

REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION.  
XX. THE ADDITION OF ALDEHYDES TO OLEFINS

M. S. KHARASCH, W. H. URRY, AND B. M. KUDERNA

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The photochemical additions of polyhalomethanes (1a),  $\alpha$ -halogenated esters (1b), etc. (1c), to olefins, as well as the similar reactions induced by acyl peroxides have been described. The present paper deals with the preparation of ketones by the addition of aldehydes to 1-alkenes.



When a high ratio (6:1) of aldehyde to olefin is used, the principal products of the reaction are: (a) the one-to-one adduct (A), (b) small amounts of higher-boiling products (formed from two or more molecules of olefin to one molecule of aldehyde), (c) alkane derived from the alkyl radical of the aldehyde, and (d) carbon monoxide. The latter two products are formed in equimolecular amounts.

The structures of the ketones formed were established by analysis, by molecular weight determination and by comparison of the physical properties of the products with the physical properties of the same ketones prepared by conventional methods. In some instances, the identity of the ketones prepared by the new method and the ketones prepared by conventional methods was established by proving the identity of the respective hydantoin derivatives.

DISCUSSION

The products formed in the addition of aldehydes to olefins may be accounted for by the following series of reactions:

1.  $\text{RCHO} + \text{CH}_3\cdot \rightarrow \text{CH}_4 + \cdot\text{C}(\text{R})=\text{O}$  or  $\text{RCHO} \xrightarrow{h\nu} \cdot\text{C}(\text{R})=\text{O} + \text{H}\cdot$   
from diacetyl peroxide
2.  $\cdot\text{C}(\text{R})=\text{O} + \text{R}'\text{CH}=\text{CH}_2 \rightarrow \cdot\text{CHR}'\text{CH}_2\text{COR}$  (I)
3.  $\text{I} + \text{RCHO} \rightarrow \cdot\text{C}(\text{R})=\text{O} + \text{RCOCH}_2\text{CH}_2\text{R}'$
4.  $\text{I} + \text{R}'\text{CH}=\text{CH}_2 \rightarrow \cdot\text{CHRCH}_2\text{CHR}'\text{CH}_2\text{COR}$  (II)
5.  $\text{II} + \text{R}'\text{CH}=\text{CH}_2 \rightarrow \cdot\text{CHR}'\text{CH}_2\text{CHR}'\text{CH}_2\text{CHR}'\text{CH}_2\text{COR}$  (III)

The formation of equimolecular quantities of an alkane and carbon monoxide is probably due to side reactions 6 and 7. Step 8 is the chain-terminating reaction, and in the addition of acetaldehyde to 1-octene the yield of biacetyl was about 30% that of the 2-decanone formed.

6.  $\cdot\text{C}(\text{R})=\text{O} \rightarrow \text{R}\cdot + \text{CO}$
7.  $\text{R}\cdot + \text{RCHO} \rightarrow \text{RH} + \cdot\text{C}(\text{R})=\text{O}$
8.  $2 \cdot\text{C}(\text{R})=\text{O} \rightarrow \text{RCOCOR}$

The non-formation of the one-to-one adducts of aldehydes and styrene is readily explained by the assumption that when  $R = C_6H_5$ , the activation energy required to enable the free radical (I) to remove a hydrogen atom from the aldehyde molecule is very high compared to the activation energy required for the addition of this free radical to another styrene molecule. Hence, reactions of the type indicated in steps 4 and 5 are favored, and the resulting products are, therefore, mixtures of polymers of high molecular weight. Bromotrichloromethane, on the other hand, adds readily to styrene at 50–60° to give a one-to-one adduct because at that temperature the free radical  $\cdot CH(C_6H_5)CH_2CCl_3$  readily removes a bromine atom from bromotrichloromethane, thus propagating the chain.

A less complex reaction mixture is formed when the additions of aldehydes to olefins are initiated photochemically rather than by acyl peroxides. In the reactions induced by acyl peroxides the acid formed causes an aldol condensation of

TABLE I  
ADDITION OF ALDEHYDES TO OLEFINS

ALDEHYDE	OLEFIN	REACTION INITIATED BY	ADDITION PRODUCT	YIELD %
Ethanal	1-Octene	Ultraviolet light	2-Decanone	
Butanal	1-Octene	Ac <sub>2</sub> O <sub>2</sub>	4-Dodecanone	57
	1-Hexene	Ac <sub>2</sub> O <sub>2</sub>	4-Decanone	41
	Styrene	Ac <sub>2</sub> O <sub>2</sub>	Polymer	
	1-Octene	Visible light	4-Dodecanone	
2-Butenal	1-Octene	Ac <sub>2</sub> O <sub>2</sub>	Polymer	
Heptanal	1-Octene	Ac <sub>2</sub> O <sub>2</sub>	7-Pentadecanone	75
	1-Octene	Visible light	7-Pentadecanone	
	Cyclohexene	Visible light	1-Cyclohexyl-1-heptanone	

the aldehyde. Frequently, the aldol thus formed boils at about the same temperature as the ketonic product; this fact often makes the isolation of the ketone difficult. In the photochemical reaction, no acid is formed, and, hence, there is little or no aldol produced.

The best yields of ketones were obtained by adding long-chain aldehydes to long-chain 1-alkenes. Thus, the addition of ethanal to olefins gave low yields of methyl ketones. Similarly, butanal and heptanal when treated with propene gave low yields of propyl ketones. On the other hand, excellent yields of ketones were obtained when butanal or heptanal were added to 1-octene. Irrespective of the aldehyde used, cyclic olefins, such as cyclohexene, gave poor yields of ketones.

It is of interest that when a mixture of 2-butenal and 1-octene was either illuminated or heated in the presence of an acyl peroxide no one-to-one adduct was found; the reaction product consisted entirely of a high polymer. Furthermore, no carbon monoxide was liberated in this reaction. In this respect, 2-butenal resembles benzaldehyde which, unlike all saturated aliphatic aldehydes, gives no carbon monoxide when treated with acetyl peroxide. The non-formation of

carbon monoxide from these aldehydes is probably due to the high resonance energy of the free benzoyl and crotonyl radicals.

#### EXPERIMENTAL

*Reagents.* Heptanal, Eastman's, was first distilled through a 10-inch Vigreux column, dried over Drierite, and then distilled through a 50-plate Podbielniak column (b.p. 56°/23 mm.;  $n_D^{20}$  1.4114).

1-Octene (Connecticut Hard Rubber Company) was distilled through a 50-plate column at atmospheric pressure (b.p. 118°;  $n_D^{20}$  1.4090).

Eastman's butanal was first distilled through a 10-inch Vigreux column and dried over Drierite; it was then distilled through a 100-plate Podbielniak column (b.p. 74.2°;  $n_D^{20}$  1.3819).

1-Hexene was distilled through the 50-plate column (b.p. 63.2°;  $n_D^{20}$  1.3880).

Eastman's ethanal was distilled before use (b.p. 20°).

Cyclohexene was distilled through a 50-plate column (b.p. 82-83°;  $n_D^{20}$  1.4454).

1-Bromohexane was prepared according to the directions of Kamm and Marvel (2). It was distilled through a 15-plate column packed with single-turn glass helices (b.p. 57°/28 mm.;  $n_D^{20}$  1.4456).

1-Bromooctane was prepared in the same way. It was distilled through a 15-plate column (b.p. 40-41°/1 mm.;  $n_D^{20}$  1.4528).

Styrene was distilled immediately before use (b.p. 144°;  $n_D^{20}$  1.5460).

Eastman's 2-butenal was distilled through a 15-plate column (b.p. 102-103°;  $n_D^{20}$  1.4375).

*The peroxide-induced addition of heptanal to 1-octene.* Acetyl peroxide (4.5 g.) dissolved in heptanal (14.2 g.) was dropped over a period of 9 hours into a solution containing 1-octene (31.4 g., 0.28 mole) and heptanal (114 g., 1.0 mole; b.p. 68°/40 mm.;  $n_D^{20}$  1.4128) held at 65°. After the peroxide addition was complete, the reaction temperature (65°) was maintained for 10 hours. During the reaction period, a gas (7.1 liters N.T.P.; molecular weight, 26.3) was evolved. This gas was shown to be a mixture of methane (13%) and carbon monoxide (87%; 0.28 mole). The carbon monoxide content was determined by ammoniacal cuprous chloride absorption in a Moorhead apparatus.

The reaction mixture was distilled through a 50-plate Podbielniak column and the following fractions were collected: hexane (23.9 g.;  $n_D^{20}$  1.3742; b.p. 63-68°; 0.28 mole); 1-octene (3.8 g.); heptanal (66.0 g.). The residue was distilled at reduced pressure through a 10-inch Vigreux column, and the fraction boiling at 63-70°/0.1 mm. (47.5 g.) was collected. This material crystallized upon standing. After two crystallizations from methanol, it melted at 32°. This substance was shown to be 7-pentadecanone.

*Anal.* Calc'd for  $C_{16}H_{30}O$ : C, 79.57; H, 13.36; Mol. wt., 226.

Found: C, 79.16; H, 13.22; Mol. wt., 236.

A residue (4.5 g.; mol. wt., 436) remained in the distilling flask.

*Identification of the heptanal-1-octene addition product (7-pentadecanone).* 7-Pentadecanol (34.7 g.) was prepared from *n*-octylmagnesium bromide (made from 1-bromooctane, 52 g., and magnesium, 7 g., in absolute ether, 180 ml.) and heptanal (23.0 g.; 0.20 mole) in 76% yield. The alcohol distilled at 95-100°/0.1 mm., and upon standing crystallized to a white solid. The solid melted at 36.5-38° after crystallization from methanol.

The 7-pentadecanol was oxidized with chromic anhydride in glacial acetic acid by the method of Karrer (3). The 7-pentadecanone isolated melted at 31-32° after two crystallizations from methanol. This material did not depress the melting point of the 7-pentadecanone obtained by the addition of heptanal to 1-octene.

The 7-pentadecanone was converted to its hydantoin derivative (4). After several crystallizations from 60% ethanol, the hydantoin (5-*n*-hexyl-5-*n*-octylhydantoin) melted at 121.5-122°.

*Anal.* Calc'd for  $C_{17}H_{32}N_2O_2$ : N, 9.45. Found: N, 9.24.

The hydantoin prepared from the product of addition of heptanal to 1-octene melted at 121-122°. It did not depress the melting point of the hydantoin derived from a known sample of 7-pentadecanone.

*The peroxide-induced reaction of butanal with 1-octene.* A mixture of butanal (42.9 g.; 0.596 mole) and 1-octene (18.1 g.; 0.162 mole) was held under reflux while a solution of acetyl peroxide (7.2 g.) in butanal (18.0 g.) was dropped in over a period of 3 hours. The reaction mixture was heated for 4 hours after the addition was complete.

The reaction mixture was distilled without further treatment. Unchanged butanal (b.p. 69–73°; 24.7 g.) distilled first. The residual reaction product was distilled at reduced pressure. A fraction was obtained (b.p. 65°/0.25 mm.; 17.2 g.;  $n_D^{20}$  1.4313) which was shown to be 4-dodecanone. A residue (7.0 g.;  $n_D^{20}$  1.4538) remaining in the distilling flask had an apparent molecular weight of 310.

The addition product of butanal to 1-octene was converted to the hydantoin. The hydantoin melted at 117–119° after three crystallizations from 60% ethanol.

*Anal.* Calc'd for  $C_{14}H_{26}N_2O_2$ : N, 11.01. Found: N, 11.22.

*Identification of the butanal-1-octene addition product (4-dodecanone).* 4-Dodecanone was prepared according to the general method outlined above for 7-pentadecanone. To *n*-octylmagnesium bromide, prepared from 1-bromooctane (52 g.; 0.27 mole) and magnesium (6.5 g.; 0.28 mole) in absolute ether (200 ml.), a solution of butanal (19.4 g.; 0.27 mole) in ether (50 ml.) was slowly added. Stirring of the reaction mixture was continued at room temperature for 24 hours.

The reaction mixture was treated with an aqueous acetic acid solution (30%), and the ether layer was washed with water and sodium carbonate solution (5%). The ether solution was dried over calcium sulfate. After the ether had been removed, the reaction product was distilled through a short Vigreux column. 4-Dodecanol (36.7 g.;  $n_D^{20}$  1.4386; b.p. 76–78°/0.1 mm.) was obtained in 61% yield.

The 4-dodecanol was oxidized by the method of Karrer (3). The alcohol (20 g.; 0.11 mole) was treated with a solution containing chromic anhydride (10 g.), concentrated sulfuric acid (32 g.), and glacial acetic acid (100 g.). 4-Dodecanone (12.9 g.;  $n_D^{20}$  1.4315; b.p. 71–73°/0.30 mm.) was obtained in 67% yield. These physical properties correspond with those of the addition product of butanal and 1-octene.

The 4-dodecanone prepared by the two methods was converted to 5-*n*-propyl-5-*n*-octylhydantoin. After one crystallization from 60% ethanol, both samples melted at 117–119°. The melting point of a mixture was not depressed.

*The light-initiated reaction of ethanal with 1-octene.* A solution containing ethanal (192.4 g.; 4.37 moles) and 1-octene (123.6 g.; 1.10 mole; b.p. 120°;  $n_D^{20}$  1.4090) was placed in an irradiation tube fitted with a long quartz mercury resonance lamp. The apparatus was swept with nitrogen before use. The tube and its contents were cooled throughout the reaction by an ice-water bath. The reaction mixture was illuminated for 72 hours. During this time, gas (2000 ml.; methane, 47%; carbon monoxide, 51%) was evolved. The gas was passed through an ice-cooled condenser, a Dry Ice-acetone trap, and into a gas receiver.

Distillation at atmospheric pressure yielded: ethanal (185 g.); a small intermediate fraction (3 g.; b.p. 80–95°) containing biacetyl (diphenylhydrazone, m.p. 243°); 1-octene (115 g.). After these substances had been removed, the residue (18 g.) was distilled at reduced pressure. A fraction (7.5 g.;  $n_D^{20}$  1.4267; b.p. 117°/37 mm.) was shown to 2-decanone by conversion to its semicarbazone (m.p. 124–125°) (5).

The distillation residue (10 g.) was a high-boiling material (molecular weight, 301).

*The peroxide-induced addition of butanal to 1-hexene.* A solution of acetyl peroxide (3.0 g.) in butanal (15.0 g.) was added dropwise over a period of 3 hours to a mixture of butanal (192.6 g.; 2.68 moles) and 1-hexene (60 g.; 0.71 mole) held at its boiling point. After the peroxide addition was completed, the reaction mixture was held under reflux for an additional 24 hours. During this period, it assumed a light-yellow color.

After residual butanal and 1-hexene had been distilled at atmospheric pressure, the reaction products were distilled at reduced pressure, and the following fractions were collected. Fraction I: 4.5 g., b.p. 60–92°/18 mm.,  $n_D^{20}$  1.4214. Fraction II: 15.4 g., b.p. 92–96.5°/18 mm.,  $n_D^{20}$  1.4253. Fraction III: 27.6 g., b.p. 96.5°/18 mm.,  $n_D^{20}$  1.4300. Residue: 15 g. Fractions II and III are presumably 4-decanone. However, the index of refraction of this material is somewhat higher than that of pure 4-decanone ( $n_D^{20}$  1.4240) prepared by conven-

tional methods. It was suspected that the impurity in the 4-decanone was *n*-butyl butyrate, formed by reaction of acetyl peroxide with butanal (6). A determination of the saponification equivalent of Fraction III indicated about ten per cent of the ester. For this reason, Fraction III was converted to 5-propyl-5-hexylhydantoin. After two crystallizations from ethanol (60%) it melted at 117–119°.

*Anal.* Calc'd for  $C_{12}H_{22}N_2O_2$ : N, 12.38. Found: N, 12.03.

This hydantoin derivative did not depress the melting point of the hydantoin prepared from an authentic sample of 4-decanone.

*The peroxide-induced addition of butanal to styrene.* A solution of acetyl peroxide (3.0 g.) in butanal (7 g.) was added dropwise (over a period of seven hours) to a mixture of styrene (17.0 g.; 0.16 mole) and butanal (110 g.; 1.53 mole) at 90°. The reaction mixture was held at that temperature for one hour after the last addition of the peroxide.

The reaction mixture was distilled at reduced pressure through a 10-inch Vigreux column. After unchanged butanal (b.p. 38°/80 mm.) had distilled, the residue became viscous. A small fraction (3.0 g.; b.p. 30–32°/0.5 mm.;  $n_D^{20}$  1.4160) distilled. The still-pot residue (14 g.) was a viscous polymeric product.

*The peroxide-induced reaction of 2-butanal with 1-octene.* A mixture of 1-octene (49 g.; 0.44 mole) and butanal (123 g.; 1.76 mole) was placed in a 250-ml. flask fitted through ground-glass joints with a dropping-funnel and a condenser. The apparatus was swept with dry carbon dioxide.

A solution of acetyl peroxide (4.5 g.) in butanal (23.4 g.) was slowly added over a period of 10 hours while the reaction mixture was held at 65–70°. After the peroxide solution had been added, heating was continued for 10 hours. A small amount of gas (250 ml.) was evolved during this time. It was shown to be almost pure methane (mol. wt., 16.5). A qualitative test for carbon monoxide was negative.

Unchanged butanal and 1-octene were removed from the reaction mixture by distillation (b.p. 40–70°/80 mm.). The residue (17 g.) was then distilled through a 10-inch Vigreux column. Only a small fraction (4.0 g.; b.p. 61–90°/0.1 mm.) distilled. The residue was a highly viscous syrup with an apparent molecular weight of 755.

*Photochemical addition of heptanal to 1-octene.* A mixture of 1-octene (29.0 g.; 0.26 mole) and heptanal (104.2 g.; 0.914 mole) was internally irradiated by a mercury vapor-neon fluorescent tube. The apparatus was thoroughly swept with nitrogen, and the light was turned on. The heat from the lamp maintained the reaction temperature at 70°. Illumination was continued for 23 hours. During that time 800 cc. of gas was evolved. The gas was passed through a trap immersed in a bath cooled by a mixture of Dry-Ice and acetone, and collected in gas reservoir.

The reaction mixture was distilled at atmospheric pressure and the following fractions were collected: Fraction I: hexane, 3 g.; Fraction II: 1-octene, 20 g.; Fraction III: heptanal, 90 g. The residue was distilled at reduced pressure, and the fraction (15 g.) boiling at 92°/2 mm. was collected. This fraction was 7-pentadecanone. It solidified upon standing. After crystallization from methanol, it melted at 31–32°. A residue (5 g.) remained in the distilling flask.

*The photochemical addition of butanal to 1-octene.* A mixture of butanal (109.5 g.; 1.52 mole) and 1-octene (33.0 g.; 0.295 mole) was illuminated internally by a mercury vapor-neon fluorescent tube. The reaction mixture was held at about 70° and illuminated for 26 hours. During this period, 2050 ml. of gas was collected. The gas was a mixture of 49% propane and 51% carbon monoxide.

The reaction mixture was distilled through a 50-plate Podbielniak column. The unchanged butanal (100 g.) and 1-octene (21 g.) were thus separated from the reaction product. The residue was distilled at reduced pressure through a 10-inch Vigreux column and the fraction boiling at 65°/0.2 mm. was collected. This material ( $n_D^{20}$  1.4315) is 4-dodecanone. A residue (4 g.) remained in the distilling flask.

*The photochemical addition of heptanal to cyclohexene.* A mixture of heptanal (112.5 g.; 0.98 mole) and cyclohexene (22.0 g.; 0.27 mole) was irradiated internally by a mercury vapor-

neon fluorescent tube for 72 hours. During this time, 1650 ml. of gas was evolved. The gas consisted of 95% carbon monoxide.

Distillation of the reaction mixture yielded unchanged cyclohexene (15 g.) and heptanal (105 g.). A product, presumably 1-cyclohexyl-1-heptanone (10 g.; b.p. 73–80°/0.05 mm.;  $n_D^{20}$  1.4486) was obtained.

#### SUMMARY

1. Ketones are formed by the addition of aldehydes to 1-alkenes. The reaction may be initiated photochemically or by acyl peroxides.

2. The following ketones have been prepared by the method indicated: 2-decanone, 4-decanone, 4-dodecanone, 7-pentadecanone, and 1-cyclohexyl-1-heptanone.

3. Polymers were obtained when mixtures of butanal and styrene, or 2-butenal and 1-octene were irradiated or treated with small quantities of acyl peroxides.

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#### REFERENCES

- (1) (a) KHARASCH, JENSEN, AND URRY, *J. Am. Chem. Soc.*, **69**, 1100 (1947); KHARASCH, REINMUTH, AND URRY, *J. Am. Chem. Soc.*, **69**, 1105 (1947). (b) KHARASCH, SKELL, AND FISCHER, *J. Am. Chem. Soc.*, **70**, 1055 (1948). (c) KHARASCH, KUDERNA, AND URRY, *J. Org. Chem.*, **13**, 895 (1948).
- (2) KAMM AND MARVEL, *Organic Syntheses, Coll. Vol. I*, 2nd ed., p. 28 (1941).
- (3) KARRER, *Helv. Chim. Acta*, **13**, 1300 (1930).
- (4) HENZE AND SPEER, *J. Am. Chem. Soc.*, **64**, 522 (1942).
- (5) ST. PFAU, *Helv. Chim. Acta*, **15**, 1270 (1932).
- (6) KHARASCH, GRAHAM, AND URRY, Unpubl. work.