[19] W. von E. Doering and R. W. Young, *ibid.*, **74**, 2997 (1952); T. Purdie and W. Marshall, *J. Chem. Soc.*, **59**, 477 (1891).

Hydrogenation Product of Tetraphenylmethane. The Cyclohexyl, Phenyl Tetrasubstituted Methanes

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It has been previously shown that the catalytic hydrogenation of tetraphenylmethane proceeds smoothly to tetracyclohexylmethane,[1] despite the failure of early attempts[2] and the suggestion that steric requirements would preclude the bonding of four cyclohexyl groups to a single carbon atom.[3] To verify this conclusion and to observe reaction intermediates, hydrogenation of tetraphenylmethane has now been performed under conditions conducive to partial reaction

Cyclohexyltriphenylmethane[4] (I) was isolated when the hydrogenation at 95° and 500 psig over rhodium was interrupted after 3 moles of hydrogen was absorbed, while dicyclohexyldiphenylmethane (II) was the major product (74%) at the point when hydrogenation slowed substantially after 6 moles was absorbed. The partial hydrogenation of II at 97.5° furnished tricyclohexylphenylmethane (II) in 19% yield.

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[1] G. R. Buell and L. Spialter, *J. Org. Chem.*, **30**, 1662 (1965).

[2] V. N. Ipatiev and B. N. Dolgov, *Compt. Rend.*, **185**, 210 (1927).

[3] M. Kanazashi and M. Takakusa, *Bull. Chem. Soc. Japan*, **27**, 441 (1954).

[4] H. Wieland and A. Meyer, *Ann.*, **551**, 249 (1942).

In earlier work[1] on the dehydrogenation of tetracyclohexylmethane (IV) to tetraphenylmethane, none of the latter could be isolated, although it was detected by gas chromatography. Tetraphenylmethane has now been obtained in 9.1% yield by aromaticization of IV thereby completing the structure proof for tetracyclohexylmethane.

The 60-Mcps proton magnetic resonance (pmr) spectra for the intermediate cyclohexyl and phenyl substituted methanes in deuteriochloroform displayed two absorption regions: a fairly sharp band at 2.65 and complex multiplets in the region 6.6–9.6 ppm. Quantitative band and coupling-constant assignments were impossible to determine. However, the ratio of the areas under the respective pmr bands agreed satisfactorily with the theoretical (see Table I) and supported the molecular structures proposed.

TABLE I

PROTON DISTRIBUTION IN $(c\text{-}C_6H_{11})_nC(C_6H_5)_{4-n}$

	Phenyl		Cyclohexyl		Cyclohexyl/phenyl	
n	Calcd	Found[a]	Calcd	Found[a]	Calcd	Found
1	15	14.8	11	11.2	0.73	0.75
2	10	9.7	22	22.2	2.20	2.26
3	5	4.7	33	33.5	6.60	7.09

[a] Based on the computed average area per proton.

Experimental Section

Gas chromatographic analysis was performed at *ca.* 210° using capillary columns coated with Carbowax 1540. Hydrogenations were carried out in a magnetically stirred autoclave. Stirring was maintained at 1000 rpm for all reactions. Thin layer chromatography was performed with Silica gel $HF_{254+366}$ (E. Merck A. G.). All reagents, solvents and catalyst are from commercial suppliers. Tetraphenylmethane was obtained from K & K Laboratories, Inc., and was purified by sublimation before use. Tetracyclohexylmethane was prepared as previously reported.[1]

Dehydrogenation of Tetracyclohexylmethane.—The dehydrogenation of IV was carried out as previously described[1] except refluxing methyl phthalate was used (bp 280°) as a heat bath. Three 100-mg batches furnished 25 mg (8%) of tetraphenylmethane, mp 284–285° (no depression), mol wt 311 (vapor osmometry), when the hot, filtered octadecane solutions were diluted with an equal volume of benzene.

Cyclohexyltriphenylmethane (I).—Tetraphenylmethane (1 g, 0.0031 mole) and 5% rhodium on charcoal (0.5 g) in methylcyclohexane (150 ml) were hydrogenated at 92° and 500-psi hydrogen pressure. Samples were taken at intervals and were analyzed by gas chromatography. After 35 hr of reaction the area under the peak for I on the chromatogram stopped increasing with respect to the total area of the reaction products and the hydrogenation was terminated. Preparative-scale, thin layer chromatography on silica gel, with 10% benzene in hexane as the developing solvent, yielded a fraction of crude I, which was further purified by recrystallization from hexane. Sublimation of the product gave 150 mg (15% of theory) of I, mp 137–138°.[5]

Anal. Calcd for $C_{25}H_{26}$: C, 91.97; H, 8.03; mol wt, 326.5. Found: C, 91.87; H, 8.06; mol wt (Mechrolab osmometer), 330.

Dicyclohexyldiphenylmethane (II).—Hydrogenation of 1 g (0.0031 mole) of tetraphenylmethane was carried out for 48 hr in 150 ml of methylcyclohexane with 1 g of 5% rhodium on charcoal at 95° and 500-psi hydrogen pressure. The reaction mixture was filtered to remove the catalyst and the components were separated by means of thin layer chromatography using hexane as the developing solvent. Sublimation of the product gave 0.77 g (74% of theory) of II, mp 195–196°.

Anal. Calcd for $C_{25}H_{32}$: C, 90.30; H, 9.70. Found: C, 90.63; H, 9.37.

Tricyclohexylphenylmethane (III).—Compound III was obtained by the hydrogenation of 1 g (0.003 mole) of II in 150 ml of methylcyclohexane with 1 g of 5% rhodium on charcoal as catalyst at 500-psi hydrogen pressure and 97.5°. Samples were taken periodically and examined by means of gas–liquid chromatography. When the peak corresponding to III reached a maximum, after approximately 7 days, the reaction was stopped and the catalyst was removed by filtration. After initial purification by thin layer chromatography on silica gel, with hexane as the developing solvent, the product was recrystallized from hexane. After sublimation, there was obtained 85 mg (19% of theory) of III, mp 240–242°.

Anal. Calcd for $C_{25}H_{38}$: C, 88.79; H, 11.31; mol wt, 338.5. Found: C, 88.69; H, 11.40; mol wt (Mechrolab osmometer), 300.

Registry No.—I, 13619-64-2; II, 13619-65-3; III, 13619-66-4; tetraphenylmethane, 630-76-2.

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[5] Reference 4 reports a melting point of 143–145°. The cause and significance of the discrepancy in values is not known.

An Anomalous Hydrocyanation

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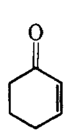
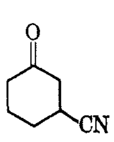
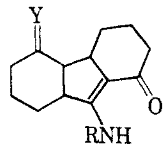
In an attempt to synthesize 3-cyanocyclohexanone (II), the unsaturated ketone I was exposed to an aqueous, alcoholic potassium cyanide solution. The sole isolable product was a crystalline substance whose elemental analysis ($C_{13}H_{17}O_2N$) revealed it to be an unexpected 2:1 enone–cyanide adduct. Its infrared spectrum (see Experimental Section) showed OH and/or NH bands and bands characteristic of a saturated keto function and a vinylogous amide unit,[1] but no C≡N absorption. The ultraviolet spectrum confirmed the presence of a vinylogous amide chromophore.[2] These facts and the mechanistic rationale of the complex reaction given by eq 1 suggest IIIa as the structure of the unusual product. Acetylation of the adduct yielded the derivative IIIb, while sodium borohydride



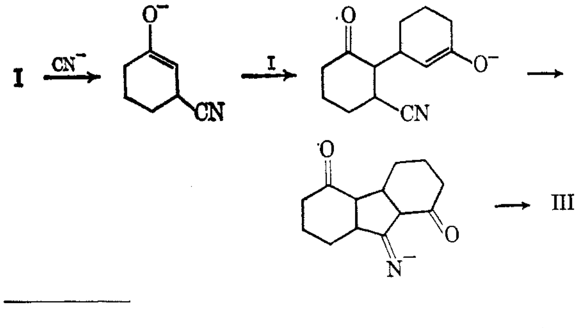
I



II



IIIa, R = H; Y = O
b, R = Ac; Y = O
c, R = H; Y = HOH
d, R = Ac; Y = HOAc



(1)

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[2] E. Wenkert and B. Wickberg, *ibid.*, **87**, 1580 (1965); E. Wenkert, K. G. Dave, and F. Haglid, *ibid.*, **87**, 5461 (1965).