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.

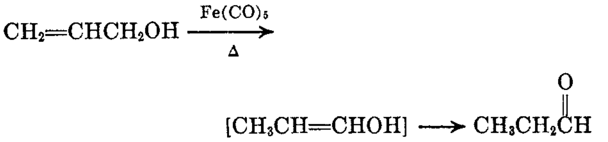
Isomerization of Unsaturated Alcohols with Iron Pentacarbonyl. Preparation of Ketones and Aldehydes[1]

RALPH DAMICO AND TED J. LOGAN

The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239

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.



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

(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-

---

(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).

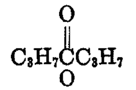
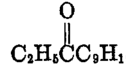
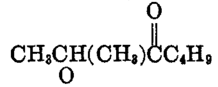
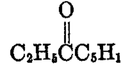
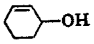
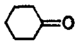
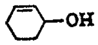
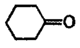
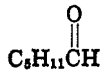
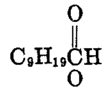
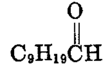
(3) R. W. Goetz and M. Orchin, *ibid.*, **85**, 1549 (1963).

(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).

TABLE I

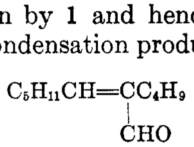
IRON CARBONYL CATALYZED ISOMERIZATION OF UNSATURATED ALCOHOLS TO ALDEHYDES AND KETONES

Entry	Alcohol	Mole % $Fe(CO)_5$	Time, hr[a]	Reacn method[b]	Product	Yield,[c] %	Purity,[c] %
1	$CH_2{=}CHCH_2CHOHC_3H_7$	10	4	*d*	 $C_3H_7\overset{O}{\overset{\parallel}{C}}C_3H_7$	80	98
2	$CH_2{=}CHCHOHC_9H_{19}$	20	6	A	 $C_2H_5\overset{O}{\overset{\parallel}{C}}C_9H_{19}$	60	98
3	$CH_2{=}C(CH_3)CHOHC_4H_9$	20	6	A	 $CH_3CH(CH_3)\overset{O}{\overset{\parallel}{C}}C_4H_9$	75	99
4	$CH_2{=}CHCHOHC_5H_{11}$	3	1	B	 $C_2H_5\overset{O}{\overset{\parallel}{C}}C_5H_{11}$	70	97
5		20	6	A		20[e]	93[e]
6		3	4	B		40[e]	95[e]
7	*cis*-$HOCH_2CH_2CH{=}CHC_2H_5$	10	6	*d*	 $C_5H_{11}\overset{O}{\overset{\parallel}{C}}H$	8	..
					1	29	..
8	$CH_2{=}CH(CH_2)_7CH_2OH$	10	5	A	 $C_9H_{19}\overset{O}{\overset{\parallel}{C}}H$	~10	..
9	$CH_2{=}CH(CH_2)_7CH_2OH$	5	5	B	 $C_9H_{19}\overset{O}{\overset{\parallel}{C}}H$	54	..

[a] The reaction time needed to reach complete conversions as determined by infrared and vapor phase chromatography is reported. [b] Reaction method A consists of heating approximately 20% solutions of unsaturated alcohols in octane solvent at 124° in the presence of 10–20 mole % of $Fe(CO)_5$. Reaction method B consists of irradiating ~5% solutions of unsaturated alcohols in pentane solvent at 20°. A quartz reactor with a 200-w high-pressure mercury lamp and with 3–5 mole % $Fe(CO)_5$ was used for these reactions. [c] Purity and yield percentages were calculated from vapor phase chromatography peak areas. [d] These reactions were conducted without solvent at 110°. [e] The values were determined by vpc after distillation of the reaction products.

complished either by direct distillation from the reaction mixtures or by first oxidizing the unreacted iron pentacarbonyl with ferric chloride solutions and then extracting the organic products. Ketones are identified by nuclear magnetic resonance (nmr), mass, and infrared spectral analyses, by vapor phase chromatography (vpc) retention time comparisons with authentic samples, and by conversion to 2,4-dinitrophenylhydrazone derivatives.

Attempts to apply the described conditions to the isomerization of unsaturated primary alcohols or cyclic olefinic alcohols give poor yields of the corresponding aldehydes or ketones. A study of the reaction of *cis*-3-hexen-1-ol with iron pentacarbonyl reveals that extensive dimerization takes place during the heating period. Thus, in addition to a 7.8% yield of hexanal, a 29% yield of hexanal dimer is obtained. Indeed, exposure of hexanal itself to the thermal isomerization conditions converts hexanal in 85% yield to this dimer. By spectral and elemental analysis data, the dimer has the structure shown by 1 and hence appears to be a dehydrated aldol condensation product.



$$C_5H_{11}CH{=}\underset{\underset{CHO}{\vert}}{C}C_4H_9$$

1

In order to find isomerization conditions applicable to the preparation and isolation of aldehydes and cyclic ketones, we explored the use of iron pentacarbonyl in combination with ultraviolet light at room temperature. Asinger and co-workers[6a,b] have recently used these conditions to isomerize undecene isomers. Equal quantities of internal undecene isomers are obtained by treating 1-undecene with 10% $Fe(CO)_5$ at 50° for 1 hr in the presence of a 300-w quartz lamp. Irradiation is necessary for this fast isomerization. Without the ultraviolet light only 29% of 1-undecene is isomerized at 100° for 1 hr with 10% $Fe(CO)_5$.[7]

We employed a 200-w high-pressure mercury lamp[8] at 20° with 3–5% iron pentacarbonyl catalyst in pentane solvent to convert cyclic olefinic alcohols and unsaturated primary alcohols to ketones and aldehydes. Yields of 40–60% are obtained within 1–6 hr of irradiation. Normally a maximum amount of ketone or aldehyde is formed during this time and continued irradiation causes loss of product through dimerization reactions. Isolation of the aldehydes or ketones is accomplished either by the ferric chloride treatment or by simple filtration of insoluble iron carbonyls[9] and evaporation of the pentane solvent. The results of some of these reactions and comparisons with the thermal method of isomerization are shown in Table I, entries 4–9.

There are at least three major advantages of using iron pentacarbonyl as an unsaturated alcohol isomerization catalyst in preference to the more conventional acid and base catalysts. Iron pentacarbonyl may be used in low concentration (3–5%) to cause rapid (1–6 hr) movement of double bonds within a molecule. An

---

(6) (a) F. Asinger, B. Fell, and K. Schrage, *Chem. Ber.*, **98**, 372 (1965); (b) F. Asinger, B. Fell, and K. Schrage, *ibid.*, **98**, 381 (1965).

(7) An explanation proposed[6b] for the rapid isomerization with irradiation is that $Fe(CO)_5$ dissociates to $Fe(CO)_4$, an electron-deficient species that readily combines with the π electrons of the α olefin. Isomerization by this complex is fast. In the absence of ultraviolet light, thermal energy is probably necessary to produce the $Fe(CO)_4$ species.

(8) A Model S-654A-36 Hanovia lamp, purchased from Engelhard Hanovia, Inc., Newark, N. J., was used in a quartz reactor.

(9) $Fe(CO)_5$ is converted to pentane-insoluble $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ upon ultraviolet irradiation.

olefin isomerization study[10] of several different strong base and acid catalysts compared to iron pentacarbonyl has indicated that iron pentacarbonyl is a faster and more complete isomerization catalyst than any of those studied. Secondly, the conditions employed with $Fe(CO)_5$ are mild and have not led to structural rearrangement or polymerization that is characteristic of acid catalysts. Thirdly, $Fe(CO)_5$ is a relatively neutral material not reacting with a variety of functional groups such as carboxylic esters, alcohols, and ketones. The results of isomerization experiments with ethers and esters will be reported in a forthcoming paper.

Experimental Section

General.—Melting and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. The nmr spectra were obtained on a Varian HA-100 instrument. Nmr samples were dissolved in either deuterated chloroform or carbon tetrachloride with tetramethylsilane as an internal reference. All vapor phase chromatograms were obtained on an Aerograph A-90-P instrument; a 10-ft Carbowax 20 M column was employed for analysis. Mass spectra results were determined on an Atlas CH-4 spectrophotometer. The ultraviolet spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer.

Materials.—Iron pentacarbonyl was purchased from Alfa Inorganics, Inc., and used as received. The unsaturated alcohols were purchased from either Aldrich Chemical Co. or Chemical Samples Co. Purity of these compounds was checked by vpc and all were found to be greater than 95% one component.

Isomerization of 1-Hepten-4-ol (Entry 1).—A solution of 10 g (0.088 mole) of 1-hepten-4-ol and 1.8 g (0.0092 mole) of iron pentacarbonyl was heated at 110° under an argon atmosphere for 4 hr. During this time the solution turned dark brown and deposits of a black solid formed on the sides of the flask. At 1-hr intervals, 0.5-ml samples were withdrawn and analyzed by infrared and vpc for appearance of 4-heptanone and disappearance of 1-hepten-4-ol. After 4 hr, the solution was cooled and 3.0 g (0.018 mole) of ferric chloride in 10 ml of 95% ethanol was added, which caused an evolution of gas (CO). This mixture was stirred for 1 hr, 50 ml of water was added, and the solution was extracted with ether. The ether layer was separated, washed with saturated sodium chloride, dried with 3A molecular sieves, and evaporated under reduced pressure. A total of 8.0 g (80% yield) of 4-heptanone was recovered. Vpc of this sample showed a major peak of 98% peak area. A 2,4-dinitrophenylhydrazone derivative was prepared, mp 70–71° (lit.[11] mp 71–72°). The mass spectrum of this product indicates a molecular ion peak at m/e 114 (calcd 114) with major fragment peaks at m/e 71 and 43 that correspond to $C_3H_7C(=O)$ and C_3H_7 groups, respectively.

Isomerization of 2-Methyl-1-hepten-3-ol (Entry 3).—A solution of 5.0 g (0.039 mole) of 2-methyl-1-hepten-3-ol and 1.5 g (0.0078 mole) of iron pentacarbonyl in 25 ml of *n*-octane solvent was refluxed at 124° for 6 hr. The solution was monitored for isomerization by infrared and vpc. After isomerization was complete, the mixture was cooled, treated with ferric chloride in 95% ethanol, diluted with ether, washed with saturated sodium chloride, and distilled to afford 3.7 g (75% yield) of 2-methyl-3-heptanone, bp 42–49° (12–15 mm) [lit.[12] bp 63–65° (25 mm)]. A vapor phase chromatogram of this product indicated a purity of 99%. The nmr spectrum of this sample has a multiplet centered at τ 7.62 (3 H, $>CHC(=O)CH_2$) and a complex band from 8.5 to 9.15 (11 H, aliphatic CH).

Isomerization of *cis*-3-Hexen-1-ol (Entry 7).—To 5.0 g (0.05 mole) of *cis*-3-hexen-1-ol was added 1.0 g (0.005 mole) of iron pentacarbonyl which caused an immediate evolution of gas (CO) and a 5° rise in temperature. Within 3 min the solution turned dark brown; however, infrared analysis indicated that the starting alcohol had not changed. The solution was heated to 110° for 6 hr and analyzed by vpc and infrared. The mixture has vpc peaks (170°) at retention times of 1.1, 2.0, 2.5, and 7.8 min. Peak 1 (1.1 min) was identical in retention time with hexanal, and peak 3 corresponded to *cis*-3-hexen-1-ol. Peak 2 probably corresponds to partially isomerized *cis*-3-hexen-1-ol. An infrared spectrum of the product mixture showed two bands at 5.8 (aldehyde C=O) and 5.95 (conjugated C=O) as well as peaks at 6.1 (conjugated C=C) and 10.35 μ (*trans* olefin). Peak 4 was collected from the gas chromatograph and analyzed by mass, ultraviolet, and nmr spectra and elemental analysis. The collected sample has a λ_{max} in 95% EtOH at 232 mμ (ϵ 13,500); nmr peaks at τ 0.62 (1 H, singlet, $>CHO$), 3.1 (1 H, triplet, $CH=CC=O$), 7.75 (4 H, multiplet, allylic CH_2), and a broad peak from 8.6 to 9.05 (16 H, aliphatic CH). The mass spectrum of the product has a molecular ion peak at 182. This data accommodates structure **1** for the product.

Anal. Calcd for $C_{12}H_{22}O$: C, 79.1; H, 12.1. Found: C, 79.2; H, 11.8.

Reaction of Hexanal with Iron Pentacarbonyl.—A solution of 20 g (0.20 mole) of freshly distilled hexanal and 3.9 g (0.02 mole) of iron pentacarbonyl was heated at 110° for 6 hr. An infrared spectrum of the mixture after this time had peaks at 5.8 (aldehyde C=O) and 5.95 μ (conjugated C=O). Vpc analysis (170°) of the mixture showed three peaks with the major component ($\sim$85%) having a retention time of 7.8 min, identical with that of **1** isolated from the reaction of *cis*-3-hexen-1-ol with iron pentacarbonyl. The major peak was collected from the gas chromatograph. An nmr spectrum of this material was found to be identical with the nmr spectrum of **1**.

Isomerization of 9-Decen-1-ol with Iron Pentacarbonyl and Ultraviolet Light (Entry 9).—A 200-w high-pressure mercury lamp in a quartz reactor was used in this irradiation procedure. A solution of 5.0 g (0.032 mole) of 9-decen-1-ol and 0.31 g (0.0016 mole) of iron pentacarbonyl in 125 ml of pentane was irradiated at $\sim$20°. Samples of 5 ml were withdrawn at 1-hr periods for 5 hr and analyzed by infrared and vpc for the appearance of decanal and loss of 9-decen-1-ol. Within 1 hr, terminal olefin peaks (10.1 and 10.95 μ) and aldehyde C=O (5.8 μ) had formed. No other carbonyl peaks were present. The solution turned a dark green but a precipitate did not form during this reaction. The vpc analysis of this reaction mixture and subsequent experiments indicated that a maximum amount of decanal had formed at a 5-hr reaction time. The reaction was stopped at this time and filtered to remove insoluble iron carbonyls, pentane was evaporated under reduced pressure, and the crude product, which showed 54% decanal by vpc, was recovered. A 2,4-dinitrophenylhydrazone derivative of the decanal in the mixture was prepared, mp 100–101° (lit.[13] mp 104.2–104.8°). A total of 7.2 g (54% yield) of 2,4-dinitrophenylhydrazone derivative was obtained.

Registry No.—**1**, 13019-16-4; 4-heptanone 2,4-dinitrophenylhydrazone, 1655-41-0; 2-methyl-3-heptanone, 13019-20-0. Table I: **1**, 3521-91-3; **2**, 4048-42-4; **3**, 13019-19-7; **4**, 3391-86-4; **5**, 822-67-3; **7**, 1708-81-2; **8**, 13019-22-2.

---

[10] F. Asinger, B. Fell, and G. Collin, *Chem. Ber.*, **96**, 716 (1963).

[11] H. Bredereck, R. Gompper, and K. Klemm, *Chem. Ber.*, **92**, 1456 (1959).

[12] J. Cason and M. P. Chang, *J. Org. Chem.*, **21**, 449 (1956).

[13] R. Ellis, A. M. Gaddis, and G. T. Currie, *Anal. Chem.*, **30**, 475 (1958)

The *ortho* Bromination of Phenols

D. E. Pearson, R. D. Wysong, and C. V. Breder

Department of Chemistry, Vanderbilt University,
Nashville, Tennessee 37203

Received January 31, 1967

One of our objectives in research work has been to manipulate orientation in various ways to obtain any isomer desired.[1] The bromination of phenol serves as one example. *para* substitution is predominant by bromination in carbon bisulfide,[2] almost exclusive in

---

[1] D. E. Pearson, *J. Tenn. Acad. Sci.*, **40**, 97 (1965).

[2] R. Adams and C. S. Marvel, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 128.