in an ice bath. After 30 min the reaction mixture was poured onto 600 ml of cold 2 *N* hydrochloric acid. An oil appeared which solidified after a few minutes. The solid material was collected on a filter and was recrystallized from ethanol to yield 10.0 g (79%) of white needles, mp 100–101°.

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 76.44; H, 5.07.

Material having the same melting point and exhibiting a superimposable infrared spectrum was obtained by the hydrogenation of an acetic acid solution of 3-benzoylcoumarin at 35 psi, using platinum oxide as catalyst.

Acknowledgment.—The author wishes to thank Dr. I. J. Pachter for valuable advice and Mr. M. Myers for expert technical assistance.

Some Reactions of Cyclobutylcarbinyl Radical Intermediates

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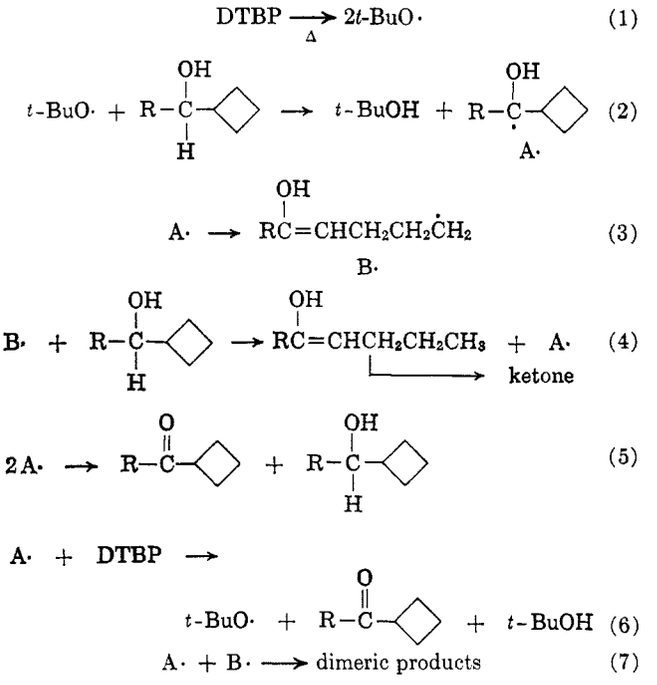
Ring-opening rearrangement reactions of cyclobutylcarbinyl free radicals have been reported to result from the peroxide-induced addition of certain polyhaloalkanes to β-pinene.[2] The quantities of rearranged product obtained, as in the case of addition reactions to certain vinylcyclopropanes,[3] are known to be a function of radical lifetime.[4] Few other examples of cyclobutylcarbinyl radical ring-opening reactions are reported.

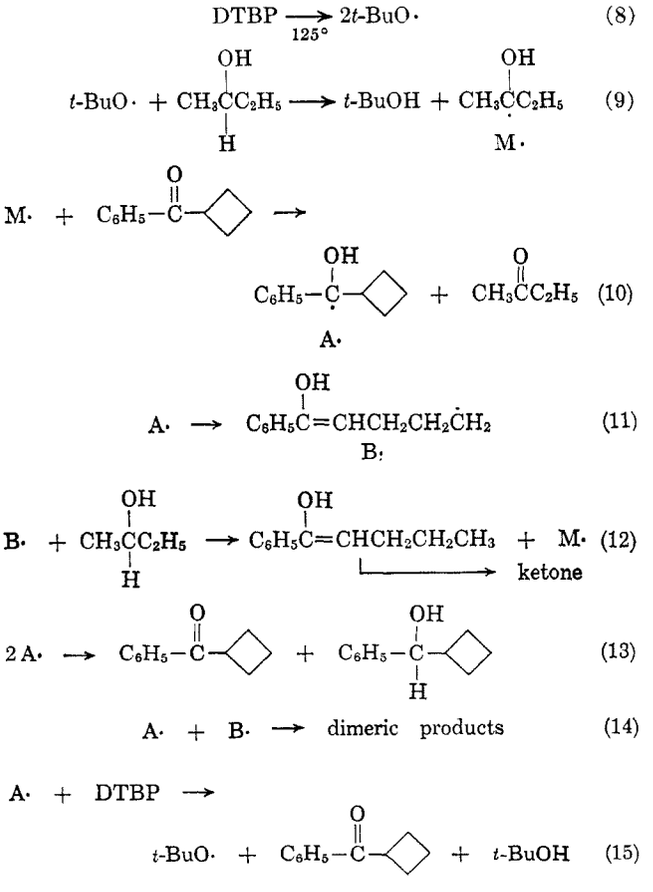
We wish to report a unique ring-opening rearrangement reaction of (α-hydroxy)cyclobutylcarbinyl free radicals. As in the case of (α-hydroxy)cyclopropylcarbinyl free radicals,[5,6] the major reaction product is a straight-chain aromatic ketone. Specifically, we have found treatment of cyclobutylphenylcarbinol with di-*t*-butyl peroxide (DTBP) at 125° to give valerophenone as a major product. Similarly, treatment of cyclobutylmethylcarbinol with DTBP at 125° gives good yields of 2-hexanone. The results of typical experiments are given in Table I.

Of interest is the fact that 2-hexanone predominates over cyclobutyl methyl ketone by a factor of about 8:1 when DTBP is decomposed in cyclobutylmethylcarbinol, whereas cyclobutyl phenyl ketone predominates over valerophenone by 2.7:1 when DTBP is decomposed in cyclobutylphenylcarbinol, a fact indicative of the increased resonance stability imparted to the cyclobutylcarbinyl free radical by the adjacent phenyl group. Details of further experiments on resonance and polar factors influencing cycloalkylcarbinyl radical stability will be reported shortly.[6]

A mechanism for the reaction of DTBP with cyclobutylmethyl- and cyclobutylphenylcarbinol may be as follows (1–7).



Cyclobutyl phenyl ketone, when treated with 2-butanol and DTBP, also yields valerophenone. Presumably a reaction intermediate similar to A· precedes the rearrangement reaction, although such an intermediate may not be totally necessary. The results of a typical experiment are given in Table II. A reasonable mechanism for the reaction may be as follows (8–15).



(1) Financial support from the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(2) (a) D. M. Oldroyd, G. S. Fisher, and L. A. Goldblatt, *J. Am. Chem. Soc.*, **72**, 2407 (1950); (b) G. Dupont, R. Dulou, and G. Clement, *Compt. Rend.*, **236**, 2512 (1953); (c) G. Dupont, R. Dulou, and G. Clement, *Bull. Soc. Chim. France*, 1056, 1115 (1950); (d) G. Dupont, R. Dulou, and G. Clement, *ibid.*, 257 (1951); (e) L. A. Goldblatt and D. M. Oldroyd, U. S. Patent 2,533,240 (1950); *Chem. Abstr.*, **45**, 2262 (1951).

(3) (a) E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, **28**, 3444 (1963); (b) E. S. Huyser and L. R. Munson, *ibid.*, **30**, 1436 (1965).

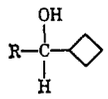
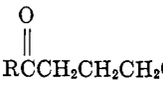
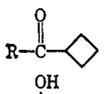
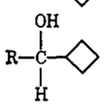
(4) F. G. Bordwell and W. A. Hewett, *J. Am. Chem. Soc.*, **79**, 3493 (1957).

(5) D. C. Neckers, *Tetrahedron Letters*, 1889 (1965).

(6) D. C. Neckers, J. Hardy, and A. P. Schaap, in preparation.

TABLE I

REACTIONS OF CYCLOBUTYLCARBINOLS WITH DTBP AT 125°[a]

Reactants	R = C_6H_5	R = Me	Products	R = C_6H_5	R = Me
	1.87	0.371	*t*-Butyl alcohol	0.45	0.060
DTBP	0.43[b]	0.069[c]	Acetone	0.07	0.020
				0.151	0.118
				0.402	0.014
				1.33	0.178
			(residual)		

[a] All quantities are millimolar. [b] 88% conversion. [c] 68% conversion.

TABLE II

REACTION OF CYCLOBUTYL PHENYL KETONE WITH 2-BUTANOL AND DTBP AT 125°

Reactants (mmoles)	Products (mmoles)
Cyclobutyl phenyl ketone (2.49)	*t*-Butyl alcohol (4.00)
DTBP[a] (2.28)	Acetone (0.44)
2-Butanol (33.00)	Methyl ethyl ketone (3.62)
	Valerophenone (1.51)
	Cyclobutyl phenyl ketone (residue) (0.69)

[a] 91.5% conversion.

Of further interest are the relative reaction rates of aryl cycloalkyl ketones with 2-butanol and DTBP (Table III). In a process that formally may be represented as the addition of a hydrogen atom to a carbonyl group, it appears that adjacent cyclopropyl and cyclobutyl groups serve very effectively to enhance the rate of hydrogen atom addition. An excuse for ring-strain relief is provided by radical formation. Probably this accounts for the rate increase of smaller over larger ring analogs.

TABLE III

REACTIONS OF ARYL CYCLOALKYL KETONES WITH DTBP AND 2-BUTANOL AT 125°

Cycloalkyl aryl ketone	$\frac{k \text{ (cycloalkyl aryl ketone)}}{k \text{ (isobutyrophenone)}}$
Cyclopropyl phenyl ketone	36.00 ± 1.00
Cyclobutyl phenyl ketone	11.30 ± 1.20
Cyclopentyl phenyl ketone	1.84 ± 0.27
Cyclohexyl phenyl ketone	1.23 ± 0.10
Isobutyrophenone	1.00

As is to be anticipated, smaller amounts of ring-opened products are isolated from cyclopentyl and cyclohexyl phenyl ketones.[7]

(7) Small quantities of hexanophenone were isolated as a result of reactions of cyclopentyl phenyl ketone.

Experimental Section[8]

Materials.—Cyclopropylphenylcarbinol (Aldrich), cycloproppl phenyl ketone (Aldrich), 2-butanol (Eastman), and di-*t*-butyl peroxide (Lucidol) were purified by conventional methods until they gave a single peak upon vapor phase chromatography. Cyclobutyl phenyl ketone [bp 78–82° (0.7 mm), lit.[9] bp 114° (7 mm)], cyclopentyl phenyl ketone [bp 78° (0.3 mm), lit.[10] bp 156–160° (15 mm)], and cyclohexyl phenyl ketone (mp 53–55.5°, lit.[11] mp 54°) were prepared from cyclobutanoyl, cyclopentanoyl, and cyclohexanoyl chlorides, using conventional Friedel–Crafts procedures. Cyclobutylphenylcarbinol [bp 105° (1.5 mm), lit.[12] bp 121–122° (5 mm)] was prepared by sodium borohydride reduction of cyclobutyl phenyl ketone, cyclobutylmethylcarbinol (bp 134–140°, lit.[13] bp 136–139°) by sodium borohydride reduction of cyclobutyl methyl ketone.[14] Cyclobutyl methyl ketone (bp 130–134°, lit.[15] bp 134–136°) was prepared from cyclobutanoyl chloride and dimethylcadmium.[15]

Reaction of Cyclobutylphenylcarbinol with DTBP.—Cyclobutylphenylcarbinol (1.87 mmoles) and DTBP (0.43 mmole) were sealed in a Pyrex tube. The tube and contents were heated to 125° in an oil bath. After 24 hr, the tube was opened, and weighed quantities of acetophenone and *n*-butyl acetate were added as internal standards for vapor phase chromatography. The higher boiling products and residual reactants were analyzed, using a Wilkens A-90-P gas chromatograph and a 5-ft 10% Carbowax 4000 on Chromosorb P column thermostated at 125° with 15 psi of helium as a carrier gas. The lower boiling products could be analyzed using the same column at 40° and 5 psi of helium, but more satisfactory results were obtained if a 10-ft 15% Carbowax 4000 column at 60° and 6–7 psi of helium was utilized. Valerophenone was identified by its retention time on several columns. In addition, the infrared spectrum of a sample of valerophenone collected from the eluate stream was identical with that of an authentic specimen of valerophenone.

Reaction of Cyclobutylmethylcarbinol with DTBP.—Cyclobutylmethylcarbinol (0.336 mmole) and DTBP (0.097 mmole) were sealed in a Pyrex tube and heated to 125° for 24 hr in a

(8) Melting points are uncorrected. All infrared spectra were taken on a Beckman Model IR-8. A Wilkens Model A-90-P vapor phase chromatograph with thermal conductivity detectors and using helium as a carrier gas was employed for gas chromatographic analysis.

(9) R. P. Mariella and R. R. Raule, *J. Am. Chem. Soc.*, **74**, 521 (1952).

(10) L. H. Groves and G. A. Swan, *J. Chem. Soc.*, 871 (1951).

(11) V. Meyer and W. Scharvia, *Ber.*, **30**, 1942 (1897).

(12) P. T. Lansbury and V. A. Pattison, *J. Am. Chem. Soc.*, **84**, 4295 (1962).

(13) G. T. Tatevosyan, M. O. Melikyan, and A. T. Terzyan, *J. Gen. Chem. USSR*, **17**, 981 (1947).

(14) The crude product, after a single distillation, was collected by preparative vapor phase chromatography. Infrared and mass spectral analysis confirmed that the carbinol was pure and that which was expected.

(15) R. Pinson and S. L. Friess, *J. Am. Chem. Soc.*, **72**, 5333 (1950).

constant-temperature bath. The products were chromatographed on the 10-ft 15% Carbowax column mentioned earlier, using *n*-butyl acetate as an internal standard. 2-Hexanone was identified by collecting the eluted material with the retention time of 2-hexanone from several 50-μl injections and comparing its infrared spectrum with that given by an authentic specimen of 2-hexanone.

Reaction of Cyclobutyl Phenyl Ketone with 2-Butanol and DTBP.—Cyclobutyl phenyl ketone (2.79 mmoles), DTBP (1.42 mmoles), and 2-butanol (30.8 mmoles) were sealed in a Pyrex tube and heated to 125° for a period of 24 hr. At the end of this period the tube was opened and the products were analyzed by vapor phase chromatography, using acetophenone and *n*-butyl acetate internal standards as previously mentioned.

Relative Reactivities of Cycloalkyl Aryl Ketones with DTBP and 2-Butanol.—Weighed quantities of the two ketones totaling 1 mmole, DTBP (0.5 mmole), and 2-butanol (30 mmoles) were sealed in Pyrex tubes and heated to 125° in a constant-temperature bath. After 6–12 hr the sample tubes were opened and a weighed quantity of an appropriate aryl alkyl ketone was added as an internal standard. Analysis for residual cycloalkyl aryl ketone was accomplished using the 5-ft 10% Carbowax 4000 column at temperatures from 125 to 150° and 15 psi of helium. Relative reactivities were calculated from $k/k_0 = (\log A_0/A)/(\log B_0/B)$ where A_0 and A are initial and final concentrations of cycloalkyl aryl ketone A, and B_0 and B are initial and final concentrations of isobutyrophenone.[16]

(16) E. S. Huyser and D. C. Neckers, *J. Am. Chem. Soc.*, **85**, 3641 (1963).

The Direct Synthesis of Phenylacetylenes from Monohydrazones

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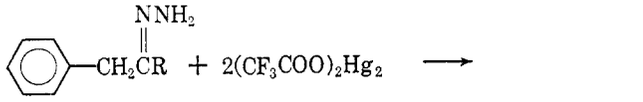
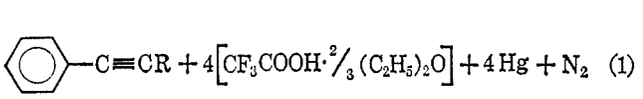
Received July 29, 1965

The oxidation of α,β-dihydrazones with various mercury and silver salts to produce acetylenes has long been known.[1-3] However, it is believed that the following is the first reported direct synthesis of acetylenes from monohydrazones.

The reaction involves oxidation of substituted benzyl ketone hydrazones with mercurous trifluoroacetate in refluxing ether or in dioxane at 40–50° according to the eq 1. Oxygenated solvents which



$$\text{C}_6\text{H}_5\text{CH}_2\overset{\overset{\text{NNH}_2}{\|}}{\text{C}}\text{R} + 2(\text{CF}_3\text{COO})_2\text{Hg}_2 \longrightarrow$$



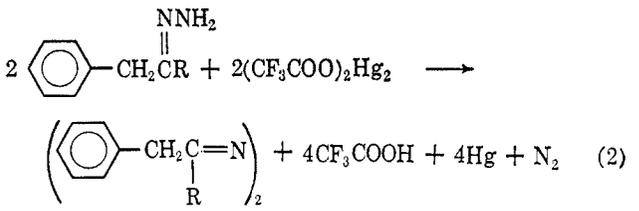
$$\text{C}_6\text{H}_5\text{C}{\equiv}\text{CR} + 4\left[\text{CF}_3\text{COOH}\cdot{}^2\!/_3(\text{C}_2\text{H}_5)_2\text{O}\right] + 4\,\text{Hg} + \text{N}_2 \quad (1)$$

form addition compounds with trifluoroacetic acid must be employed to prevent the addition of trifluoroacetic acid to the acetylenes. Diethyl ether and *p*-dioxane form 2:3 and 3:4 addition complexes with trifluoroacetic acid, respectively.[4,5] Bases cannot be employed to neutralize the acid formed, since they disproportionate the mercurous salt.

(1) T. Curtius, *Ber.*, **22**, 2161 (1889).
(2) T. Curtius and K. Thun, *J. Prakt. Chem.*, **44**, 168 (1891).
(3) M. S. Newman and D. E. Reid, *J. Org. Chem.*, **23**, 665 (1958).
(4) M. Hauptscheim and A. von Grosse, *J. Am. Chem. Soc.*, **73**, 5139 (1951).
(5) J. Lichenberger, *Bull. Soc. Chim. France*, 687 (1954).

The solvent and reactants employed must be thoroughly dried and the reaction run under anhydrous conditions. The presence of water lowers the yield considerably, owing to hydrolysis of the hydrazone.

The principle side reaction observed is the formation of azines from the reaction of 1 equiv of hydrazone with 1 equiv of mercurous trifluoroacetate. This



$$2\,\text{C}_6\text{H}_5\text{CH}_2\overset{\overset{\text{NNH}_2}{\|}}{\text{C}}\text{R} + 2(\text{CF}_3\text{COO})_2\text{Hg}_2 \longrightarrow \left(\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{R})=\text{N}\right)_2 + 4\text{CF}_3\text{COOH} + 4\text{Hg} + \text{N}_2 \quad (2)$$

reaction is minimized by dropwise addition of a hydrazone solution to a stirring slurry of the mercurous salt.

When R = phenyl or alkyl, the yields were 60 ± 10% based on the ultraviolet spectra of the reaction solution. Yields were considerably lower in the cases where R = α-naphthyl and ferrocenyl. Table I summarizes the results obtained.

Attempted oxidation of hydrazones which lacked the benzyl moiety, *e.g.*, acetophenone and propiophenone hydrazones, did not yield any acetylene products. Phenylacetaldehyde hydrazone, where R = H, likewise failed to yield any phenylacetylene. With 1 equiv of mercurous trifluoroacetate, the above hydrazones reacted to produce the respective azine. With 2 equiv of mercurous trifluoroacetate, azine was formed first, followed by a further slow reaction with mercurous trifluoroacetate to give products which could not be identified. One attempt was made to synthesize a heterocyclic acetylene using this route. When R = 3-pyridyl, the basic nitrogen caused disproportionation of the mercurous salt. Oxidation of deoxybenzoin hydrazone with mercuric oxide, mercurous chloride, thallic chloride, ferric chloride, and silver trifluoroacetate yielded only the azine. When mercuric trifluoroacetate and mercurous nitrate were employed as the oxidizing agent, only trace amounts of diphenylacetylene were produced. The oxidation potential of the metal does not appear to be an important factor. Silver and mercury(I) have nearly identical oxidation potentials, yet silver trifluoroacetate does not yield any diphenylacetylene in the oxidation of deoxybenzoin hydrazone. Since the general concensus of opinion appears to be that HgO oxidation of hydrazones yields diazo intermediates, the $(\text{Hg}^{\text{I}}\text{O}_2\text{CCF}_3)_2$ oxidation must involve some new factor.

The mechanism of the hydrazone oxidation reaction is at present unknown. Several analogous derivatives of deoxybenzoin were synthesized and reacted with mercurous trifluoroacetate under the same conditions. The hydroxylamine, phenylhydrazone, and N,N-dimethylhydrazone did not yield any diphenylacetylene. However, oxidation of the monomethylhydrazone of deoxybenzoin did produce diphenylacetylene in 5–10% yield. This fact also argues against a diazo compound as an intermediate in the production of the acetylene.