Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.79; H, 6.91.

3-Bromo-3-phenyltetrahydro-2-pyrone (7).—Compound **6** (9.4 g, 0.0534 mole) in 25 ml of reagent grade CCl_4 was added to 9.5 g (0.0534 mole) of N-bromosuccinimide suspended in 25 ml of CCl_4. The mixture was heated to boiling on a steam bath and 0.1 g of freshly recrystallized benzoyl peroxide was added. The reaction mixture was refluxed for 2 hr, during which time the originally colorless solution turned reddish. The cooled mixture was filtered and the solvent was removed from the filtrate under reduced pressure. The residual caramel-colored oil solidified on standing overnight at room temperature. Recrystallization from ethanol yielded 7.0 g (52%) of white needles: mp 85.5–86.5°; infrared absorption ($CHCl_3$) at 5.85 (C=O) and 6.2 and 6.7 μ (phenyl); nmr peaks ($CDCl_3$) at δ 7.4 (5 H, multiplet), 4.38 (2 H, multiplet), 2.72 (2 H, quartet), and 1.9 (2 H, unresolved).

Anal. Calcd for $C_{11}H_{11}BrO_2$: C, 51.78; H, 4.35; Br, 31.32. Found: C, 51.76; H, 4.35; Br, 31.06.

3-Phenyl-5,6-dihydro-2-pyrone (3). Method A.—A mixture of 1.0 g (0.0052 mole) of **2**[6] and 15 ml of 5% H_2SO_4 was refluxed for 3 hr, after which it was cooled and extracted with ether. This extract was dried (Na_2SO_4) and filtered, and the solvent was removed from the filtrate under reduced pressure. The residual oil was dissolved in hot Skellysolve B and upon cooling, white crystals appeared: mp 98–100°; yield, 0.60 g (66%); infrared absorption ($CHCl_3$) at 5.83 (C=O) and 6.7 μ (phenyl); nmr absorption ($CDCl_3$) at δ 7.35 (5 H, singlet), 6.96 (1 H, triplet), 4.44 (2 H, triplet), and 2.60 (2 H, sextet).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79; mol wt, 174. Found: C, 75.91; H, 6.04; mol wt, 175.[8]

Method B.—A mixture of 15 ml of sodium hydroxide dried pyridine, 5 ml of anhydrous ethanol, and 2.0 g (0.0078 mole) of **7** was refluxed for 12 hr. The solvents were removed from the deep brown solution under reduced pressure; the oily residue was dissolved in $CHCl_3$ and this solution was extracted with two 25-ml portions of water. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed from the filtrate under reduced pressure. The residual, brown oil was taken up in hot Skellysolve B and upon cooling, 1.1 g (70%) of white crystals separated, mp 98–100°. The infrared spectrum ($CHCl_3$) was identical with that of the product of method A.

Deamination of *dl*-Cyclopropylphenylglycine.—To an ice-chilled solution of 10 g (0.052 mole) of *dl*-cyclopropylphenylglycine (Pierce Chemical Co., Rockford, Ill.) in 250 ml of 50% H_2SO_4 was added 6.9 g (0.1 mole) of $NaNO_2$ in 15 ml of water. The mixture was stirred in an ice bath for 42 hr, then 30 ml of 10% sulfamic acid solution was added to decompose the excess nitrite. The resulting mixture was diluted to a convenient volume with water and was extracted with four 50-ml portions of ether. The combined ethereal extracts were washed with 5% Na_2CO_3, then with water, dried (Na_2SO_4), and filtered, and the solvent was removed from the filtrate under reduced pressure. The yellow residue was taken up in hot Skellysolve B and on cooling, 3.5 g (38%) of white crystals appeared, mp 96–97°. An infrared spectrum ($CHCl_3$) of this material was superimposable upon a similar spectrum of an authentic sample of **3**.

(±)-2-Phenyl-1,5-pentanediol (8).—Compound **3** (25 g, 0.144 mole) in 100 ml of anhydrous ether was added slowly to 12 g (0.316 mole) of lithium aluminum hydride suspended in 200 ml of anhydrous ether. The resulting mixture was refluxed for 24 hr, water was added slowly to the ice-cooled solution, and the resulting mixture was poured over ice. Sulfuric acid (200 ml of 10%) was added; two layers separated, and the ether layer was washed with 5% Na_2CO_3 then with water, dried ($MgSO_4$), and filtered. The filtrate was evaporated under reduced pressure leaving a colorless oil which distilled at 144–145° (0.1 mm): yield, 15 g (57%) of a colorless oil [lit.[9] bp 150–155° (1.0 mm)]; infrared absorption (film) at 2.8 and 3.0 (OH) and 6.2 and 6.7 μ (phenyl).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95; O, 17.75. Found: C, 73.46; H, 8.98; O, 17.09.

A di(*p*-toluenesulfonate) of **8** was prepared according to the method of Kawazu and Fujita[9] and was recrystallized from methanol, mp 88–89° (lit.[9] mp 89–90.5°).

Cyclopropylphenylglycolamide.—A mixture of 5.4 g (0.026 mole) of methyl cyclopropylphenylglycolate[6] and 150 ml of liquid NH_3 was permitted to stand in a bomb at room temperature for 36 hr. The excess NH_3 was permitted to evaporate, leaving a tan, crystalline solid which was recrystallized several times from $CHCl_3$ (charcoal), to yield 1.0 g (20%) of a white, crystalline solid: mp 120–122°; infrared absorption ($CHCl_3$) at 2.93 and 3.0 (OH, NH) and at 6.0 μ (amide).

Anal. Calcd for $C_{11}H_{11}NO_3$: C, 69.1; H, 6.80; N, 7.33. Found: C, 68.78; H, 6.74; N, 7.24.

Rearrangement of Cyclopropylphenylglycolic Acid (2) with Boron Trifluoride Etherate.—A mixture of 1.0 g (0.052 mole) of **2**, 2 ml of boron trifluoride etherate (Eastman White Label), and 40 ml of sodium-dried benzene was refluxed for 3 hr and then was permitted to stand at room temperature for 24 hr. The reaction mixture was washed with six 25-ml portions of water, dried (Na_2SO_4), and filtered, and the solvent was removed from the filtrate under reduced pressure. The residual, deep amber oil was taken up in a minimum amount of hot ethanol and on cooling, crystalline material separated which was recrystallized from ethanol to yield rosettes of needles: mp 97–98.5°, yield 0.28 g (31%). The infrared spectrum ($CHCl_3$) of this material was identical with a similar spectrum of an authentic sample of **3**. The mother liquor from the first crystallization was diluted with water; an amber oil separated whose infrared spectrum ($CHCl_3$) showed a broad band between 3.2 and 3.6 μ and peaks at 5.7, 5.82, and 5.92 μ. Column chromatographic treatment of this oil gave rise to no identifiable material.

Treatment of Cyclopropylphenylglycolamide with Aqueous Sulfuric Acid.—Cyclopropylphenylglycolamide (1.3 g, 0.0068 mole) was heated under reflux for 6 hr with 13 ml of 5% H_2SO_4. The cooled reaction mixture was extracted repeatedly with ether; the combined extracts were washed with water until the washings were neutral, then the ether was removed on a steam bath. An off-white solid remained which recrystallized from ethanol to yield 0.6 g of needles, mp 98–100°. From the mother liquor was isolated an additional 0.1 g of material, mp 98–100°. Total yield was 0.7 g (58%). A sodium fusion indicated the absence of nitrogen. An infrared spectrum ($CHCl_3$) was identical with a spectrum of an authentic sample of **3**.

Registry No.—**2**, 1460-46-4; **3**, 13019-35-7; **4**, 13019-36-8; **6**, 13019-37-9; **7**, 13019-38-0; **8**, 13019-39-1; cyclopropylphenylglycolamide, 13019-40-4.

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[8] Mass spectroscopic determination was by Varian Associates, Palo Alto, Calif.

[9] K. Kawazu and T. Fujita, *J. Am. Chem. Soc.*, **81**, 932 (1959).

The Synthesis of Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane[1]

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In the course of our investigations on the behavior of polycyclic carbonium ions, it became desirable to prepare the interesting and symmetrical hydrocarbon pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (**4c**). Our first thought was to build on the successful photoisomerization of *exo*-tricyclo[3.2.1.0^{2,4}]octene-6 (**1**) to tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane (**2**) which we have recently reported.[2] The addition of a methano bridge connecting C-3 and C-8 in structure **1** produces ring skeleton **3c** (deltacyclene),[3] and a photoisomerization of delta-

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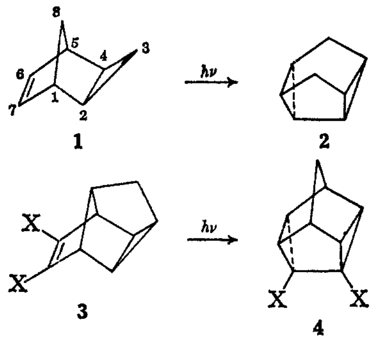
[1] This work was supported in part by the National Science Foundation, Grant GP-6228.

[2] P. K. Freeman, D. G. Kuper, and V. N. M. Rao, *Tetrahedron Letters*, 3301 (1965). For similar photoisomerizations of the *anti*-3,6,7-tricarbomethoxy and *anti*-3,6,7-tricarboxylic acid derivatives of **1**, see H. Prinzbach, W. Eberbach, and G. von Veh, *Angew. Chem. Intern. Ed. Engl.*, **4**, 436 (1965).

[3] The name "deltacyclene" has been suggested for structure **3c** and "deltacyclane" for the related saturated tetracyclononane **5d** by A. Nickon and H. R. Kwasnik, private communication, and ref 4b.

[4] (a) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, **87**, 1613 (1965); **87**, 1615 (1965); (b) H. R. Kwasnik, Ph.D. Thesis, Johns Hopkins University, 1966.

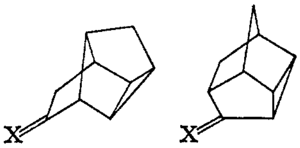


a, X = CO_2CH_3
b, X = CO_2H
c, X = H

cyclene or a derivative, analogous to that observed for **1**, should generate the desired hydrocarbon skeleton **4**.

The first substrate tested was the easily synthesized addition product of norbornadiene and dimethyl acetylenedicarboxylate (**3a**).[5] Irradiation of this diester, however, resulted in the generation of at least seven components. Using the same reaction conditions, the diacid **3b** gave a 63% yield of a saturated isomer whose spectral properties corresponded to those for **4b**, which has been prepared in a nearly identical fashion by Wenkert and co-workers and reported subsequent to our own experimental work.[6] Since attempts to generate **4c** by decarboxylation of **4b** were unsuccessful, we turned our attention to the more direct photoisomerization of deltacyclene (**3c**).

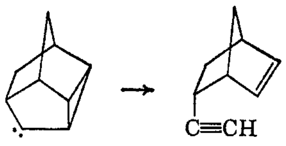
The preparation of **3c** was accomplished by conversion of tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonan-8-one (**5a**)[7] to the *p*-toluenesulfonylhydrazone **5b** and then to the sodium salt **5c**, which, in turn, was pyrolyzed to give



5 **6**
a, X = O
b, X = NNHTs
c, X = NNNaTs
d, X = H = H

the desired starting olefin (**3c**) in 56% yield. The structural assignment for this olefin is based upon an nmr absorption band at τ 3.86 (triplet, J = 1.7 cps, 2 H), absorptions in the infrared (ν_{max} 3060, 1575, and 803 cm^{-1}) which are characteristic of both norbornene[8] and nortricyclene[8] skeletal units, nmr and infrared spectral comparison with a sample of **3c** prepared by pyrolysis of the homo-Diels–Alder dimer of norbornadiene,[9] and its conversion to the tetracyclic hydrocarbon deltacyclane (**5d**)[3,4] by catalytic hydrogenation. Irradiation of **3c** using a 450-w Hanovia high-pressure mercury lamp resulted in the production of a 24% yield of the desired photoisomerization product, pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (**4c**).[9a]

The assignment of structure **4c** to the photoisomerization product is based upon 100-Mc nmr (τ 7.47, 2 H; 7.81, 2 H; 8.05–8.21, 6 H) and infrared (ν_{max} 3090 cm^{-1}, no absorption from 2700 to 1480 cm^{-1}) spectral properties and synthesis by an independent route. The sodium salt of the *p*-toluenesulfonylhydrazone of the known ketone **6a**[4] (**6c**) was pyrolyzed and a 93% yield of C_9 hydrocarbons was obtained; vapor phase chromatography indicated four components in a ratio of 29:4:4:63. The 63% component proved to be the expected carbenoid insertion product **4c** and its identity with the photoisomerization product of **3c** was demonstrated by comparison of vpc retention times, melting points, and nmr and infrared spectra. The two different 4% components were not investigated further. The infrared spectrum of the 29% component [ν_{max} 3310 (C≡CH), 3080 (=CH), 2110 (C≡C), and 1570 cm^{-1} (norbornene C=C)] suggests an ethynylnorbornene structure. Since the bivalent carbenoid intermediate expected as a result of decomposition of **6c** is a 2-carbenabicyclo[3.1.0]hexane[10] intermediate (**7**), by analogy to previous studies of this type of carbene[11–13] *endo*-5-ethynylnorbornene (**8**) is the anticipated product. The assignment of structure **8** to the



7 **8**

29% component is supported by the nmr spectrum (τ 3.82, 2 H; 6.75–7.50, 3 H; 7.67–9.17, 5 H). Thus, it is clear that bivalent intermediate **7** has undergone ring fragmentation involving cleavage of two rings and that this reaction pathway is the minor route and carbenoid insertion is the major route, in contrast to the predominant ring fragmentation found for 2-carbenabicyclo[3.1.0]hexane.[11]

Experimental Section[14]

Photoisomerization of Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene-8,9-dicarboxylic Acid (3b).—A saturated solution of **3b** (3.8 g) in 500 ml of anhydrous ether was irradiated in a Rayonet photochemical reactor for 12 hr. During this time a small amount of material crystallized out of solution. Concentration of the ether solution to approximately 80 ml gave crystals (2.4 g, 63% yield), which were essentially pure **4b**. Physical and spectral properties

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[5] C. F. Huebner, E. Donoghue, L. Dorfman, F. A. Stuber, N. Danieli, and E. Wenkert, *Tetrahedron Letters*, 1185 (1966).

[6] C. F. Huebner, E. Donoghue, L. Dorfman, E. Wenkert, W. E. Streth, and S. W. Donely, *Chem. Commun.*, 419 (1966).

[7] P. K. Freeman and D. M. Balls, *Tetrahedron Letters*, 437 (1967); H. K. Hall, Jr., *J. Org. Chem.*, **25**, 42 (1960).

[8] E. R. Lippencott, *J. Am. Chem. Soc.*, **73**, 2001 (1951); K. Alder, H. D. Schafer, H. Esser, H. Krieger, and R. Reubke, *Ann.*, **593**, 23 (1955); J. D. Roberts, E. R. Trumbull, W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

[9] T. J. Katz, J. C. Carnahan, Jr., and R. Boecke, in press. We express our appreciation to Professor Katz for providing us with nmr and infrared spectra of deltacyclene and a preprint of his paper. L. G. Cannell [*Tetrahedron Letters*, 5967 (1966)] has reported a similar synthesis of **3c**.

[9a] Note Added in Proof.—H. Prinzbach and D. Hunkler [*Angew. Chem. Intern. Ed. Engl.*, **6**, 247 (1967)] have just reported that the pyrolysis of the di-*t*-butyl peroxy ester related to **4b** [**4**, X = $CO_3C(CH_3)_3$] in triisopropylbenzene yields **4c**. Their infrared and nmr spectral data correspond with ours. H-D. Scharf and G. Weisgerber [*Tetrahedron Letters*, No. 16, 1567 (1967)] have just recently noted that irradiation of **3c** in acetone produces a 1,2-cycloaddition dimer, rather than pentacyclic **4c**.

[10] The nomenclature used here is that suggested by W. Kirmse ("Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 3). 2-Carbenabicyclo[3.1.0]hexane designates a bicyclo[3.1.0]hexylidene intermediate with the carbenoid carbon at C-2.

[11] P. K. Freeman and D. G. Kuper, *J. Org. Chem.*, **30**, 1047 (1965).

[12] S. J. Cristol and J. K. Harrington, *ibid.*, **28**, 1413 (1963).

[13] L. Friedman and H. Schechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960).

[14] Melting points are uncorrected. The nmr spectra were recorded with a Varian Associates A-60 nmr spectrometer using tetramethylsilane as the internal standard. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and by Max Bernhardt, Microanalytisches Laboratorium, Max-Planck Institute, Mülheim, Germany.

corresponded to those described[6] except that the nmr spectrum in pyridine showed absorptions at τ 6.96 (4 H, cyclopropyl), 7.28 (2 H, methine), and 8.05 (2 H, methylene); the reported nmr spectrum of the sodium salt in D_2O exhibits absorption at τ 7.08 (4 H, cyclopropyl), 6.71 (2 H, methine), and 7.64 (2 H, methylene).

Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 63.88; H, 4.95.

Preparation of Tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nonan-8-one *p*-Toluenesulfonylhydrazone (5b).—Tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]nonan-8-one (**5a**,[7] 28.5 g, 0.213 mole) was added to a refluxing solution of 41.2 g of *p*-toluenesulfonylhydrazine, 8 drops of acetic acid, and 160 g of absolute ethanol. After heating the resulting mixture at reflux for 2 min, the solution was allowed to cool overnight in a refrigerator. The product was collected and dried to give 60.0 g of colorless crystals, mp 179–181°. An additional 2.6 g of slightly less pure product was obtained by dilution of the filtrate with water.

Anal. Calcd for $C_{16}H_{18}N_2O_2S$: C, 63.55; H, 6.00. Found: C, 63.26; H, 6.17.

Preparation of Tetracyclo[4.3.0.0.^{2,4}.$0^{3,7}$]non-8-ene (3c).—*p*-Toluenesulfonylhydrazone **5b** (62.6 g, 0.206 mole) was dissolved in a solution of sodium methoxide prepared from 5.3 g (0.23 g-atom) of sodium and 500 ml of anhydrous methanol. The solvent was removed under vacuum and the dried sodium salt was heated slowly under vacuum (*ca.* 0.1 mm). When an external flask temperature of 180–190° was reached, decomposition began as indicated by an increase in pressure and a puffing of the salt. The product was collected in two traps which were connected in series to the pyrolysis flask and cooled in Dry Ice–isopropyl alcohol baths. Distillation of this material on a 30-in. spinning-band column gave 14.2 g of distillate, bp 71–72° (70 mm). Vapor phase chromatography of this fraction on an 18-ft column, which was packed with 12% SE 30 on 110–120 mesh Anakron AS, using a column temperature of 130° and nitrogen flow rate of 72 ml/min, showed evidence of two components in the ratio 89:11. The 89% component was eluted first and proved to be tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]non-8-ene (**3c**): ν_{max} 3060, 2990, 2900, 1610, 1575, 1320, 1268, 1255, 930, 803, 778, and 700 cm^{-1}; the nmr spectrum exhibited absorptions at τ 3.86 (triplet, J = 1.7 cps, 2 H), 7.47 (broad multiplet, 2 H), 8.12–8.55 (broad multiplet, 4 H), and 8.82 (doublet, J = 5 cps, 2 H).

Anal. Calcd for C_9H_{10}: C, 91.47; H, 8.52. Found: C, 91.31; H, 8.53.

The 11% component was identical with the known tetracyclo-[4.3.0.$0^{2,4}$.$0^{3,7}$]nonane (**5d**) as shown by comparison of nmr and infrared spectra.[4b] Hydrogenation of the mixture of two hydrocarbons **3c** and **5d** over a 10% palladium-on-carbon catalyst in ethyl acetate in a semimicro, low-pressure hydrogenation apparatus produced pure **5d**.

Preparation of Pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonane (4c). Method A.—A solution of 89% **3c** and 11% **5d** (5.2 g) in 200 ml of anhydrous ethyl ether was irradiated with a 450-w Hanovia high-pressure mercury lamp using a water-cooled quartz probe. Removal of aliquots at different times during the irradiation and examination by vpc (using the same column and conditions as in the preparation of **3c**) revealed the growth of a new component which eluted after **3c** and **5d** and was later proved to be the photoisomerization product **4c**. Using **5d** as an internal standard, it was calculated that the maximum yield of **4c** occurred at 46 hr and was 1.11 g (24%). A sample of **4c** was purified by vpc and had mp 87.5–88.0°; ν_{max} 3090, 3000, 2880, 1300, 900, 892, 882, 785, 765, and 755 cm^{-1}; the 100-Mc nmr spectrum (benzene solvent) exhibited absorptions at τ 7.41–7.54 (broad multiplet, 2 H), 7.73–8.05 (broad multiplet 2 H), and complex absorption from 8.05 to 8.21 (6 H).

Anal. Calcd for C_9H_{10}: C, 91.47; H, 8.52. Found: C, 91.34; H, 8.67.

Method B.—Ketone **6a** (3.5 g), prepared from *endo*-bicyclo-[2.2.1]hept-5-ene-2-carboxylic acid *via* the acid chloride and diazoketone as previously described,[4] was converted to the *p*-toluenesulfonylhydrazone **6b** by the method described above for the preparation of **5b** using proportional amounts of reagents and reactants. The yield amounted to 6.7 g, mp 183–188° dec.

Anal. Calcd for $C_{16}H_{18}N_2O_2S$: C, 63.55; H, 6.00. Found: C, 63.38; H, 6.25.

p-Toluenesulfonylhydrazone **6b** (6.0 g) was converted to **6c** and pyrolyzed under vacuum, as described above for the conversion of **5b** to **3c**. Vapor phase chromatographic analysis of the 2.9 g of liquid product collected indicated that 2.2 g (93% yield) of a mixture of C_9 hydrocarbons was generated in the ratio 29:4:4:63 (in order of increasing retention time). The 29% component was assigned the structure of *endo*-5-ethynylnorbornene on the basis of its mode of formation and its infrared (ν_{max} 3310, 3080, 2110, 1570 cm^{-1}) and nmr (τ 3.82, 2 H; 6.75–7.50, 3 H; 7.67–9.17, 5 H) spectra.

Anal. Calcd for C_9H_{10}: C, 91.47; H, 8.52. Found: C, 91.31; H, 8.59.

The 63% component proved to be the expected carbenoid insertion product **4c** and was shown to be identical with the photoisomerization product of **3c** by comparison of infrared and nmr spectra, vpc retention times, and melting points. A mixture melting point determination showed no depression (87.5–88.0°). The two 4% components were not characterized.

Registry No.—**3c**, 7785-10-6; **4b**, 13084-55-4; **4c**, 13084-56-5; **5b**, 13084-57-6; **6b**, 13084-53-2; **8**, 13084-54-3.

Isomerization of Unsaturated Alcohols with Iron Pentacarbonyl. Preparation of Ketones and Aldehydes[1]

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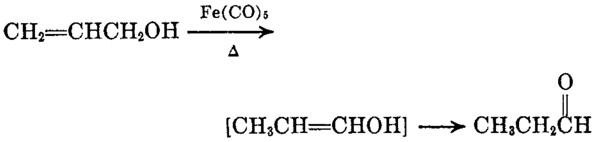
Received February 13, 1967

Although Emerson and Pettit[2] have reported that treatment of allyl alcohol with iron pentacarbonyl causes isomerization to propionaldehyde (eq 1), the experimental details and the limitations of this general type of isomerization reaction have not been disclosed.



$$CH_2{=}CHCH_2OH \xrightarrow[\Delta]{Fe(CO)_5} [CH_3CH{=}CHOH] \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}H \quad (1)$$

More recently, Goetz and Orchin[3] described the cobalt hydrocarbonyl catalyzed isomerization of allyl and substituted alkyl allyl alcohols to aldehydes and ketones. Under their conditions large amounts of hydroformylation products are found. The yields of aldehydes and ketones formed from isomerization alone ranged from 3 to 21%. Other workers[4,5] have examined the isomerization of unsaturated alcohols with iron carbonyls either in the presence of strong alkali or under carbon monoxide pressure.

We wish to report the results of a study of iron carbonyl catalyzed isomerization of some alkene and cycloalkene alcohols to saturated ketones or aldehydes, and the experimental details necessary to obtain high yields of products from these reactions.

Heating acyclic unsaturated secondary alcohols either neat or in hydrocarbon solvents to 110–125° with 10–20 mole % iron pentacarbonyl for 2–6 hr gives 60–80% conversions to ketones of greater than 95% purity (see Table I, entries 1–3). Isolation of the ketones is ac-

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[1] Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967, Abstracts, Paper O-159.

[2] G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, **84**, 4591 (1962).

[3] R. W. Goetz and M. Orchin, *ibid.*, **85**, 1549 (1963).

[4] R. T. Olsen, U. S. Patent 2,548,171 (1951).

[5] S. F. Chappell and C. E. Sibert, Netherlands Patent Application 64/14033 (1964).