mers were made with 0.7% sulfur. The mercaptan-modified polymers were prepared in the same way, substituting 0.30–1.0% of dodecyl mercaptan for the sulfur. Likewise, for the unmodified polymer no change in the system was made except omission of the modifier. Samples of the latex were removed, treated with 2.5% of tetraethyl thiuram disulfide in emulsion or with 0.5% of phenothiazine and 1.0% of phenyl-α-naphthylamine in emulsion. They were then coagulated with ethanol and dried at room temperature *in vacuo*. Analysis indicated that polymers prepared in this way contained only small amounts of residual soap and other adjuvants.

Preparation of Samples.—As indicated in the Discussion, the polymer samples were extracted or precipitated to remove uncombined sulfur and sulfur compounds. For elemental sulfur and some mercaptan samples the polymers were extracted continuously with acetone or methanol for three to four days in ASTM rubber extractors or Soxhlet apparatus. In other experiments the samples were dissolved in benzene to make 1–5% solutions and the polymer precipitated completely by addition of about 2 volumes of methanol or acetone. Further addition of methanol produced no cloudiness in the clear supernatant liquid.

Radioactivity Assay.—The dry polymer samples were oxidized by the Carius method to obtain a clear solution of sodium sulfate. The sulfate was precipitated as the benzidine salt on special funnels, dried and counted directly with Geiger counters.[28] A control from the labeled sulfur compound under study was always counted at the same time as the unknowns to eliminate the necessity of reliance on decay calculations and to check counter operation with theory based on decay. Sufficient sodium sulfate carrier was added to both control and unknowns to make the sample sizes comparable so that errors due to absorption were eliminated. Furthermore, the control samples were adjusted to roughly the same order of magnitude of counts as the unknowns.

Acknowledgments.—The authors gratefully acknowledge the assistance of Miss Doris Peterson in the radioactivity determinations and of Dr. J. B. Nichols and Miss Beverly Price for the osmotic pressure measurements. We also extend our sincere thanks to Drs. D. M. McQueen, B. C. Pratt and G. D. Patterson for their aid and encouragement, and to Professors F. T. Wall and C. S. Marvel for many helpful discussions during the course of this research.

Summary

By use of radioactive sulfur it has been shown that sulfur-modified neoprene, *i. e.*, Neoprene Type GN, is essentially a copolymer of chloroprene and sulfur in the approximate ratio of 100 chloroprene units per sulfur atom. The sulfur units, possibly disulfides, are cleaved by an alkaline emulsion of tetraethyl thiuram disulfide, so that a gel polymer containing combined sulfur can thus be converted to a soluble, plastic product. The mechanism of this cleavage reaction has not been completely elucidated as yet.

Potassium persulfate, used as initiator for the polymerization of neoprene, appears to be combined with the polymer in Neoprene Type GN in amounts equivalent to 8–17 polymer molecules formed for each sulfur-containing initiator fragment. However, when dodecyl mercaptan is used as modifier, a large proportion of the polymer molecules contain essentially no combined sulfur from the persulfate and it appears that the true initiator is the RS· free radical formed by reaction of the mercaptan with potassium persulfate.

Dodecyl mercaptan used as a polymerization modifier or chain transfer agent, is combined in a greater amount than the one mercaptan per polymer molecule expected on the basis of simple chain transfer. High molecular weight fractions contained 3–4 mercaptan sulfur atoms per polymer molecule and the results suggest that mercaptan addition to the double bonds of the polymer had occurred.

WILMINGTON, DELAWARE RECEIVED SEPTEMBER 23, 1948

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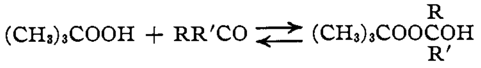
[28] Henriques, Kistiakowsky, Margnetti and Schneider, *Ind. Eng. Chem., Anal. Ed.*, **18**, 349 (1946).

[CONTRIBUTION FROM THE EMERYVILLE LABORATORIES OF SHELL DEVELOPMENT COMPANY]

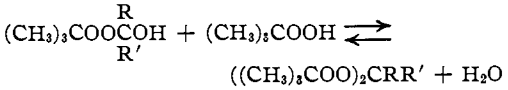
Some *t*-Butyl Hydroperoxide Derivatives of Aldehydes and Ketones

BY FRANK H. DICKEY, FREDERICK F. RUST AND WILLIAM E. VAUGHAN

t-Butyl hydroperoxide combines with aldehydes and ketones to form a series of new compounds which contain either one or two peroxide groups for each carbonyl group. The synthesis is in accord with the equations



$$\mathrm{(CH_3)_3COOH + RR'CO \rightleftarrows (CH_3)_3COO\overset{R}{\underset{R'}{C}}OH} \qquad (1)$$



$$\mathrm{(CH_3)_3COO\overset{R}{\underset{R'}{C}}OH + (CH_3)_3COOH \rightleftarrows ((CH_3)_3COO)_2CRR' + H_2O} \qquad (2)$$

where R and R′ may be organic radicals or hydrogen.

Reaction 1 is exemplified by formaldehyde and chloral in which cases reaction 2 apparently is of little or no consequence. Rieche[1] mentions the reaction of alkyl hydroperoxides with aldehydes to form hydroxydialkyl peroxides (monoperoxides). However, the ketones investigated in the present work all form liquid bis-(*t*-butylperoxy)-alkanes, as does benzaldehyde.

Experimental

Reactants.—The *t*-butyl hydroperoxide was a commercial product which was purified by steam distillation. After the low boiling fractions had been removed and the distilling temperature had reached 92–93°, the kettle contents were cooled and the phases separated. The upper, hydroperoxide phase, after drying with sodium sulfate, analyzed 78–82%. The ketones and aldehydes were all

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[1] Rieche, "Alkylperoxyde und Ozonide," Theodor Steinkopf, Dresden, 1931.

TABLE I

t-BUTYL HYDROPEROXIDE DERIVATIVES OF CARBONYLIC COMPOUNDS

Peroxide β = (*t*-butylperoxy)	Derivative of	$n^{20}\text{D}$	%C		%H		% Active O^d		Mol. wt.		Conversion of hydroper.
			Found	Theory	Found	Theory	Found	Theory	Found	Theory	%
2,2-bis-(β)-propane	Acetone	1.4098	59.6	59.9	11.1	11.0	14.6	14.5	220	220	90
2,2-bis-(β)-butane	Methyl ethyl ketone	1.4140	61.1	61.5	11.2	11.2	13.9	13.7	232	234	85
2,2-bis-(β)-pentane	Methyl propyl ketone	1.4168	62.6	62.9	11.4	11.4	13.2	12.9	266	248	83
3,3-bis-(β)-pentane	Diethyl ketone	1.4155	62.4	62.9	11.4	11.4	12.6	12.9	245	248	79
2,2-bis-(β)-4-methylpentane	Methyl isobutyl ketone	1.4200	64.2	64.1	11.5	11.5	12.2	12.2	258	262	74
1,1-bis-(β)-cyclohexane	Cyclohexanone	1.4420	64.4	64.6	11.2	10.8	11.6	12.3	259	260	88
bis-(β)-phenylmethane	Benzaldehyde	1.5770	67.5	67.1	9.0	9.0	11.8	11.9	252	268	95
I	Formaldehyde	1.4128	51.5	50.0	10.9	10.0	13.3	13.3	120	120	85
II	Chloral	50–51^a	44.7^b	44.7^b	0.47^c	0.44^c	6.7	6.7	246	238	90

^{a} M. p., °C. ^{b} %Cl. ^{c} Acetyl value, eq./100 g. ^{d} See text "Analytical-Total Peroxide." I = *t*-butyl hydroxymethyl peroxide. II = *t*-butyl α-hydroxy-β,β,β-trichloroethyl peroxide.

commercial products which were purified when necessary by careful fractionation.

bis-(*t*-Butylperoxy)-alkanes.[2]—The bis-(*t*-butylperoxy)-alkanes were prepared by treating 0.67 mole of the carbonyl compound with 0.133 mole of *t*-butyl hydroperoxide (78–82%) at room temperature in the presence of concentrated hydrochloric aid (0.1 ml.) as the catalyst. In each case 15 g. of boric anhydride was used to dry the mixture and take up the water of reaction. Each mixture was allowed to stand for about one month after which it was analyzed in accordance with the procedure described in the following section. High yields of the acetone and methyl ethyl ketone derivatives have been obtained in periods of time as short as a few hours.

Isolation of the pure compounds from reaction mixtures in the cases of acetone and methyl ethyl ketone can be easily accomplished by simply extracting the unreacted starting materials with water. In these instances the yields of the isolated products approach the conversions indicated by the analytical method, 80% in the case of acetone and 75% in the case of methyl ethyl ketone (see Table I). However, with the higher carbonylic compounds, water extraction is not satisfactory because of their limited solubility. In the present work, these derivatives were isolated for determination of physical constants and analysis by repeated extraction of the reaction mixture with aqueous 50% ethyl alcohol; this procedure obviously removes a major portion of the desired compound because of solubility in the extractant and the yields ranged from *ca.* 15% on input hydroperoxide in the case of benzaldehyde to *ca.* 65% for methyl propyl ketone. A more efficient procedure would be removal of the remaining starting materials by low pressure distillation; the yields would then approach the conversions indicated by the titration analyses. It is emphasized that great care should be exercised in such operation as it is known[3] that heat will cause these compounds to decompose, in some cases with explosive violence.

***t*-Butyl Hydroxymethyl Peroxide.**[4]—Two hundred eighty grams (2.4 moles) of 78% *t*-butyl hydroperoxide was gradually stirred into 200 g. of 36–38% formalin solution (2.4 moles) at room temperature and the product then vacuum distilled. The peroxide came over at 52–53° at 8–9 mm. A yield of 65.5%, 188 g., was obtained.

***t*-Butyl α-Hydroxy-β,β,β-trichloroethyl Peroxide.**—Chloral (0.1 mole, 15 g.) was introduced a few drops at a time into a cooled (0°) solution of *t*-butyl hydroperoxide (0.2 mole) in 75 ml. of hexane. A small amount of calcium chloride was included in the mixture to remove the water. Reaction time was one hour, after which the calcium chloride was filtered off. The peroxide crystallized out when the hexane solution was cooled to −40°. The yield was 8.2 g., 27%.

Analytical

Total Peroxide.—A 1.0-ml. sample of the reaction mixture was added to 10 ml. of acetic acid and *ca.* 2 g. of solid potassium iodide. The solution was heated on the steam-bath under reflux for twenty minutes, cooled and the free iodine titrated with thiosulfate.

***t*-Butyl Hydroperoxide.**—A 1.0-ml. sample of the product was added to a solution containing 50 ml. of isopropyl alcohol, 2 ml. of acetic acid and 2 ml. of saturated potassium iodide solution. The mixture was heated to boiling for two minutes, cooled and the liberated iodine titrated.

bis-(*t*-Butylperoxy)-alkanes.—The difference between the total peroxide value and the hydroperoxide value is taken as the bis-(*t*-butylperoxy)-alkane. Control experiments have shown that 97–99% of the hydroperoxide present is determinable by the above procedure. There is also some participation by the carbonyl derivatives in the analysis for copresent hydroperoxide, which may vary from as high as 6–7% in the case of the acetone derivative to 1% or less for the cyclohexanone derivative. The conversions of *t*-butyl hydroperoxide to the bis-(*t*-butylperoxy)-alkanes given in Table I are, therefore, subject to these limitations of accuracy.

Results and Discussion

Some new diperoxy compounds derived from *t*-butyl hydroperoxide and ketones are listed in Table I, together with analytical data obtained on the purified products. Also included are data on the diperoxy derivative of benzaldehyde and on the monoperoxy compounds obtained from formaldehyde and chloral. All except the solid chloral derivative are clear, colorless liquids with mild, pleasant odors. They show excellent potentialities as polymerization catalysts and the methyl ethyl ketone derivative in particular is highly effective in the polymerization of allyl esters.[3]

When 2,2-bis-(*t*-butylperoxy)-butane was decomposed[5] in cumene at 110°, 92% of the *t*-butoxy radicals was accounted for as *t*-butyl alcohol and at least 82% of the reacted cumene was found as dicumyl. This is related to the corre-

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[2] Dickey, U. S. Patent No. 2,455,569 (Dec. 7, 1948).

[3] Unpublished data from these laboratories.

[4] Dickey, U. S. Patent No. 2,400,041 (May 7, 1946).

[5] This work will be presented in the future.

sponding decomposition of *di-t*-butyl peroxide[6] and is an indication of the structure of the molecule as a perketal. Likewise, the observation that equations (1) and (2) are reversible—the pure peroxide can be hydrolyzed by acid to the original hydroperoxide and ketone—is pertinent.

[6] Raley, Rust and Vaughan, THIS JOURNAL, **70**, 1336 (1948).

Summary

A series of new liquid peroxides derived from reaction of aldehydes and ketones with *t*-butyl hydroperoxide is presented together with methods of synthesis.

EMERYVILLE 8, CALIFORNIA RECEIVED[7] JANUARY 6, 1949

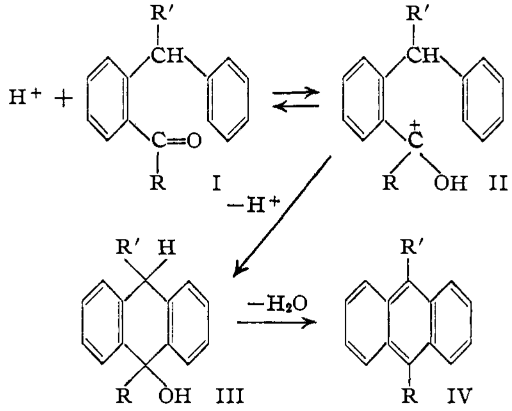
[7] Original manuscript received April 12, 1948.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

Aromatic Cyclodehydration. XXII.[1] The Mechanism of the Cyclization of *o*-Benzylphenones. III

BY CHARLES K. BRADSHER AND FRANK A. VINGIELLO[2]

In acid media, *o*-benzylphenones (I) may be cyclized to yield anthracene hydrocarbons[3,4,5] (IV). Berliner[5] has found (where R′ = CH_3) that the rate of cyclization decreases with increasing length of group R until *n*-butyl is reached, and remains approximately the same for *n*-pentyl and *n*-hexyl.



This was explained in terms of an increasing order of electron release with increase in size of the alkyl group[6] up to butyl, resulting in an increase in electron density on the positive central carbon atom, thus making the substitution reaction more difficult.

The present investigation was undertaken to determine (1) whether a similar difference in cyclization rates exists in the series in which R′ = H, (2) the effect on the cyclization rate when the inductive effect is varied, while steric factors are kept essentially constant and (3) the effect of varying R′ while R remains constant.

The procedure used in our rate studies differs from that employed by Berliner in that the reaction mixture was not refluxed, but heated in a thermostat in glass-stoppered tubes, and the weight of product isolated was corrected to allow for solubility in the cyclizing medium.[7]

TABLE I

RATES OF CYCLIZATION OF SOME *o*-BENZYLPHENONES (I)[a]

R	K, (hr.$^{-1}$) × 10^{-2}
H	540
CH_3	70
C_2H_5	30
$C_6H_5CH_2$	23
p-$CH_3C_6H_4$	4.2
p-BrC_6H_4	4.2
p-ClC_6H_4	4.1
p-FC_6H_4	2.8
C_6H_5	4.4
C_6H_5 (R′ = CH_3)	13
C_6H_5 (R′ = C_6H_5)	13

[a] R′ = H unless otherwise noted.

Like Berliner,[5] we have found the rate of cyclization to be of first order with respect to ketone concentration, and, as he has pointed out, the earlier statement by one of us and Smith that "the rate of cyclization of *o*-benzylphenones is roughly independent of the nature of the R group" is erroneous.[8]

In addition to the ketones mentioned, we have measured the rate of cyclization of *o*-benzylbenzaldehyde[9] (I, R = H; R′ = H). Under the conditions we have used, the rate of formation of anthracene was so great as to make accurate timing difficult.

The comparison of the rates shown by the *para*-substituted phenyl ketones (R′ = H; R = *p*-XC_6H_4) affords a test of the relative importance

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[1] For the preceding communication of this series see *J. Org. Chem.*, **13**, 786 (1948).

[2] Present address: Virginia Polytechnic Institute, Blacksburg Va.

[3] Bradsher, THIS JOURNAL, **62**, 486 (1940).

[4] Bradsher and Smith, *ibid.*, **65**, 451 (1943).

[5] Berliner, *ibid.*, **66**, 533 (1944).

[6] Berliner has been careful to emphasize that equally plausible explanations might be obtained from purely stereochemical considerations.

[7] While the solubility of the aryl anthracenes was small, that of the methyl- and ethylanthracenes was large enough to make errors in the solubility determination a significant source of error in the final rate.

[8] This statement, for which the senior author accepts full responsibility, was based upon only a few yields obtained under conditions which were not comparable.

[9] The cyclization of this compound was first observed by Bergmann, *J. Org. Chem.*, **4**, 1 (1939).