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# REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XXXIII. PHOTOCHEMICAL AND PEROXIDE-INDUCED ADDITION OF CYCLOHEXANONE TO 1-OCTENE[1]

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*Received April 4, 1953*

The vapor-phase photolysis of alicyclic ketones has been studied by many investigators (1). Carbon monoxide as well as mixtures of cyclic hydrocarbons and olefins have been isolated and identified as the main reaction products. For cyclohexanone, it is claimed that vapor-phase illumination (mercury arc) gives carbon monoxide (50%), ethylene (40%), propylene (4%), and cyclopentane (46%) at room temperature, but at higher temperatures (181–300°) it gives cyclopentane (74%), pentene-1 (24%), ethylene (2%), propylene, carbon monoxide, some cyclohexenyl cyclohexanone, water, and some polymer (2). It has been suggested that the primary process in these reactions is formation of a diradical by cleavage of the ring. This diradical may then (a) reform the original

$$\overline{\lfloor (CH_2)_n C}{=}O + h\nu \rightarrow \cdot(CH_2)_nC({=}O)\cdot$$

ketone, (b) react with another molecule of the ketone, or (c) undergo further cleavage to carbon monoxide and a pentamethylene diradical, which in turn gives cyclopentane or isomerizes to the olefin (pentene-1) (3).

The liquid-phase photolysis of cyclic ketones has not been carefully investigated. It is claimed that prolonged exposure (6–18 months) to sunlight in the presence of water, and in the presence or absence of oxygen, gives acids and unsaturated aldehydes. The structures of the latter compounds have not, however, been carefully established (4).

Irradiation of cyclohexanone with ultraviolet light for a period of 24 hours gave little reaction product. However, similar irradiation of a mixture of cyclohexanone and 1-octene (the latter present in large excess) gave a large quantity of the following products (Table I): (a) 5-hexenal; (b) a mixture of *cis*- and *trans*-2-octene; (c) 2-*n*-octylcyclohexanone (the 1:1 adduct); (d) a "dimer" of octene; (e) high-boiling adducts containing two or more molecules of octene to one molecule of cyclohexanone; (f) traces of volatile compounds. It has been estimated that the 1:1 adduct, the 2:1 adduct, and the higher polymerization adducts are formed in the approximate proportions 1:1.5:4. It is also noteworthy that little if any carbon monoxide is formed in this reaction.

Products similar to those described above were obtained when a mixture of cyclohexanone and 1-octene was heated in the presence of acetyl peroxide (5).

[1] The addition of simple aliphatic ketones to olefins will be reported in a future publication.

TABLE I

ADDITION OF CYCLOHEXANONE TO 1-OCTENE IN THE PRESENCE OF ULTRAVIOLET LIGHT

| EXPERIMENT NUMBER | A | B | C |
|---|---|---|---|
| Cyclohexanone-1-Octene ratio (moles) | 1:8 | 1:8 | 1:6 |
| Reaction period (hrs.) | 73 | 55 | 48 |
| MAJOR PRODUCTS | MOLES OF PRODUCTS FORMED, PER MOLE OF CYCLOHEXANONE CONSUMED IN THE REACTION | | |
| 5-Hexenal | 0.14 | 0.16 | 0.32 |
| 2-Octene | .20–0.26 | .20 | .32 |
| Octene dimer | .09 | .09 | .08 |
| $C_{12}H_{22}O_2$ (?) | .03 | .03 | — |
| 2-Octylcyclohexanone | .20 | .22–0.26 | .20–0.28 |
| 2:1 Adduct | .13–0.18 | .20–0.25 | .04 |
| 3:1 Adduct | .10 | .07–0.11 | — |
| High polymers* | .16 | .14 | .20 |

* Average molecular weight 800.

## DISCUSSION

The following schematic representation accounts for the products formed when a mixture of cyclohexanone and 1-octene is illuminated with ultraviolet light, or heated in the presence of an acyl peroxide.

*Initiating steps*

1.[2] $$\overline{\mathrm{OC(CH_2)_5}} + \mathrm{C_6H_{13}CH{=}CH_2} \xrightarrow[\text{(u.v.)}]{h\nu} \mathrm{O}\underset{\bullet}{\mathrm{C}}\overline{\mathrm{CH(CH_2)_4}}\ (\mathbf{A}) + \mathrm{C_6H_{13}}\underset{\bullet}{\mathrm{C}}\mathrm{HCH_3}\ (\mathbf{B})$$

2. **A** may also be produced by treating cyclohexanone with an acyl peroxide (6).

*Formation of 1:1 adduct of cyclohexanone with 1-octene, and polymeric products.*

3. $$\mathbf{A} + \mathrm{C_6H_{13}CH{=}CH_2} \longrightarrow \mathrm{C_6H_{13}}\underset{\bullet}{\mathrm{C}}\mathrm{HCH_2}\overline{\mathrm{CH{-}CO(CH_2)_4}}\ (\mathbf{C})$$ [3]

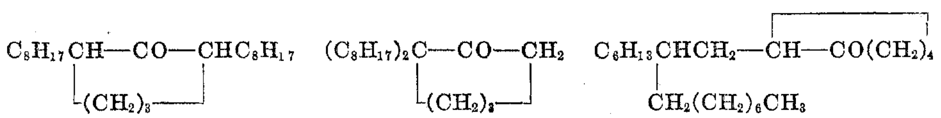
4. $$\mathbf{C} + \mathrm{O{=}}\overline{\mathrm{CCH_2(CH_2)_4}} \longrightarrow \mathrm{C_6H_{13}CH_2CH_2}\overline{\mathrm{CHCO(CH_2)_4}}\ (\mathbf{D}) + \mathrm{O{=}}\overline{\mathrm{C{-}}\underset{\bullet}{\mathrm{C}}\mathrm{H(CH_2)_4}}$$

The structure of the adduct of one molecule of cyclohexanone and two molecules of 1-octene was not established since it was somewhat outside the scope of

[2] Note that none of the products formed in the photochemical vapor-phase breakdown of cyclohexanone (carbon monoxide or cyclopentane) are formed in this reaction. The formation of the reaction products when cyclohexanone and 1-octene are illuminated is, therefore, best explained as an induced reaction as indicated in equation 1.

[3] Some of the free radicals (**C**) could disproportionate to give a mixture of a saturated compound (**D**) and unsaturated compounds. The non-isolation of the unsaturated compound does not preclude the presence of some of the compound in the reaction mixture. The corresponding unsaturated compound was isolated when a mixture of cyclohexanone and 2-methyl-2-butene was irradiated with ultraviolet light (unpublished work, Kharasch and Dobry).

the present investigation. It may be either **E**, **F**, **G**, or a mixture of these compounds. The presence of unsaturated derivatives of **E**, **F**, and **G** is also not precluded.



(E) (F) (G)

Similarly, it was not deemed desirable at this time to undertake determination of the structure of the so-called "octene dimer". This "dimer" may have arisen by union of two free radicals of the type **B**, or by dimerization of the free radical **H**, formed from **B** and 1-octene. The three possible "dimers" derived from **H**

$$\mathbf{B} + C_5H_{11}CH_2CH{=}CH_2 \rightarrow C_8H_{18} + \left[\begin{array}{c} C_5H_{11}\dot{C}HCH{=}CH_2 \\ \updownarrow \\ C_5H_{11}CH{=}CHCH_2\cdot \end{array}\right] \quad (\mathbf{H})$$

have been previously identified (7). The free radical **H**, by abstracting a hydrogen atom from cyclohexanone (or other hydrogen donors present in the reaction mixture), may form 1-octene and 2-octene. This postulated method of forming 2-octene is in some respects preferable to the one which assumes disproportionation of the free radicals **B** into octane, 1-octene, and 2-octene.

*Formation of 5-hexenal.* The formation of 5-hexenal has not been observed in the vapor-phase ultraviolet irradiation of cyclohexanone. On the other hand, it is claimed that prolonged exposure of a mixture of cyclohexanone and water to sunlight gives caproic acid and presumably 5-hexenal (4). The identity of the latter compound had, however, not been established. The formation of 5-hexenal in the liquid-phase irradiation of cyclohexanone and its non-formation in the vapor-phase irradiation may be explained by assuming that in the vapor-phase the diradical (produced as indicated below) breaks down to give carbon monoxide and cyclopentane. At lower temperatures the diradical might rearrange to give

$$O{=}\overline{C(CH_2)_5} + \xrightarrow[\text{(u.v.)}]{h\nu} \left[O{=}\overline{C(CH_2)_5}\right]^* \rightarrow \cdot CH_2(CH_2)_4C({=}O)\cdot$$

5-hexenal. It is of interest to speculate whether the 5-hexenal might not originate from the free radical **A**. In this connection, it is noteworthy that no 5-hexenal was isolated in the reaction of cyclohexanone and 1-octene when the reaction was initiated with acyl peroxide. However, a mixture of cycelopentanone and 1-octene gave allylacetaldehyde (5) both when it was irradiated with ultraviolet light and when it was treated with acetyl peroxide. In both instances, the other reaction products were also similar. Therefore, at least in the case of cyclopentanone, there is some evidence that in solution the rupture of the carbon-to-carbon bond takes place through the intermediate formation of the free radical $O{=}\overline{\dot{C}CH(CH_2)_3}$.

## EXPERIMENTAL

*Reagents. Cyclohexanone* (Paragon) was purified through the bisulfite addition compound and then distilled through a 100-plate Podbielniak column, the middle fraction being used (b.p. 155°; $n_D^{20}$ 1.4505).

*1-Octene* (Connecticut Hard Rubber Company) was distilled through a 100-plate column at atmospheric pressure (b.p. 121°; $n_D^{20}$ 1.4090).

*n-Hexanal* was prepared according to the directions of Bachman (8).

*Trans-2-octene* was obtained from a mixture of isomeric octenes (Connecticut Hard Rubber Company) by fractionation through a 100-plate column (b.p. 124–124.5°; $n_D^{20}$ 1.4132).

*1-Bromoöctane* (Halogen Chemicals Inc.) was used without further purification ($n_D^{20}$ 1.4519).

*Cyclohexene oxide* was prepared by the oxidation of cyclohexene with peroxybenzoic acid (9).

*Di-n-octyl magnesium* was prepared by adding a large quantity of dioxane to the stirred ethereal solution of *n*-octylmagnesium bromide (made from 1-bromoöctane, 87 g., and magnesium, 12.2 g., in absolute ether, 300 ml.). The whole was centrifuged and the clear, nearly colorless solution decanted from the magnesium halide. The solution gave a negative test for bromine with silver nitrate.

*Aluminum tert-butoxide* was prepared in the manner described by Wayne and Adkins (10).

*Photochemical addition of cyclohexanone to 1-octene.* A mixture of cyclohexanone (39.2 g., 0.4 mole) and peroxide-free 1-octene (358.4 g., 3.2 moles) was placed in an irradiation tube fitted with a long quartz mercury resonance lamp (11). The air in the apparatus was displaced by nitrogen, and the reaction mixture was internally illuminated at a temperature of about 40° for periods ranging from 48–73 hours. No gas (or at the utmost a minute amount) was evolved during the first 48 hours.

The reaction mixture was distilled through a 100-plate Podbielniak column at atmospheric pressure and the following fractions were collected: a very small quantity, insufficient for identification, of volatile materials boiling at 25–45°; Fraction I, 5-hexenal (5–6 g., b.p. 118.0–118.5°, $n_D^{20}$ 1.4109); Fraction II, b.p. 121°, $n_D^{20}$ 1.4089, 1-octene (280–290 g.); Fraction III, a mixture of *cis*- and *trans*-2-octene (8–10 g., b.p. 125°, $n_D^{20}$ 1.4140).

The unreacted cyclohexanone was removed at reduced pressure (b.p. 30° at 0.5 mm.) and 5–10 g. was recovered, depending upon the length of the irradiation period. The residue (95–98 g.), a mobile, light amber-colored oil, was distilled at reduced pressure through a short-path Claisen distillation apparatus, and the following fractions were collected:[4] Fraction IV, 4–8 g., b.p. 65–70°/0.05 mm., $n_D^{20}$ 1.439–1.440, $d_4^{20}$ 0.77; Fraction V, 1–2 g., b.p. 70–75°/0.05 mm., $n_D^{20}$ 1.443–1.445; Fraction VI, 14–16 g., b.p. 75–80°/0.05 mm., $n_D^{20}$ 1.4580, $d_4^{20}$ 0.88; Fraction VII, 8–10 g., b.p. 110–120°/0.05 mm., $n_D^{20}$ 1.4665. The viscous syrup which remained was molecularly distilled in a Hickman apparatus over a period of several days to yield the following additional products: Fraction VIII(a), 10–12 g., the same as Fraction VII; Fraction VIII, 10–15 g., b.p. 130–140° (bath temperature), $n_D^{20}$ 1.4720. The non-distillable portion of the residue consisted of polymers of high molecular weight (35–45 g., $n_D^{20}$ 1.478–1.479, molecular weight, 700–800).

Fraction IV is believed to be a somewhat impure "dimer" (derived from radicals B or H) or a mixture of these "dimers" containing either a minute amount of cyclohexanone or of Fraction V.

*Anal.* Calc'd for $C_{16}H_{34}$: C, 84.9; H, 15.1; Mol. wt., 226; $M_R$, 76.1.

Found: C, 83.6; H, 14.2; Mol. wt., 225; $M_R$, 76.8.

The physical constants of Fraction IV are similar to those of dimeric fraction obtained by Kharasch and Jerome (12), when 1-octene was treated with acetyl peroxide. There is also a similarity in the physical constants of Fraction IV and the product obtained by

[4] In some instances it was necessary to repeatedly fractionate the samples in order to effect a satisfactory separation of the products.

Nametkin and Abakumovskaya (13) when 1-octene was treated with sulfuric acid. They report the following constants for the saturated dimer, containing 19% of the unsaturated dimer: b.p. 130–140°/15 mm.; $d_4^{20}$ 0.785; $n_D^{20}$ 1.44; $M_R$ (obs.) 75.97; $M_R$ (Calc'd) 76.09; mol. wt., 226.6.

Fraction V has the approximate composition $C_{12}H_{22-24}O_2$. It has not been further identified. It rapidly decolorizes a solution of bromine in carbon tetrachloride, and does not react with 2,4-dinitrophenylhydrazine.

*Anal.* Calc'd for $C_{12}H_{24}O_2$: C, 72.0; H, 12.0; Mol. wt., 200.

Found: C, 71.9; H, 11.6; Mol. wt., 210.

Fraction VI has been identified as 2-octylcyclohexanone; the separation of this compound from the products of Fractions IV and V has proven to be exceedingly difficult inasmuch as repeated careful fractionation at reduced pressure is necessary for the isolation of even moderately pure samples.

*Anal.* Calc'd for $C_{14}H_{26}O$: C, 80.0; H, 12.4; Mol. wt., 210; $M_R$ 64.7.

Found: C, 79.6; H, 12.8; Mol. wt., 210–224; $M_R$ 65.1.

The *2,4-dinitrophenylhydrazone* of 2-octylcyclohexanone melts at 112–113° and the *phenylsemicarbazone* melts at 114–114.5°.

*Anal.* Calc'd for $C_{20}H_{30}N_4O_4$: N, 14.4; Found: N, 14.6.

Calc'd for $C_{21}H_{33}N_3O$: N, 12.2; Found: N, 12.4.

The proof of structure of the 2-octylcyclohexanone here obtained is given in a later section.

Fraction VII is believed to be an adduct corresponding to two molecules of olefin and one of cyclohexanone.

*Anal.* Calc'd for $C_{22}H_{42}O$: C, 81.9; H, 13.0; Mol. wt., 322.

Found: C, 81.5; H, 13.1; Mol. wt., 325.

Crystalline derivatives of this compound could not be obtained with 2,4-dinitrophenylhydrazine, phenylsemicarbazide, or hydroxylamine sulfate[5] although there were indications that the compound reacted with 2,4-dinitrophenylhydrazine. The hydrazone gave a permanent carmine color when treated with alcoholic potassium hydroxide.

Fraction VIII appears to be an adduct of three molecules of the olefin and one of cyclohexanone.

*Anal.* Calc'd for $C_{30}H_{58}O$: C, 82.9; H, 13.3; Mol. wt., 434.

Found: C, 82.2; H, 13.3; Mol. wt., 439.

*Identification of Fraction I (5-hexenal).* The structure of 5-hexenal was established by the following reactions:

1. $CH_2{=}CH(CH_2)_3CHO \xrightarrow[Pt]{H_2} CH_3CH_2CH_2CH_2CH_2CHO$
2. $CH_3(CH_2)_4CHO + H_2NNHC_6H_3(NO_2)_2 \rightarrow CH_3(CH_2)_4CH{=}NNHC_6H_3(NO_2)_2$
3. $CH_2{=}CH(CH_2)_3CHO \xrightarrow[H_2O]{O_3} HCHO + HO_2C(CH_2)_3CHO$
4. $HO_2C(CH_2)_3CHO + H_2NNHC_6H_3(NO_2)_2 \rightarrow HO_2C(CH_2)_3CH{=}NNHC_6H_3(NO_2)_2$

Fraction I (0.8 g.) dissolved in absolute ethanol was hydrogenated in the presence of Adams' catalyst. The solvent was carefully removed by distillation and the residual oil was fractionated (b.p. 127°; $n_D^{20}$ 1.4270). The 2,4-dinitrophenylhydrazone of the compound thus obtained melted at 103°. The melting point of this material was not depressed by admixture with 2,4-dinitrophenylhydrazone of an authentic sample of *n*-hexanal.

The position of the double bond in the 5-hexenal obtained in this study was established by ozonolysis. Fraction I (2.45 g.) was dissolved in 200 cc. of absolute ethanol and cooled to −50°, and a stream of ozone (5% $O_3$) was passed through the mixture for 50 minutes. The volatile products were collected in a large trap containing 50 cc. of distilled water. After completion of the ozonolysis the water solution was treated with an alcoholic solution of methone. The crystalline precipitate which separated was collected. The material melted

[5] Failure to obtain crystalline derivatives of this and other polyalkyl cyclohexanones obtained in this study is not surprising in view of previous observations recorded in the literature [Haller, *Compt. rend.*, **156**, 1199 (1913)].

at 187° and did not depress the melting point of an authentic sample of the methone derivative of formaldehyde (lit. m.p. 187°).

The ethanol was removed from the ozonized sample at reduced pressure and the residue was worked up in the usual way. Upon treating the solution with a solution of the 2,4-dinitrophenylhydrazine reagent, a yellow solid separated which melted at 167°. The 2,4-dinitrophenylhydrazone of glutaric dialdehyde is reported to melt at 169–172°.

A few drops of Fraction I were added to an alcoholic solution of 2,4-dinitrophenylhydrazine and the crystalline precipitate which separated was twice recrystallized from 95% ethanol. The compound melted at 93–94° and is presumably the 2,4-dinitrophenylhydrazone of 5-hexenal.

*Anal.* Calc'd for $C_{12}H_{14}N_4O$: N, 20.1. Found: N, 20.0.

*Identification of Fraction III (cis- and trans-2-octene).*

1. $n\text{-}C_5H_{11}CH{=}CHCH_3 \xrightarrow{O_3} n\text{-}C_5H_{11}CHO + CH_3CHO$
2. $n\text{-}C_5H_{11}CHO + H_2NNHC_6H_3(NO_2)_2 \rightarrow n\text{-}C_5H_{11}CH{=}NNHC_6H_3(NO_2)_2$
3. $CH_3CHO + C_8H_{12}O_2 \rightarrow CH_3CH(C_8H_{11}O_2)_2$
   (methone) (acetaldimethone)

Fraction III (2 g.) was dissolved in carbon tetrachloride and cooled to 0°, and ozone was passed through the mixture until no further absorption took place. The volatile products were collected in a trap containing about 15 ml. of distilled water. The water solution was added to an alcoholic solution of methone, and the resulting mixture was warmed briefly over a steam cone. Upon cooling there was deposited from the solution a crystalline precipitate, the melting point of which was 139°. This material was identified as acetaldimethone since it did not depress the melting point of an authentic sample prepared from reagent grade acetaldehyde and methone.

The solvent was removed from the ozonide at room temperature, and the latter was decomposed by warming with water on a steam-bath for three hours. The layers were separated, and the water layer discarded. The oil layer was added to an alcoholic solution of 2,4-dinitrophenylhydrazine and warmed for 5–10 minutes. Upon cooling, a precipitate separated. It was collected and twice recrystallized from 95% ethanol. The substance melted at 102°, and did not depress the melting point of an authentic sample of 2,4-dinitrophenylhydrazone of *n*-hexanal. Furthermore, a pure sample of *trans*-2-octene was ozonized in the manner described above, and the 2,4-dinitrophenylhydrazone obtained from the oil layer (following decomposition of the ozonide) was found to be identical in all respects to the two products previously obtained.

The presence of a mixture of *cis*- and *trans*- forms of octene-2 in Fraction III (b.p. 125°; $n_D^{20}$ 1.4140) was surmised from melting point data obtained by freezing the sample and plotting temperature of the melt *versus* time. The indices of refraction at 20° of pure *cis*- and *trans*-2-octene are 1.4150 and 1.4132, respectively.

*Identification of the cyclohexanone-1-octene addition product (2-octylcyclohexanone).* 2-Octylcyclohexanol was prepared from cyclohexene oxide (11 g., 0.11 mole) and an excess of di-*n*-octyl magnesium according to the method of Bartlett (14). There was obtained 6 g. of the alcohol (26%) (b.p. 81–82°/0.03 mm., $n_D^{20}$ 1.4583). The oxidation of the alcohol to 2-octylcyclohexanone (73%) was by the method of Oppenauer (15), using aluminum *tert*-butoxide. The synthetic sample (b.p. 78–79°/0.01 mm.; $n_D^{20}$ 1.4579) when treated with 2,4-dinitrophenylhydrazone gave a compound which melted at 112–113°. This material did not depress the melting point of the 2,4-dinitrophenylhydrazone of the 2-octylcyclohexanone obtained by the interaction of 1-octene and cyclohexanone. Similarly, the synthetic sample when treated with phenylsemicarbazide gave a product which melted at 114–114.5°. This product did not depress the melting point of the phenylsemicarbazone derived from the product of addition of cyclohexanone to 1-octene.

*Hydrogenation of the cyclohexanone-1-octene addition product (2-octylcyclohexanone).* Hydrogenation of the 1:1 adduct to form the corresponding alcohol was undertaken as a further step in establishing the structure of the reaction product.

Fraction VI (0.77 g.), dissolved in glacial acetic acid, was hydrogenated in the presence of Adams' catalyst over a period of several hours. The reaction was carried out at room temperature, and under a slight positive pressure of hydrogen. By measuring the hydrogen uptake with time and comparing the data with that obtained for a blank run containing catalyst alone it was computed that the compound contained one carbonyl group and no double bonds.

*Attempted photochemical addition of cyclohexanone to 1-octene in the presence of visible light.* A mixture of cyclohexanone (25 g., 0.25 mole) and 1-octene (114 g., 1.0 mole) was illuminated internally with a mercury vapor-neon fluorescent tube for a period of 48 hours. Distillation of the reaction mixture through a 100-plate Podbielniak column at atmospheric pressure yielded only unchanged reactants, and no high-boiling residue was found.

*Behavior of 1-octene in the presence of ultraviolet light.* 1-Octene (348 g.) was placed in the usual irradiation tube fitted with a quartz mercury resonance lamp, and the irradiation was carried out in a manner exactly analogous to that employed in the photochemical addition of cyclohexanone to the olefin. The air in the apparatus was displaced by nitrogen, and the liquid was internally illuminated at 40° for 72 hours. At the conclusion of this period it was carefully fractionated through the Podbielniak column, and unchanged 1-octene was the only compound which was found.


## SUMMARY

1. Illumination of a mixture of 1-octene and cyclohexanone with ultraviolet light gave the following products: (a) 5-hexenal; (b) a mixture of *cis-* and *trans-*2-octene; (c) 2-*n*-octylcyclohexanone (the 1:1 adduct); (d) a "dimer" of octene; (e) high-boiling adducts containing two or more molecules of octene to one mole cule of cyclohexanone.

2. It was noted that cyclopentanone, dissolved in 1-octene, gives allylacetaldehyde when illuminated with ultraviolet light or when treated with acetyl peroxide. The other reaction products were similar to those obtained with cyclohexanone.

3. A mechanism is suggested that accounts satisactorily for the products formed in 1.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