*Anal.* Calcd. for $C_{10}H_{16}$: C, 88.2; H, 11.8. Found: C, 88.3; H, 12.0.

*cis*-**8-Methylhydrindane (XXV).**—The foregoing product (1 g.) was hydrogenated in 20 ml. of ether in the presence of 50 mg. of palladium–charcoal (10%) at ordinary temperature and pressure. The product boiled at 151° (690 mm.) and had $n^{20}\mathrm{D}$ 1.4702.

*cis*-**1-Methylcyclopentane-1,2-diacetic Acid (XVII).**—To a solution of 2 g. of sodium metaperiodate in 10 ml. of water, 40 mg. of ruthenium dioxide and 0.8 g. of XIX, dissolved in 20 ml. of acetone, were added with stirring.[16] The yellow solution turned black. A second portion of 7.5 g. of solid sodium metaperiodate was added, whereupon the temperature rose to 40°. After one hour, the solution became yellow again. Isopropyl alcohol was added, the inorganic solid filtered and washed with acetone, and the filtrate diluted with 50 ml. of water. Thorough extraction with ether, followed by transfer into 10% sodium carbonate solution, acidification with 10% hydrochloric acid and renewed extraction with ether gave a product which was recrystallized repeatedly from aqueous acetone (1:1); m.p. 197°, yield 0.3 g. (10%).

*Anal.* Calcd. for $C_{10}H_{16}O_4$: C, 60.0; H, 8.0. Found: C, 60.1; H, 8.0.

*cis*-**8-Formyl-5,6-dimethyl-4,7,8,9-tetrahydroindane (XVI).**—A mixture of 10 g. of 1-formylcyclopentene, 30 g. of 2,3-dimethylbutadiene and 1 g. of hydroquinone was heated at 200° for 24 hours. The adduct boiled at 80° (0.7 mm.), yield 12 g. (60%).

*Anal.* Calcd. for $C_{12}H_{18}O$: C, 80.9; H, 10.1. Found: C, 80.8; H, 10.2.

**The 2,4-dinitrophenylhydrazone** was recrystallized from methanol; m.p. 154°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 365 mμ (4.23). *Anal.* Calcd. for $C_{18}H_{22}N_4O_4$: C, 60.3; H, 6.2. Found: C, 60.2; H, 6.0.

*cis*-**5,6,8-Trimethyl-4,7,8,9-tetrahydroindane.**—A mixture of 3 g. of XVI, 8 ml. of hydrazine hydrate, 4.6 g. of potassium hydroxide and 30 ml. of propylene glycol was treated in the usual manner; the reaction mixture was poured into dilute hydrochloric acid and extracted with petroleum ether. The product boiled at 187° (690 mm.), yield 2.5 g. (90%), $n^{25}\mathrm{D}$ 1.4965.

*Anal.* Calcd. for $C_{12}H_{20}$: C, 87.8; H, 12.2. Found: C, 87.4; H, 12.0.

*cis*-**1-Methyl-1,2-diacetonylcyclopentane (XXI).**—A solution of 1 g. of the foregoing hydrocarbon in 10 ml. of acetone was added slowly to a well-stirred mixture of 9 g. of sodium metaperiodate and 40 mg. of ruthenium dioxide in 20 ml. of 50% aqueous acetone. After 30 minutes, a solution of 30 mg. of ruthenium dioxide and 1.5 g. of sodium metaperiodate in 40 ml. of 50% acetone was added and the stirring continued for 12 hours. Then isopropyl alcohol was added, the solution filtered, diluted with water and extracted thorougly with ether. The ether residue boiled at 140° (0.1 mm.), $\bar{\nu}_{\max}^{\mathrm{liq}}$ 1710 cm.$^{-1}$ (carbonyl).

*Anal.* Calcd. for $C_{12}H_{20}O_2$: C, 73.5; H, 10.2. Found: C, 73.2; H, 9.7.

**The bis-2,4-dinitrophenylhydrazone**, from nitromethane, had m.p. 205°.

**1-Vinylcyclohexene.**—For the synthesis of this compound, two methods were used: (a) 1-Ethynylcyclohexanol,[31] (b.p. 97° (14 mm.)) was dehydrated with phosphorus oxychloride in pyridine.[32] 1-Ethynylcyclohexene so obtained in 80% yield (b.p. 148°) was hydrogenated with the Lindlar catalyst[33] in pentane solution; yield 95%, b.p. 147°.

(b) A solution of 50 g. of ethynylcyclohexanol in 200 ml. of pyridine (dried over barium oxide) was hydrogenated with 1 mole of hydrogen in the presence of 0.5 g. of palladium–charcoal (10%). The crude 1-vinylcyclohexanol (45 g.), which contained some unchanged starting material and some 1-ethylcyclohexanol, was selectively dehydrated by means of anilinium *p*-toluenesulfonate[34] (5 g.) in 100 ml. of boiling toluene (azeotropic distillation, 6 hours). Thus, 27 g. (6%) of 1-vinylcyclohexene, b.p. 147°, was obtained.

**1,2-Cyclopentano-2**(or 1)-**formyl-1,2,3,5,6,7,8,9-octahydronaphthalene (XXIII or XXII)** was obtained from 17 g. of 1-formylcyclopentene, 23 g. of 1-vinylcyclohexene and 1 g. of hydroquinone by heating at 200° for 20 hours; b.p. 114° (1.2 mm.), yield 23 g. (80%), $n^{25}\mathrm{D}$ 1.5243 $\bar{\nu}_{\max}^{\mathrm{liq}}$ 1724 cm.$^{-1}$ (carbonyl).

*Anal.* Calcd. for $C_{14}H_{20}O$: C, 82.3; H, 9.8. Found: C, 82.1; H, 9.6.

**The 2,4-dinitrophenylhydrazone**, from ethanol, showed m.p. 175°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 365 mμ (4.29). *Anal.* Calcd. for $C_{20}H_{24}N_4O_4$: C, 62.5; H, 6.3. Found: C, 62.6; H, 6.6.

**1,2-Cyclopentano-2**(or 1)-**methyl-1,2,3,5,6,7,8,9-octahydronaphthalene.**—A mixture of 4 g. of the foregoing compound, 4 ml. of hydrazine hydrate, 6 g. of potassium hydroxide and 30 ml. of propylene glycol was treated as usual; b.p. 126–128° (14 mm.), yield 3 g. (89%), $n^{15}\mathrm{D}$ 1.5163, $\bar{\nu}_{\max}^{\mathrm{liq}}$ 3000 cm.$^{-1}$ (methyl).

*Anal.* Calcd. for $C_{14}H_{22}$: C, 88.4; H, 11.6. Found: C, 88.3; H, 11.7.

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[31] E. D. Bergmann, M. Sulzbacher and D. F. Herman, *J. Appl. Chem.*, **3**, 39 (1953).

[32] J. C. Hamlet, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.* 2652 (1951).

[33] H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

[34] Ch. Weizmann, U. S. Patent 2,381,148 (*C. A.*, **40**, 346 (1946)).

JERUSALEM, ISRAEL

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY]

# The Reactions of N,N'-Dicyclohexylcarbodiimide with Benzoyl Peroxide and *t*-Butyl Perbenzoate

BY DONALD B. DENNEY AND GERALD FEIG

RECEIVED JULY 25, 1958

N,N'-Dicyclohexylcarbodiimide reacts with benzoyl peroxide in isopropyl alcohol to give N-benzoyl-N,N'-dicyclohexylurea, acetone, benzene and carbon dioxide. The same reactants in carbon tetrachloride gave N-cyclohexylbenzamide, chlorobenzene, cyclohexyl isocyanate and carbon dioxide.

*t*-Butyl perbenzoate and N,N'-dicyclohexylcarbodiimide reacted in *n*-butyl alcohol to give N-cyclohexylbenzamide, *n*-butyraldehyde and *n*-butyl N-cyclohexylcarbamate. Mechanisms are suggested for the formation of these compounds.

The reactions of organic peroxides have been the subject of many investigations.[1] They have received continued interest because of their complex character and fundamental value. It is the purpose of this paper to report on the course of the reactions of benzoyl peroxide (I) and *t*-butyl perbenzoate (II) with N,N'-dicyclohexylcarbodiimide (III) in several solvents.

When benzoyl peroxide was allowed to react with N,N'-dicyclohexylcarbodiimide in refluxing chloroform, the 5.60 and 5.68 μ bands of the benzoyl peroxide and the 4.75 μ band of the N,N'-dicyclohexylcarbodiimide steadily diminished in intensity. New strong bands appeared at 4.45 and 6.08 μ.

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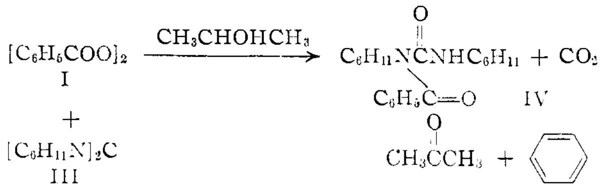
[1] (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957; (b) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954.

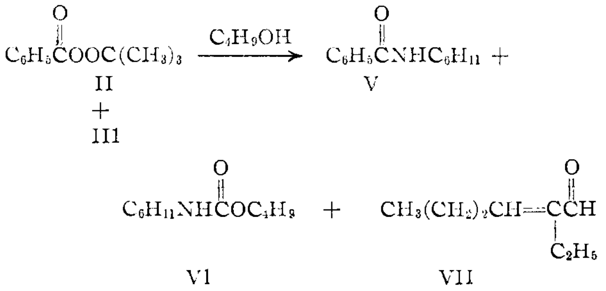
It was shown in other experiments that these bands were those of cyclohexyl isocyanate and N-cyclohexylbenzamide. The reaction mixture obtained after evaporation of the chloroform proved to be rather intractable and the only product isolated was impure N-cyclohexylbenzamide.

When the solvent was changed to methanol or isopropyl alcohol, the reaction took a different course and the major product obtained after removal of the solvent was N-benzoyl-N,N′-dicyclohexylurea, 92% yield. An aliquot of the isopropyl alcohol, which was distilled from the reaction mixture, was treated with 2,4-dinitrophenylhydrazine. The yellow precipitate which formed was shown to be the 2,4-dinitrophenylhydrazone of acetone. The yield, based on the assumption that one mole of acetone was formed for every mole of benzoyl peroxide used, was 52%. A control experiment showed that 2,4-dinitrophenylhydrazine did not react with isopropyl alcohol under these conditions. The ultraviolet absorption spectrum of the isopropyl alcohol distillate showed that benzene was present. The yield, calculated from the spectral data and assuming one mole of benzene produced for every mole of benzoyl peroxide used, was 60%. In another experiment nitrogen was passed through the reaction mixture and then through a saturated solution of calcium hydroxide. A precipitate of calcium carbonate formed thus indicating that carbon dioxide was a product of the reaction.



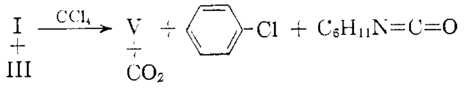
From the reaction of *t*-butyl perbenzoate with III in isopropyl alcohol, N-cyclohexylbenzamide (V) and acetone, as the 2,4-dinitrophenylhydrazone, were isolated. It seemed reasonable to suggest that the acetone arose by oxidation of the solvent or by decomposition of a *t*-butoxy radical. In order to distinguish between these two possibilities, the solvent was changed to *n*-butyl alcohol.

When II and III were allowed to react in *n*-butyl alcohol, V was isolated in 90% yield. The recovered *n*-butyl alcohol was treated with 2,4-dinitrophenylhydrazine. From this reaction there was isolated a red compound, which was shown to be the 2,4-dinitrophenylhydrazone of 2-ethyl-2-hexenal (VII). Presumably *n*-butyraldehyde was formed first and then condensed to give VII. From the reaction mixture there was also obtained a 44% yield of *n*-butyl N-cyclohexylcarbamate (VI). It was not possible to determine the fate of the *t*-butyl group of the starting perester; however, it probably was transformed into *t*-butyl alcohol.

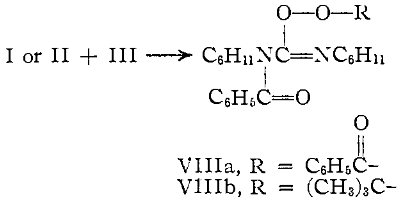


$$\underset{\text{II}}{C_6H_5\overset{O}{\overset{\|}{C}}OOC(CH_3)_3} + \underset{}{\text{III}} \xrightarrow{C_4H_9OH} \underset{\text{V}}{C_6H_5\overset{O}{\overset{\|}{C}}NHC_6H_{11}} + \underset{\text{VI}}{C_6H_{11}NH\overset{O}{\overset{\|}{C}}OC_4H_9} + \underset{\text{VII}}{CH_3(CH_2)_2CH{=}\underset{C_2H_5}{\underset{|}{C}}\overset{O}{\overset{\|}{C}}H}$$

The last reaction to be reported here was between benzoyl peroxide and N,N′-dicyclohexylcarbodiimide in carbon tetrachloride. After the reaction was completed, the solvent was removed by distillation and the solid residue was treated with water. The product isolated from this residue after purification was N-cyclohexylbenzamide. The infrared spectrum of the carbon tetrachloride distillate had a strong band at 4.40 $\mu$, which indicated that an isocyanate was present. Treatment of this solution with cyclohexylamine gave N,N′-dicyclohexylurea. This result in conjunction with the infrared spectrum indicates that cyclohexyl isocyanate was a product of the reaction. The carbon tetrachloride, which had been treated with cyclohexylamine, was fractionated to give a small amount of chlorobenzene. The formation of carbon dioxide during the reaction was proved as before.



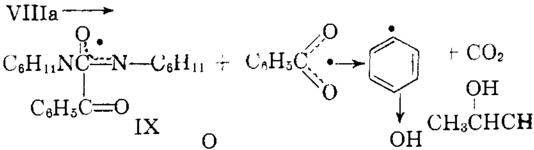
It is of interest to consider mechanisms for these reactions. It seems reasonable to suggest that the initial reaction of the peroxide and the carbodiimide is the same irrespective of the solvent. This reaction is formulated as



$$\text{I or II} + \text{III} \longrightarrow C_6H_{11}N\overset{O-O-R}{\overset{|}{\underset{\underset{C_6H_5C=O}{|}}{C}}}{=}NC_6H_{11}$$

$$\text{VIIIa, } R = C_6H_5\overset{O}{\overset{\|}{C}}- \qquad \text{VIIIb, } R = (CH_3)_3C-$$

VIII could be formed by a one-step process involving a four-center transition state.[2] Another possibility is a two-step reaction sequence in which there is initial addition of the nitrogen to the carbonyl carbon atom of the peroxide followed by expulsion of a peroxy anion, which then rapidly adds to give VIII. The formation of the products from VIII appears to depend on the nature of R and the solvent. For example a reasonable mechanism for the decomposition of VIIIa in alcohols involves cleavage of the oxygen-oxygen bond to give a benzoyloxy radical and IX. Under these conditions, the benzoyloxy radical rapidly loses carbon dioxide to give a phenyl radical,[3]



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[2] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 453–465.

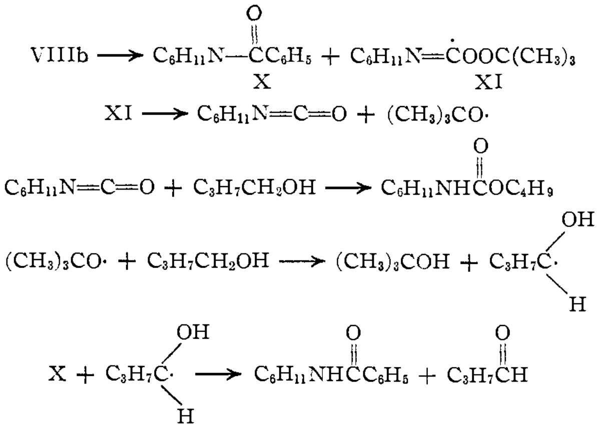
[3] D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 188 (1937).

which in turn abstracts a hydrogen atom from isopropyl alcohol to yield an α-hydroxyalkyl radical.[4] The α-hydroxyalkyl radical and IX react to give acetone and N-benzoyl-N,N′-dicyclohexylurea (IV).

The same reactants in carbon tetrachloride probably give IX in a similar fashion. Since there is no ready source of hydrogen to convert IX to IV it evidently cleaves to cyclohexyl isocyanate and the radical X. The infrared spectrum of the reaction mixture showed that the N–H bond was present which indicates that X can abstract a hydrogen from starting material, isocyanate, etc., to give N-cyclohexylbenzamide. The benzoyloxy radical reacts at least in part to give chlorobenzene and carbon dioxide.

$$\mathrm{IX} \longrightarrow C_6H_{11}N{=}C{=}O + C_6H_{11}N\cdots\overset{O}{\overset{\vdots|}{C}}C_6H_5$$

When II and III were allowed to react in alcohols VIIIb was most probably formed; VIIIb might have been expected to decompose to give IX and a *t*-butoxy radical. Evidently this was not the case since no IV was formed. A reasonable sequence of reactions is



$$\mathrm{VIIIb} \longrightarrow \underset{\mathrm{X}}{C_6H_{11}N{-}\overset{O}{\overset{\|}{C}}C_6H_5} + \underset{\mathrm{XI}}{C_6H_{11}N{=}\dot{C}OOC(CH_3)_3}$$

$$\mathrm{XI} \longrightarrow C_6H_{11}N{=}C{=}O + (CH_3)_3CO\cdot$$

$$C_6H_{11}N{=}C{=}O + C_3H_7CH_2OH \longrightarrow C_6H_{11}NH\overset{O}{\overset{\|}{C}}OC_4H_9$$

The decomposition of VIIIb probably gives X and XI rather than IX and a *t*-butoxy radical. It is possible that the decomposition of VIIIb is a concerted process which leads directly to X, a *t*-butoxy radical and cyclohexyl isocyanate. The *t*-butoxy radical can abstract an α-hydrogen from the alcohol to give *t*-butyl alcohol and an α-hydroxyalkyl radical.[4] The benzamido radical X would be expected to abstract a hydrogen from the α-hydroxyalkyl radical to yield the amide and aldehyde.

## Experimental

**Benzoyl Peroxide and N,N′-Dicyclohexylcarbodiimide in Chloroform.**—A solution of 2.42 g. (0.010 mole) of benzoyl peroxide and 2.06 g. (0.010 mole) of N,N′-dicyclohexylcarbodiimide in 50 ml. of chloroform was refluxed for 70 hr. Aliquots, 5 ml., were removed after 3, 8, 35, 58 and 70 hr. The aliquots were examined in the infrared and it was observed that the 5.60 and 5.68 μ bands of the benzoyl peroxide as well as the 4.75 μ band of the N,N′-dicyclohexylcarbodiimide diminished in intensity and had disappeared after 70 hr. At the same time new bands at 4.45 and 6.08 μ appeared. These have been assigned to cyclohexyl isocyanate and N-cyclohexylbenzamide. Evaporation of the chloroform afforded a rather intractable mixture from which a small amount of crude N-cyclohexylbenzamide was isolated. Further work was not carried out since the reaction in other solvents seemed more promising.

**Benzoyl Peroxide and N,N′-Dicyclohexylcarbodiimide in Methanol.**—A solution of 4.84 g. (0.020 mole) of benzoyl peroxide and 4.12 g. (0.020 mole) of N,N′-dicyclohexylcarbodiimide in 150 ml. of methanol was refluxed for 21 hr. The reaction mixture was added to 250 ml. of water, and the precipitate which formed was filtered and dried. The crude product, 5.1 g. (79%), was recrystallized from methanol–water to yield pure N-benzoyl-N,N′-dicyclohexylurea, m.p. 160–162° (lit.[5] 160–161°). The infrared spectrum of this material was commensurate with the assigned structure.

*Anal.* Calcd. for $C_{20}H_{28}N_2O_2$: N, 8.53. Found: N, 8.56.

**Benzoyl Peroxide and N,N′-Dicyclohexylcarbodiimide in Isopropyl Alcohol.**—A solution of 9.68 g. (0.040 mole) of benzoyl peroxide and 8.24 g. (0.040 mole) of N,N′-dicyclohexylcarbodiimide in 130 ml. of dry isopropyl alcohol was refluxed for 12 hr. The isopropyl alcohol was distilled and the solid residue was recrystallized from ethanol to yield 12.1 g. (92%) of N-benzoyl-N,N′-dicyclohexylurea, m.p. 164–165.5°. A mixed melting point with the analytical sample showed no depression. The infrared spectra of these two samples were identical.

A 10-ml. portion of the isopropyl alcohol distillate was allowed to react with 2,4-dinitrophenylhydrazine. A yellow precipitate formed, 0.40 g., m.p. 124–125°. A mixed melting point determination with an authentic sample of the 2,4-dinitrophenylhydrazone of acetone showed no depression. A 5-ml. sample of isopropyl alcohol gave no precipitate with 2,4-dinitrophenylhydrazine. From the weight of the 2,4-dinitrophenylhydrazone and the total volume of the distillate, 120 ml., it can be calculated that the yield of acetone was 52%.

The ultraviolet spectrum of the isopropyl alcohol distillate was identical to that of a known spectrum of benzene in isopropyl alcohol. A calculation of the concentration of the benzene in the distillate indicated that 60% of the theoretical amount was present. The infrared spectrum of the isopropyl alcohol distillate indicated that benzene was present.

In another experiment nitrogen was bubbled through the reaction mixture and then through a solution of calcium hydroxide. Calcium carbonate was formed thus indicating that carbon dioxide was evolved during the reaction.

**Benzoyl Peroxide and N,N′-Dicyclohexylcarbodiimide in Carbon Tetrachloride.**—A solution of 9.68 g. (0.040 mole) of benzoyl peroxide and 8.24 g. (0.040 mole) of N,N′-dicyclohexylcarbodiimide in 100 ml. of dry carbon tetrachloride was refluxed for 71 hr. The solvent was distilled and the solid residue was triturated with water. The water was decanted and the residue was washed with ether. The residue, 5.72 g. (70%) of N-cyclohexylbenzamide, was purified by crystallization from acetone–hexane to yield material, m.p. 147.5–149° (lit.[6] 148–149°). A mixed melting point determination with an authentic sample showed no depression. The infrared spectrum was identical to that of a known sample.

In another experiment the carbon tetrachloride distillate was treated with 3.4 ml. of cyclohexylamine. A precipitate formed which was filtered and crystallized from ethanol to afford 2.0 g. (22%) of N,N′-dicyclohexylurea, m.p. 230–232° (lit.[7] 229–230). The infrared spectrum of this material was in agreement with the assigned structure.

The carbon tetrachloride filtrate was extracted three times with dilute hydrochloric acid, washed with water and dried over magnesium sulfate. The carbon tetrachloride was removed by distillation through a 36″ spinning-band column. The residue was distilled in a conventional apparatus to yield a small fraction, b.p. 120–126°, $n^{25}D$ 1.5140. The infrared spectrum of this material was identical to that of a known sample of chlorobenzene.

In another experiment the evolution of carbon dioxide from the reaction mixture was proved as before.

***t*-Butyl Perbenzoate and N,N′-Dicyclohexylcarbodiimide in 1-Butanol.**—A solution of 7.76 g. (0.040 mole) of *t*-butyl perbenzoate and 8.24 g. (0.040 mole) of N,N′-dicyclohexyl-

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[4] W. H. Urry, F. W. Stacey, E. S. Huser and O. O. Juveland, THIS JOURNAL, 76, 450 (1954).

[5] F. Zetzsche and A. Fredrich, *Ber.*, 72B, 1735 (1939).

[6] H. W. Grimmel, A. Guenther and J. F. Morgan, THIS JOURNAL, 68, 539 (1946).

[7] A. Skita and H. Rolfes, *Ber.*, 53, 1248 (1920).

carbodiimide in 100 ml. of dry 1-butanol was refluxed 120 hr. The reaction mixture was distilled to dryness. A 5-ml. aliquot of the distillate was allowed to react with 2,4-dinitrophenylhydrazine. A reddish-orange precipitate formed which after recrystallization from ethanol had m.p. 123–123.5°. A 5-ml. sample of 1-butanol gave no precipitate with 2,4-dinitrophenylhydrazine. The 2,4-dinitrophenylhydrazone obtained above showed melting point depressions when mixed with authentic samples of the 2,4-dinitrophenylhydrazones of acetone and *n*-butyraldehyde. The m.p. 123–123.5° compares favorably with those reported for the 2,4-dinitrophenylhydrazone of 2-ethyl-2-hexenal,[8,9] m.p. 123° and m.p. 124–125°. The ultraviolet spectrum in ethanol was identical to that reported in the literature.[8]

The residue obtained from the distillation was triturated with hexane to yield 7.3 g. (90%) of crude N-cyclohexylbenzamide. The amide was purified by crystallization from acetone–hexane to yield pure material, m.p. 147–148.5°.

The hexane extracts were evaporated to give a residue which was sublimed at 49° (bath) and 0.01 mm. By this procedure there was isolated 3.51 g. (44%) of *n*-butyl N-cyclohexylcarbamate which was crystallized from pentane m.p. 51.5–54°.

*Anal.* Calcd. for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62. Found: C, 66.50; H, 10.63.

***t*-Butyl Perbenzoate and N,N'-Dicyclohexylcarbodiimide in Isopropyl Alcohol.**—A solution of 3.88 g. (0.020 mole) of *t*-butyl perbenzoate and 4.12 g. (0.020 mole) of N,N'-dicyclohexylcarbodiimide in 50 ml. of isopropyl alcohol was refluxed for 98 hr. The isopropyl alcohol was removed by distillation and the residue was recrystallized from ethanol to yield 3.28 g. (81%) of N-cyclohexylbenzamide, m.p. 147–150°, no depression with an authentic sample.

A 5-ml. portion of the distillate yielded a yellow 2,4-dinitrophenylhydrazone, m.p. 120–123°. A mixed melting point determination with the 2,4-dinitrophenylhydrazone of acetone showed no depression.

NEW BRUNSWICK, N. J.

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[8] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

[9] S. G. Powell and D. A. Ballard, THIS JOURNAL, **60**, 1914 (1938).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

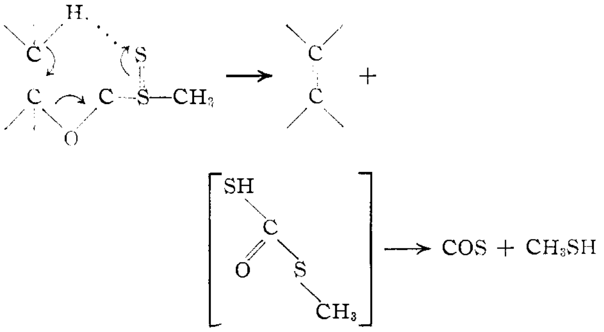
# Factors Influencing the Direction of Elimination in the Chugaev Reaction

BY ROBERT A. BENKESER AND JAMES J. HAZDRA

RECEIVED JULY 21, 1958

The xanthate esters of a series of 1-alkylcyclohexanols and alkylcyclohexylcarbinols were pyrolyzed (Chugaev reaction) and the resulting olefin mixtures analyzed by gas chromatography. In every instance isomers containing double bonds *exo* to the six-membered ring were disfavored. In two of the five eliminations studied, the system followed the Hofmann rather than the Saytzeff rule. In three cases, a primary or secondary hydrogen was removed, rather than the expected tertiary. It is concluded that the unifying feature underlying all of these reactions is the preferred formation of the more thermodynamically stable olefin. In this respect the Chugaev reaction closely resembles acetate pryolyses. In keeping with this observation (but contrary to published reports) it was noted that pyrolysis of 1-methylcyclohexylacetate produced a ratio of 1-methylcyclohexene/methylenecyclohexane of approximately 4. A very similar isomer distribution was noted when 1-methylcyclohexylcarbinol was dehydrated by the Chugaev procedure. Evidence is presented to indicate that steric factors are very likely of importance in controlling the direction of Chugaev elimination.

It is well known that acid-catalyzed dehydrations of alcohols frequently result in bond or group migrations.[1] This complication can be avoided if the alcohol is dehydrated *via* the Chugaev reaction,[2] which involves the thermal decomposition of its xanthate ester. Invariably this reaction proceeds by the preferential removal of hydrogen from an adjacent carbon atom, resulting in the formation of an unrearranged olefin.[3] The stereochemistry[4–6] of the Chugaev reaction has received much attention, and it is generally conceded that the preferred reaction path involves the elimination of a *cis*-hydrogen.[7] This observation, together with the demonstration of first-order kinetics,[8] lends credence to the belief the reaction proceeds by an intramolecular cyclic process.[9] However no systematic study has been made to determine how the nature of the hydrogen to be removed influences the course of the reaction. However, based upon rather numerous examples (but of widely different types of compounds), it now seems accepted that the preference for hydrogen removal in the Chugaev reaction[10] is 3° > 2° > 1°. Stated another way, the Saytzeff rule is normally followed in Chugaev eliminations. Curiously, the opposite sequence of hydrogen perference (*i.e.*, 1° > 2° > 3°) (Hofmann



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[1] E. E. Royals, "Advanced Organic Chemistry," Prentice–Hall Inc., New York, N. Y., 1954, p. 230.

[2] L. A. Chugaev, *Ber.*, **32**, 332 (1899), and subsequent papers.

[3] This fact seems well established despite a recent statement to the contrary (W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956)). A classic example of the utility of the Chugaev is the dehydration of pinacolyl alcohol to *t*-butylethylene (W. Fomin and N. Sochanski, *Ber.*, **46**, 244 (1913)). Acid dehydration of this compound leads to extensive rearrangement (F. C. Whitmore and H. S. Rothrock, THIS JOURNAL, **55**, 1106 (1933)).

[4] W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

[5] D. J. Cram, THIS JOURNAL, **71**, 3883 (1949).

[6] E. R. Alexander and A. Mudrak, *ibid.*, **72**, 1810, 3194 (1950).

[7] See F. G. Bordwell and P. S. Landis, *ibid.*, **80**, 2450 (1958), where an interesting example of a *trans* elimination is disclosed.

[8] G. L. O'Connor and H. R. Nace, *ibid.*, **74**, 5454 (1952); **75**, 2118 (1953).

[9] P. G. Stevens and J. H. Richmond, *ibid.*, **63**, 3132 (1942).

[10] J. A. Mills, *J. Chem. Soc.*, 260 (1953); see also "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 313.