isomeric compound (B) prepared above. Distinction was verified by infrared spectral differences (see Spectral Data) and mixed melting point depression.

**4,5-Dihydroxy-3,6-methylenehexahydrophthalic Acid Dilactone (IXB).**—The procedure of Alder and Stein[15] was followed. From 16 g. of the bromolactone acid (m.p. 157°) there was obtained 8 g. of the dilactone melting at 264–266°.

In compound A, the broad band at 5.9 to 6.0 $\mu$ is due to the 4-keto group while the sharper band at 5.8 $\mu$ is due to the carbonyl functions of the carboxylic acid groups. Compounds (B) and (C) did not display the first absorption band mentioned above, but they both absorbed strongly at 5.8 $\mu$. This is identical with the carbonyl absorption of the carboxylic acid functions in compound (A). Compound (C) could possibly be the corresponding anhydride, but since only one absorption band is present in the carbonyl region (typical aliphatic anhydrides display two carbonyl absorption bands at 5.4 and 5.6 $\mu$) we prefer the dicarboxylic acid structure consistent with the chemical analysis.

The spectra of compounds (B) and (C) were identical in the region of 2–8 $\mu$ and only slight differences existed in the region between 8–16 $\mu$. These latter differences could be ascribed to the respective *cis–trans* relationships of the carboxyl groups.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# The Low Reactivity of Cyclopropane Derivatives toward Free Radicals

BY GEORGE S. HAMMOND AND ROBERT W. TODD

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Cyclopropyl cyanide, methyl cyclopropyl ketone and phenylcyclopropane have been found to be unreactive toward a variety of free radicals despite the fact that their olefinic analogs undergo radical propagated polymerization with ease.

Various authors have pointed out similarities between olefins and cyclopropanes with respect to both their chemical and physical properties.[1] Since these correlations are based upon reactivity toward electrophilic and nucleophilic reagents and physical properties it was of interest to consider extension of the observations to include reactivity toward free radicals.

Other work has supplied interesting but fragmentary evidence on the subject. Roberts and Dirstine[2] have carried out the photochemical chlorination of cyclopropane. Although the rate of the reaction was somewhat slow the results show that at least one radical, the chlorine atom, attacks the hydrocarbon by hydrogen abstraction rather than by attack on carbon to effect ring opening. Similarly, Brown and Borkowski[3] observed that in the chlorination of methylcyclopropane only hydrogen abstraction from the methyl group occurred despite the presence of a tertiary structure at one of the ring atoms. Trotman-Dickenson and Steacie[4] have reported that the rate of hydrogen abstraction from cyclopropane by the methyl radical is slower than are the rates of the corresponding reactions with cycloalkanes of larger ring size.

Several examples of what appear to be ring opening by atoms or radicals have been reported. Probably the most conclusive of these is the photosensitized polymerization of cyclopropane.[5] Opening by halogen atoms is probably involved in the photochemical conversion of cyclopropane and bromine to 1,3-dibromopropane[6] and the thermal and photochemical synthesis of 1,3-diiodopropane from cyclopropane and iodine.[7]

## Experimental

**Cyclopropyl cyanide** was prepared in 55–66% yield by the method of Cloke and co-workers.[8] The product was distilled through a 40-plate glass center rod column and material boiling at 131.5–132.0°, $n^{20}{}_{\mathrm{D}}$ 1.4161, was used throughout the study.

**Cyclopropyl methyl ketone**, Matheson Co., was distilled through the center rod column and material boiling at 110–111° was taken for use.

**Phenylcyclopropane** was prepared by an adaptation of the method of Kishner.[9] A mixture of 118 g. of 5-phenyl-3-pyrazoline, prepared by the method of Lardelli and Jeger,[10] 30 g. of pulverized potassium hydroxide and 2.5 g. of platinized asbestos[11] was heated in a one-liter, three-necked flask equipped with a stirrer and a Claisen distillation head. The temperature was raised slowly by means of a Glas-Col mantle and the heat was shut off at the first sign of reaction. When the exothermic reaction ceased the temperature was again raised and the product was distilled. Both the distillate and the residue were steam distilled and the steam distillate was taken up in ether and dried first with sodium sulfate and then with sodium and redistilled. The product was collected at 60–63° (11 mm.) and was finally redistilled giving a colorless oil, wt. 11.5 g. (12%), b.p. 173.5° (740 mm.), $n^{20}{}_{\mathrm{D}}$ 1.5320.

**β-Methylstyrene** was prepared by the dehydration of phenylethylcarbinol with phosphoric acid.[12] The product was a colorless liquid, b.p. 53–56° (11 mm.).

**Decomposition of Benzoyl Peroxide in Cyclopropyl Cyanide.**—A solution of 0.529 g. of benzoyl peroxide in 10.58 g. of cyclopropyl cyanide was degassed by evacuation to 1 mm. at −78°, sealed and heated at 82° for 24 hours. The contents of the tube were distilled giving essentially quantitative recovery of the nitrile.

In another experiment a solution of 20.13 g. of peroxide and 11.10 g. of nitrile in 250 cc. of carbon tetrachloride was degassed, sealed and heated at 82° for 24 hours.

The product mixture was fractionally distilled through

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(1) For a general summary see R. A. Raphael, "Chemistry of Carbon Compounds," Vol. IIA, "Alicyclic Compounds," Elsevier Press, Houston, Texas, 1953, pp. 25–28.

(2) J. D. Roberts and P. H. Dirstine, THIS JOURNAL, **67**, 1281 (1945).

(3) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

(4) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

(5) H. E. Gunning and E. W. R. Steacie, *ibid.*, **17**, 351 (1949).

(6) M. S. Kharasch, M. Z. Fineman and F. R. Mayo, THIS JOURNAL, **61**, 2139 (1939).

(7) R. A. Ogg and W. J. Priest, *J. Chem. Phys.*, **7**, 736 (1939).

(8) J. B. Cloke, R. J. Anderson, J. Lachmann and G. E. Smith, THIS JOURNAL, **52**, 2791 (1921).

(9) N. Kishner, *J. Russ. Phys. Chem. Soc.*, **45**, 949 (1913); *C. A.*, **7**, 3965 (1913).

(10) G. Lardelli and O. Jeger, *Helv. Chim. Acta*, **32**, 1817 (1849).

(11) D. O. Shelis, *J. Phys. Chem.*, **33**, 1167 (1929).

(12) W. M. Dehn and K. E. Jackson, THIS JOURNAL, **55**, 4285 (1933).

the center rod column and a 10-cc. fraction was obtained at 126–127°. A residual solid was left which consisted mostly of *p*-trichloromethylbenzoic acid as indicated by mixed melting point. The liquid fraction was found to be an azeotrope containing approximately equal amounts of cyclopropyl cyanide and chlorobenzene.

**Decomposition of Bis-azo-diethylacetonitrile in Cyclopropyl Cyanide.**—Cyclopropyl cyanide (8.91 g.) and the azonitrile (0.92 g.) were heated under nitrogen at 82° for 22 hours. Distillation of the mixture gave only one liquid fraction which was essentially pure cyclopropyl cyanide. Tetraethylsuccinonitrile was isolated from the residue by recrystallization from ethanol, m.p. 87–88°.

**Decomposition of Acetyl Peroxide in Cyclopropyl Cyanide.** Acetyl peroxide (0.67 mole in 95 ml. of carbon tetrachloride[13]) was added slowly through a long-stemmed separatory funnel to 5 ml. of cyclopropyl cyanide which was heated on a steam-bath. The final mixture was heated for an additional half hour, washed with aqueous sodium hydroxide, dried and distilled. After the solvent and three ml. of the original nitrile had been removed, a solid separated from the residue. Distillation was discontinued and the residue was worked up by recrystallization from ethanol. Hexachloroethane was the only product isolated, m.p. 180–183°.

**Polymerization of Styrene in the Presence of Cyclopropyl Cyanide.**—Equal volumes (10 cc. each) of cyclopropyl cyanide and styrene were mixed, degassed, sealed and heated for 20 hours at 78°. The mixture was then distilled at 23 mm. The distillate was collected in two fractions, 9.2 ml. boiling at 41–41.5°, $n^{20}\text{D}$ 1.4653; and 4.8 ml. boiling at 41.5–44°, $n^{20}\text{D}$ 1.4826. The first fraction was considered to be an azeotrope of the starting materials. Polymer was isolated from an identical batch by methanol precipitation. The infrared spectrum of the product was identical to that of polystyrene. Of particular significance was the absence of a triple bond stretching frequency in the vicinity of 2200 cm.$^{-1}$.

**Decomposition of Benzoyl Peroxide in the Presence of Cyclopropyl Methyl Ketone and Acetone.**—Solutions of benzoyl peroxide in the ketone were placed in ampules, degassed and sealed under vacuum. The samples were heated at 78°. Individual tubes were removed periodically, opened and the contents were assayed for residual peroxide by an iodometric analysis.[14]

In a separate experiment a solution of 20 g. of benzoyl peroxide in 80 ml. of cyclopropyl methyl ketone was degassed, sealed and heated for 20 hours at 78°. A total of 72 ml. of cyclopropyl methyl ketone was recovered from the final mixture by distillation. The residue was extracted with ether and the ether solution was extracted, in turn, with 5% aqueous sodium hydroxide. The extract was acidified and steam distilled. Five grams of benzoic acid was recovered from the steam distillate. The dark, acidic residue was recrystallized from water giving about 0.5 g. of *p*-phenylbenzoic acid, m.p. 209–211°. The identity of the product was established by a mixed melting point determination and comparison of the infrared spectrum of the product with that of authentic material.

**Decomposition of Acetyl Peroxide in Cyclopropyl Methyl Ketone.**—Acetyl peroxide (8.8 g. in 89 g. of cyclopropyl methyl ketone) was added dropwise to 35 g. of the ketone which was heated to 100–105°. Low-boiling materials were removed by distillation at 50 mm. and the residue was distilled at 35–40° at 2 mm. giving 2 g. of a colorless oil, b.p. 174–175° (740 mm.), $n^{25}\text{D}$ 1.4311. This product gave a copious yield of amorphous solid when treated with dinitrophenylhydrazine reagent but gave only a very weak iodoform test.

**Polymerization of Styrene in the Presence of Cyclopropyl Methyl Ketone and in Acetone.**—Small, weighed amounts of benzoyl peroxide were dissolved in equimolar mixtures of styrene and one of the ketones. Individual samples were degassed, sealed and heated at 78°. Samples were removed periodically and analyzed for benzoyl peroxide and styrene (by bromination). The rates are not reported in detail since they showed the usual half-order dependence on initiator concentration and were virtually identical in the presence of the two ketones. Polymer was isolated from some samples by precipitation with methanol. The infrared spectra of films evaporated from benzene solutions showed no ketone carbonyl frequency although a maximum was found at 1760 cm.$^{-1}$ which was attributed to the benzoate end groups derived from initiator fragments.

**Decomposition of Benzoyl Peroxide in Cyclopropyl Methyl Ketone and Acetone.**—Solutions were prepared, degassed, sealed and heated at 78° in individual ampules. Periodically tubes were removed and residual peroxide was determined iodometrically. The results were analyzed graphically using the integrated form of the first-order rate law.

**Decomposition of Benzoyl Peroxide in Phenylcyclopropane.**—Twenty ml. of phenylcyclopropane was heated overnight at 80° with 10 g. of benzoyl peroxide in a sealed, evacuated tube. The mixture was then distilled yielding 15 cc. of phenylcyclopropane, b.p. 60° (9 mm.). The residue was extracted with 5% aqueous sodium hydroxide and with chloroform. On acidification the aqueous extract gave 4.5 g. of solid. The product was found to consist largely of benzoic acid, which was removed by sublimation leaving a residue of about 100 mg. of impure *p*-phenylbenzoic acid; the latter was identified by its infrared spectrum. Evaporation of the chloroform extract left a small amount of amorphous solid which was apparently polymeric in nature.

Finally, 11 ml. of phenylcyclopropane recovered from the previous experiment was heated with 5.5 g. of benzoyl peroxide. After the mixture was heated for 20 hours at 78° the volatile constituents were distilled at 12 mm. yielding 8.5 cc. of phenylcyclopropane at 61–62°. An additional 0.5 ml. of liquid was collected at 62–112°. Both fractions had $n^{20}\text{D}$ 1.5316. The residue was extracted with aqueous sodium hydroxide. Upon acidification of the extract a solid was obtained which was shown to be largely benzoic acid by careful sublimation. The sublimation residue was recrystallized from ethanol giving a few milligrams of white crystals m.p. 206–210°. The recrystallized product caused no m.p. depression when mixed with authentic *p*-phenylbenzoic acid.

A comparison of the infrared spectra of the various samples of phenylcyclopropane with that of β-methylstyrene showed that the latter compound was present in small amount in the original sample but was destroyed selectively by treatment with the peroxide. The progress of the fractionation was easily followed by the observation of the very strong band at 948 cm.$^{-1}$ in the spectrum of β-methylstyrene. The peak was barely discernible in the spectrum of the distillate obtained after the second treatment with peroxide.

## Discussion

Cyclopropyl cyanide and cyclopropyl methyl ketone showed no tendency to undergo additional polymerization in the presence of decomposing acetyl peroxide, benzoyl peroxides or bis-azo-diethylacetonitrile. Likewise, the infrared spectra of polystyrene prepared in the presence of these compounds showed no evidence for the incorporation of the cyclopropanes in the polymer. Since the C≡N and C=O stretching frequencies are quite prominent in the spectra of the parent compounds it is reasonable to conclude that no more than minor amounts were included by either chain transfer or copolymerization reactions.

As another test of the reactivity of the ketone toward the radicals produced in the decomposition of benzoyl peroxide the rates of decomposition were compared with the decomposition rates in ace-

TABLE I

DECOMPOSITION OF BENZOYL PEROXIDE IN ACETONE AND METHYL CYCLOPROPYL KETONE (MCK) AT 78°

| Solvent | $[P]_0$, mole/liter | $k_1 \times 10^{-5}$, sec.$^{-1}$ |
|---|---|---|
| Acetone | 0.0591 | 2.54 |
| Acetone | .0404 | 2.73 |
| MCK | .0768 | 2.94 |
| MCK | .0592 | 2.50 |
| MCK | .0292 | 2.42 |

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[13] M. S. Kharasch, *et al.*, THIS JOURNAL, **63**, 526 (1941).

[14] G. S. Hammond, *ibid.*, **72**, 3737 (1950).

tone as solvent. The data for individual runs could be fitted to the first-order rate law as is usually the case.[15] The data are summarized in Table I.

As would be expected from the small range of observed rates, attempts to fit the data by the method of Nozaki and Bartlett[15] led to trivial results. The rates are somewhat faster than the "true" unimolecular rates observed in other solvents in the presence of inhibitors[16,17] or at very high dilution.[14] This suggests that a first-order induced decomposition may be of some importance. This could be the consequence of the crossed termination of induced chains as is the case in ether solution.[16,18] However, the similarity of the rates in the two ketones suggests that no unusual reactivity toward the radicals from the peroxide can be attributed to the cyclopropyl group. It is entirely possible that interaction, if it does occur, involves the methyl group. The same conclusion is reached on the basis of coupling experiments with cyclopropyl methyl ketone. Kharasch and co-workers[19] have reported that acetone is converted to 2,5-hexandione by decomposing acetyl peroxide. A high-boiling fraction was obtained in a similar experiment with cyclopropyl methyl ketone. However, the product gave only a slight reaction with hypoiodite indicating that coupling was largely through the methyl groups. No yield of coupling product was obtained in a similar decomposition conducted in cyclopropyl cyanide. When gross amounts of benzoyl peroxide were decomposed in cyclopropyl methyl ketone a 20% yield of benzoic acid and a small yield of *p*-phenylbenzoic acid were produced. The significance of the latter product is to suggest that the ketone is not able to scavenge phenyl radicals well enough to prevent their reacting with either unreacted peroxide or benzoic acid.

Phenylcyclopropane proved to be entirely inert toward polymerization by benzoyl peroxide. Interestingly enough it was found that $\beta$-methylstyrene could be removed very selectively from the cyclopropane by decomposing benzoyl peroxide in a mixture of the two hydrocarbons.

The results of this study are consistent with the previous observations of Trotman-Dickenson and Steacie[4] and the predictions of Brown and Gerstein[20] in that they imply that the abstraction of hydrogen from the cyclopropane ring by free radicals is a relatively slow reaction. It is further shown that ring opening by free radicals is much more difficult than is the analogous addition reaction of olefins.

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(15) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946); P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

(16) C. G. Swain, W. H. Stockmeyer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

(17) A. T. Blomquist and I. A. Berstein, *ibid.*, **73**, 5546 (1951).

(18) W. E. Cass, *ibid.*, **68**, 1976 (1946).

(19) M. S. Kharasch, H. C. McVay and W. H. Urry, *ibid.*, **70**, 1269 (1948).

(20) H. C. Brown and M. Gerstein, *ibid.*, **72**, 2926 (1950).

AMES, IOWA

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# Preparation of Nitro Compounds from Oximes. III. The Synthesis of Nitroalkanes

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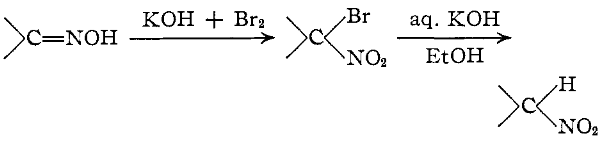
A synthesis of secondary nitroalkanes from aliphatic ketoximes *via* bromonitroso and bromonitro intermediates is described. The sequence is shown to be free of rearrangement. Ten nitroalkanes were prepared and characterized.

In 1900, Forster prepared nitrocamphane from camphor oxime by the steps[2]



Recently this sequence of reactions was examined in this Laboratory in order to determine its generality as an adjunct to existing preparations of nitro compounds.[3] With alicyclic ketoximes it was found that the alkaline solution of bromine produced a bromonitroso compound which, however, could be oxidized to a bromonitro compound with the aid of concentrated nitric acid. Although the sequence was completed with this additional step, the over-all yields of nitrocycloalkanes were poor. It was only after finding that the bromination and debromination steps could be considerably improved by the use of N-bromosuccinimide (NBS) and sodium borohydride, respectively, that a practical synthesis of nitrocycloalkanes resulted.

These improvements in the synthesis of nitrocycloalkanes from oximes now have been extended successfully to the preparation of ten secondary nitroalkanes from aliphatic ketoximes, in spite of the complete failure in this series by conditions originally used by Forster.[3a] In this series, the bromonitroso and bromonitro intermediates were not isolated or purified in order to simplify the laboratory procedure and, in particular, to minimize personal contact with these lachrymatory substances. Thus, the crude bromonitro compound was converted to the nitro compound by the action of sodium borohydride. As the crude bromonitro compounds were contaminated with the related ketone, the reduction mixtures contained small amounts of the corresponding alcohol. No difficulty was experienced, however, in the purification of the nitro compound in the procedure described in the Experimental part.

The reaction of the lower molecular weight ali-

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[1] Taken in part from the M.S. Thesis of T.-F. Yen, West Virginia University, August, 1953.

[2] M. O. Forster, *J. Chem. Soc.*, **77**, 254 (1900).

[3] (a) D. C. Iffland, G. X. Criner, M. Koral, F. J. Lotspeich, Z. B. Papanastassiou and S. M. White, THIS JOURNAL, **75**, 4044 (1953); (b) D. C. Iffland and G. X. Criner, *ibid.*, **75**, 4047 (1953).