TABLE V

HYDANTOINS OBTAINED FROM CERTAIN MORPHOLINYL KETONES

Ketone $OC_4H_8N-CH(CH_3)COR$, R =	5-R'-5, R' =	Hydantoin R =	Yield, %	Nitrogen, % Calcd.	Found
$-CH_2C_6H_5$	H	$-CH_2C_6H_5$	189–190[a]	14.73	14.78
$-CH_2C_6H_4C_2H_5$-*p*	H	$-CH_2C_6H_4C_2H_5$-*p*	177–178	12.86	12.98
$-CH_2C_6H_4CH(CH_3)_2$-*p*	H	$-CH_2C_6H_4CH(CH_3)_2$-*p*	186–187	12.12	12.15
$-CH_2CH_2CH_2CH_3$	C_4H_9	$-CH(CH_3)NC_4H_8O$	218–220 d.	15.72	15.70

[a] H. T. Bucherer and V. A. Lieb [*J. prakt. Chem.*, [2] 141, 5 (1934)] reported m.p. 190°. The m.p. of the product here reported was not depressed when mixed with an authentic sample of 5-benzylhydantoin.

Anal. Calcd. for $C_{11}H_{20}N_2O$: C, 67.30; H, 10.27; N, 14.27; mol. wt., 196.3. Found: C, 67.29; H, 10.62; N, 14.38; mol. wt. (ebulliometric), 710.

Interaction of Organolithium Reagents with α-Methyl-4-morpholineacetonitrile.—Three organolithium compounds (*n*-butyl, *sec*-butyl and phenyl) were allowed to react with this substituted nitrile in 0.15:0.5 mole ratio; hydrolysis was accomplished by the use of 50 ml. of water. The ether layer was separated and made acidic by addition of hydrochloric acid (6 *N*). After standing for 15 min., sodium carbonate was added until the aqueous phase was alkaline, then the ether layer was recovered, dried over anhydrous sodium sulfate and fractionated. In all three cases, the sole product was a ketone; certain properties of the latter are collected in Table IV.

Conversion of α-(4-Morpholinyl)-ethyl Ketones into Hydantoins.—An attempt was made to convert certain of these ketones with potassium cyanide and ammonium carbonate. After about 12 hr., the reaction mixture was concentrated to about one-third of its original volume and was acidified to *p*H 7 to precipitate the hydantoin. Purification was achieved through re-solution in alkali, with subsequent acidification, and by crystallization from ethyl alcohol. The formulas and certain physical properties of the hydantoins produced from these ketones are listed in Table V.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Stereochemistry of the Primary Carbon. VIII. Acetolysis of Optically Active 1-Butyl-1-*d* *p*-Nitrobenzenesulfonate[1-3]

BY ANDREW STREITWIESER, JR., AND WILLIAM D. SCHAEFFER[4]

RECEIVED MAY 18, 1957

The reaction of 1-butyl-1-*d* *p*-nitrobenzenesulfonate with acetic acid at 114° gives butyl-1-*d* acetate with 85% net inversion of configuration (15% racemization). The ester is shown to be optically stable to the reaction conditions; consequently, a primary carbonium ion or its solvated equivalent is demonstrated to be involved to a significant extent. Addition of nitrobenzene or dioxane but not *o*-dichlorobenzene to the solvent causes a marked increase in the amount of racemization. These results are explained in terms of "covalently solvated" carbonium ions.

Previous results[5] on the acetolysis and formolysis of optically active 1-butyl-1-*d* brosylate demonstrated that the solvolyses proceeded with 96 ± 8% and 98 ± 5%, respectively, of net inversion of configuration. The relatively large experimental uncertainties were due to systematic and non-systematic errors associated with the polarimetric measurement in narrow bore tubes of the small quantities of deuterated materials available at that time. With the preparation of a relatively large quantity of optically active 1-butanol-1-*d*[6] (I) a more extensive and precise investigation of the stereochemistry of solvolysis reactions of primary compounds was undertaken.

The optically active alcohol I was converted to the *p*-nitrobenzenesulfonate II which had a higher melting point than the brosylate and which could be purified more readily by crystallization. In the solvolysis experiments, it is obviously important to use sulfonate esters free from alcohol, for the presence of such alcohol would give rise to a corresponding amount of product ester of retained configuration. A 0.3 *M* solution of II in acetic acid was maintained at 114.4° for 24 hr. and produced 1-butyl-1-*d* acetate (III) having an optical rotation of $\alpha^{25}D$ −0.171 ± 0.003° (*l* 2). III prepared directly from I with acetyl chloride and pyridine had $\alpha^{25}D$ +0.200 ± 0.003° (*l* 2); therefore, the acetolysis product shows 85 ± 2% net inversion of configuration. Optically active III was maintained in acetic acid 0.45 *M* in *p*-toluenesulfonic acid for 24 hr. at 114.4°. It was recovered with 98 ± 10% of retention of its optical activity. Racemization of III under these conditions is undoubtedly acid catalyzed. At the completion of the solvolysis reaction of II, the medium is only 0.3 *M* in strong acid; hence, III produced in the solvolysis reaction could have suffered only 1 ± 7% racemization by an acid-catalyzed reaction after its formation. In similar solvolyses described below, II recovered from a partial solvolysis was found to have essentially no loss in optical activity. Thus, at least part of the 15% racemization described above is due neither to racemization of the starting II nor of the product III but must be a property of the solvolytic displacement reaction itself. The demonstration of racemization is an accepted and sensitive criterion for the production of symmetrically solvated carbonium ions in solvolytic reactions. The present results demonstrate unequivocally the

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(1) Paper VII, THIS JOURNAL, **79**, 2893 (1957).

(2) Taken from the Ph.D. dissertation of W.D.S., June, 1956.

(3) This research was supported in part by the Petroleum Research Fund of the American Chemical Society and was presented at the 129th Meeting of the American Chemical Society, Dallas, Texas, April 13, 1956; Abstracts, p. 52-N.

(4) General Electric Fellow, 1955–1956.

(5) A. Streitwieser, Jr., THIS JOURNAL, **77**, 1117 (1955).

(6) A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **78**, 5596 (1956).

TABLE I

ACETOLYSES OF 1-BUTYL-1-*d* *p*-NITROBENZENESULFONATE

Solvent[a]	Temp., °C.	Time, hr.	No. of half-lives[b]	$\alpha^{25}D$ (l 2) of III obtained	Net % inversion
Acetic acid	114.4	24	~22	−0.171 ± 0.003°[c]	85 ± 2
90% Nitrobenzene–10% acetic acid	114.4	24	1.5	− .102 ± .004[c]	51 ± 2
90% Nitrobenzene–10% acetic acid	90.8	259	1.4	− .118 ± .003[c]	59 ± 2
75% Dioxane–25% acetic acid	97.1	113.5	1.2	+ .099 ± .003[d]	47 ± 2
75% *o*-Dichlorobenzene–25% acetic acid	97.1	96	~3	+ .200 ± .008[d]	94 ± 6

[a] Solvent composition by volume; 0.3–0.45 *M* solutions of II were used. [b] Rate in acetic acid was estimated from the rate of acetolysis of *n*-butyl brosylate (ref. 5) using $k_{\text{nitrosylate}}/k_{\text{brosylate}} = 4$ (ref. 10). The rate constants for the solvent mixtures are given in the Experimental section (Table IV). [c] III prepared from I used had $\alpha^{25}D$ +0.200 ± 0.003° (l 2). [d] III prepared from I used had $\alpha^{25}D$ −0.213 ± 0.004° (l 2).

TABLE II

OPTICAL STABILITY OF 1-BUTYL-1-*d* ACETATE TO SOLVOLYSIS CONDITIONS

Solvent[a]	Temp., °C.	Hours run	$\alpha^{25}D$ (l 2) Start	$\alpha^{25}D$ (l 2) Recovered	Racemization, %
Acetic acid	114.4	24	−0.042 ± 0.004°	−0.041 ± 0.003°	2 ± 10
90% Nitrobenzene–10% acetic acid	114.4	24	+ .092 ± .004	+ .090 ± .003	2 ± 5
75% Dioxane–25% acetic acid	97.1	200	− .042 ± .004	− .040 ± .003	5 ± 10

[a] Solutions were 0.45 *M* in *p*-toluenesulfonic acid and 0.2 *M* in III.

involvement to a significant degree of primary carbonium ions in some solvolytic reactions.

The stereochemistry of the methanolysis of hydrogen 2,4-dimethylhexyl 4-phthalate (IV) has been shown[7] to depend sensitively on the presence of other solvent components capable of effectively solvating carbonium ion intermediates. Consequently, solvolyses of optically active II were run in binary mixtures of acetic acid and nitrobenzene, dioxane and *o*-dichlorobenzene. The results, summarized in Table I, demonstrate that addition of either nitrobenzene or dioxane to the acetic acid caused a substantial increase in the amount of racemization which accompanied the formation of III in the solvolysis. When optically active III was maintained under the solvolytic conditions with *p*-toluenesulfonic acid, the recovered ester had the same optical rotation as the starting ester within experimental error. These results, which are summarized in Table II, demonstrate that the racemized ester produced in the acetolysis does not arise from racemization of the ester after it is formed. The acetolysis in the 90% nitrobenzene–10% acetic acid mixture at 114.4° was stopped before completion. The acetic acid and III were distilled from the mixture, and a mixture of acetic acid and sodium acetate was added to the residue. The III produced by the reaction of sodium acetate with the unreacted II was isolated and was found to have 84 ± 12% inversion of configuration. If the racemized III produced in the acetolysis were due to a racemization of the starting II, the unreacted sulfonate in this experiment would be expected to have been extensively racemized. The large degree of configurational inversion found in the acetate obtained by reaction of the unreacted sulfonate with sodium acetate demonstrates that racemization of the sulfonate under the solvolysis conditions is unimportant. The presence of some residual III solvolysis product, not completely removed in the first distillation, undoubtedly accounts for the fact that completely inverted acetate was not obtained in the displacement. In a similar manner, the solvolysis of II in 75% dioxane–25% acetic acid at 97.1° was stopped before the reaction was completed. The unreacted sulfonate, which was isolated in this case in crystalline form, was treated with sodium acetate in methanol. The III obtained from this displacement reaction had a rotation which corresponded to 92 ± 5% inversion of configuration. Again racemization of II under the solvolysis conditions is not important. These control experiments demonstrate unequivocally that the extensively racemized III obtained in the solvolyses is formed in the acetolysis reaction itself.

On the other hand, acetolysis of II in 75% *o*-dichlorobenzene–25% acetic acid was not accompanied by additional racemization.

Although we did not specifically look for the formation of *sec*-butyl acetate in the solvolyses, substantial quantities of this ester, if formed, would not have escaped notice. We found no evidence for the formation of any *sec*-butyl products. In the present experiments, the racemization observed could not be due to the intervention of olefin, for olefin formation would undoubtedly lead to *sec*-butyl acetate rather than *n*-butyl acetate. In a prolonged acetolysis of *n*-propyl tosylate, Huisgen and Rüchardt[8] report the formation of less than 3% of isopropyl acetate. The important amount of racemization found in our work and the small amount of rearrangement in the solvolysis is of important significance in the understanding of the amine–nitrous acid reaction.[9]

Discussion

The increased racemization in the acetolysis of our primary system produced by the presence of nitrobenzene or dioxane seems completely analogous to the increased racemization in the methanolysis of IV produced by the presence of nitromethane, acetonitrile or dioxane.[7] The interpretation of the latter results in terms of "covalently solvated" carbonium ion intermediates would seem

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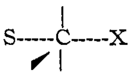
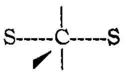
[7] W. E. Doering and A. Streitwieser, Jr., THIS JOURNAL, forthcoming.

[8] R. Huisgen and C. Rüchardt, *Ann.*, **601**, 1 (1956).

[9] A. Streitwieser, Jr., and W. D. Schaeffer, THIS JOURNAL, **79**, 2888 (1957).

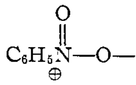
to be directly applicable to the present system.[10] In this interpretation, the racemization observed in the acetolysis of II is due to the formation of symmetrically solvated intermediates of the type VI.

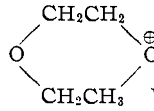

V


VI

Because of the free electron pairs on oxygen in nitrobenzene and in dioxane, these compounds, when present, can take the place of an acetic acid molecule as the covalently solvating species, S, in the first intermediate, V, in which **X** is the leaving group. However, such intermediates cannot collapse to give a stable product with inversion and must give rise to increased amounts of disolvated intermediates such as VI, in which the two S molecules may be the same or different compounds. The collapse of intermediates such as VI when one of the solvating species is acetic acid must give product acetate with racemization. *o*-Dichlorobenzene is insufficiently nucleophilic to compete with acetic acid effectively in solvating the carbonium ion intermediates. Consequently, a product of almost unchanged stereochemistry results. It is interesting and significant that the character of the results obtained in this work so completely parallel the related results on the tertiary system.[7,10] Clearly, primary carbonium ions are not of such high energy that they are unimportant in solvolytic reactions. Furthermore, because in the present case the leaving group leaves as an anion, the first intermediate, V, could conceivably be discussed in terms of an ion-pair. In the case of the methanolysis of IV, however, the leaving group is a neutral phthalic acid molecule, and the corresponding intermediate such as V is charged and cannot be considered as an ion-pair. The distinction between ion-pair and ionic intermediates seems unnecessary and undesirable in solvolytic reactions, at least as far as stereochemical factors are concerned. Of far greater apparent significance are the nucleophilicities of the solvating species and the extent of covalent bonding to solvent in these intermediates.

An alternative explanation is that nitrobenzene and dioxane partake in direct displacement reactions on II to yield the unstable intermediates VII and VIII, respectively, with inversion of configuration, followed by a second displacement by acetic acid to give the retained ester, III. This retained ester combined with the predominantly inverted ester from the direct reaction of II with acetic acid leads to the effective result of greater racemization. This interpretation, although allowed by the present facts taken alone, belies the analogy to the tertiary system in which such direct displacements are highly unlikely. Nevertheless, further work is now in progress to decide this point conclusively.


VII


VIII

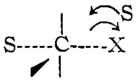
As discussed in greater detail by Doering and Streitwieser,[11] the stereochemistry of a given solvolysis at different temperatures can provide the differences in energies of activation and entropies of activation, ΔE and $\Delta\Delta S^{\ddagger}$, respectively, for inverting and racemizing reactions by equation 1 in which k_i and k_r are the effective rates of formation of inverted and racemized product, respectively, and E_i and E_r are the respective Arrhenius energies of activation.

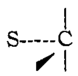
$$d \ln \frac{k_i}{k_r} = -\frac{(E_r - E_i)}{RT^2}\, dT \qquad (1)$$

k_i/k_r is related to the percentage net inversion obtained, **I**, by equation 2. The stereochemical results for the acetolyses of I in 90% nitrobenzene–10% acetic acid at 114.4 and 90.8° lead to a value of ΔE of 3.9 ± 0.7 kcal./mole. Since $E = RT + \Delta H^{\ddagger}$,[12] $\Delta E = \Delta\Delta H^{\ddagger}$. Using the absolute rate

$$\frac{k_i}{k_r} = \frac{\mathrm{I}}{100 - \mathrm{I}} \qquad (2)$$

equation[12] these results lead to a $\Delta\Delta S^{\ddagger}$ value 10 ± 2 e.u. As observed for solvolysis of IV, the process leading to racemization has both a greater energy and entropy of activation. Consequently, the transition state for the process V → VI must be "looser" than the transition state for the reaction V → inverted product. As in the case of the tertiary system, it seems improbable that a frontside displacement of one solvent moiety by another, IX, is an adequate representation of the reaction leading to racemization because of the entropy requirements for fixation of a solvent molecule implied in this formulation. It is conceivable that this reaction involves an intermediate such as **X** which is unsolvated on the frontside.


IX


X

Optically Active 1-Butanol-1-*d*.—Although most of the optically active I used in the present work was part of a large batch described earlier,[6] some of the experiments were performed using material prepared by an alternate method. The recent preparation[13] of benzyl-α-*d* alcohol having a relatively high optical rotation from the reaction of isobornyloxymagnesium bromide and benzaldehyde-*d* suggested application to the *n*-butyl system. Camphor was reduced with lithium aluminum deuteride and the mixture of deuterated borneol and isoborneol was converted to the Grignard salt and treated with butyraldehyde. The deuterobutanol obtained was converted with phthalic anhydride to the hydrogen phthalate which, after two crystallizations from benzene–cyclohexane, had $[\alpha]^{25}\mathrm{D}$ $-0.238 \pm 0.008°$. A third crystallization gave product having $[\alpha]^{25}\mathrm{D}$ $-0.229 \pm 0.010°$. Cleavage of this material with lithium aluminum hydride gave a deuterated

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[10] *Cf.* A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

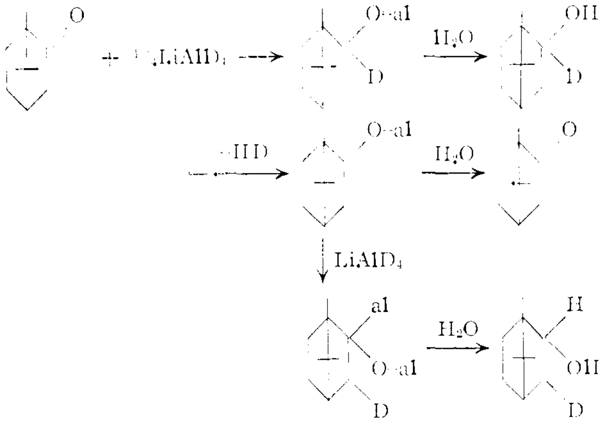
[11] W. E. Doering and A. Streitwieser, Jr., THIS JOURNAL, forthcoming.

[12] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

[13] A. Streitwieser, Jr., and J. R. Wolfe, Jr., THIS JOURNAL, **79**, 903 (1957).

butanol having $\alpha^{25}\text{D}$ 0.154 ± 0.004° (*l* 2). This rotation is more than twice as great as that obtained by the procedure using 2-octanol as the reducing agent. However, the infrared spectrum of this material indicated the presence of only 0.56 deuterium atom per molecule. The density of the alcohol indicated the presence of 0.54 deuterium atom per molecule. Consequently, the 1-butanol-1-*d* prepared in this way has a rotation 3.9 times as high as the product from optically active 2-octanol. For further use the optically active I obtained by this method was diluted with ordinary *n*-butyl alcohol to a final rotation of $\alpha^{25}\text{D}$ 0.145 ± 0.005° (*l* 4). This material also was used in some previously published experiments with 1-butyl-1-*d* chlorosulfite.[14]

The loss of deuterium probably occurred in the reduction of camphor with lithium aluminum deuteride. Using equivalent amounts of reagents at the boiling point of ether, substantial unreacted camphor was recovered. The following reaction sequence is postulated to account for the observed results



The reaction of cyclopentanone with lithium aluminum hydride is reported to give initially an insoluble complex.[15] Refluxing in ether[16] or preferably tetrahydrofuran[15] is required to give good yields of cyclopentanone. We suggest that to a significant extent the enolate salt is formed which is reduced by more vigorous treatment. Reaction of cyclopentanone with lithium aluminum hydride proceeds smoothly at −80° to give good yields of cyclopentanol.[17] With lithium aluminum deuteride under these conditions, cyclopentanol-1-*d* is obtained with no evidence of isomeric deutero compounds.[18] At low temperatures enolate salt formation clearly is not important.

Camphor contains a cyclopentanone ring system and similar chemistry may be expected. It was found subsequently that reaction of camphor with equivalent amounts of lithium aluminum hydride or deuteride at low temperatures gives complete reduction without the intervention of significant amounts of enolate salts.[19]

Experimental

1-Butyl-1-*d* *p*-Nitrobenzenesulfonate (II).—To a mixture of 10 g. (0.133 mole) of 1-butanol-1-*d*, $\alpha^{25}\text{D}$ −0.140 ± 0.004° (*l* 4),[6] and 150 ml. of dry pyridine contained in a flask protected by a drying tube and immersed in an ice-salt-bath was added 39.2 g. (0.177 mole) of freshly recrystallized *p*-nitrobenzenesulfonyl chloride. After stirring magnetically in the cooling bath for 40 minutes, the mixture was poured into 150 ml. of concentrated hydrochloric acid in 700 ml. of ice and water. The precipitated solid was filtered, dried and recrystallized from benzene–cyclohexane, yielding 22.8 g. (66% yield) of light yellow crystals, m. 61.8–62.5°, $[\alpha]^{25}\text{D}$ 0.032 ± 0.009° (*c* 28.1, acetone).

Anal.[20] Calcd. for $C_{10}H_{12}DO_5NS$: C, 46.1; H + D, 5.4; N, 5.4. Found: C, 46.5; H + D, 5.4; N, 5.6.

Kinetics of Acetolysis of *n*-Butyl *p*-Nitrobenzenesulfonate.—In order to judge the time required for desired extents of reactions in the solvolyses, kinetic measurements were carried out by the following procedure: A weighed quantity of *n*-butyl *p*-nitrobenzenesulfonate was added to a weighed amount of solvent which was preheated in a thermostat. The infinity titer was calculated on the basis of these weights. The solution was placed in a thermostat and samples were withdrawn periodically, weighed and titrated potentiometrically with a standardized solution of sodium acetate in acetic acid. Instantaneous rate constants were calculated using the first-order rate equation for the first 20 to 30% of reaction. In the several cases in which points were taken after greater extents of reaction, the rate constants showed a tendency to increase gradually, probably because of the salt effect of the liberated sulfonic acid. A typical run is shown in Table III. A summary of all of the rate constants obtained is recorded in Table IV. The composition of the solvents is given in volume per cent.

TABLE III

KINETICS OF ACETOLYSIS OF *n*-BUTYL *p*-NITROBENZENESULFONATE IN 75% DIOXANE–25% ACETIC ACID AT 97.1 ± 0.1°

Time, 10^{-4} sec.	Titer	$10^6 k$, sec.$^{-1}$
0.36	0.075	2.29
1.08	.181	2.16
2.28	.349	2.08
4.85	.811	2.34
8.64	1.124	2.08
17.28	2.38	2.19
24.92	3.52	(2.42)
34.56	4.41	(2.53)
∞	7.54	..
		Av. 2.19 ± 0.08

TABLE IV

RATES OF ACETOLYSIS OF *n*-BUTYL *p*-NITROBENZENESULFONATE

Solvent	Temp., °C.	$10^5 k$, sec.$^{-1}$
90% Nitrobenzene–10% acetic acid	114.4	1.19 ± 0.10[a]
	90.8	0.105 ± .004[a]
	97.1	(.208)
75% Dioxane–25% acetic acid	97.1	.219 ± .008
75% *o*-Dichlorobenzene–25% acetic acid	97.1	.55[b]

[a] $\Delta H^{\ddagger} = 28.2 \pm 1.1$ kcal./mole; $\Delta S^{\ddagger} = -4.0 \pm 3.0$ e.u. [b] Based on only two points.

Acetolysis of 1-Butyl-1-*d* *p*-Nitrobenzenesulfonate.—Fifteen grams (0.058 mole) of 1-butyl-1-*d* *p*-nitrobenzenesulfonate was dissolved in 200 ml. of dry acetic acid which

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[14] A. Streitwieser, Jr., and W. D. Schaeffer, THIS JOURNAL, **79**, 379 (1957).

[15] W. G. Brown, "Organic Reactions," Vol. VI, J. Wiley and Sons, Inc., New York, N. Y., 1951, p. 475.

[16] J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3928 (1949).

[17] A. Streitwieser, Jr., S. Suzuki and R. C. Fahey, unpublished results; *cf.* A. Streitwieser, Jr., R. H. Jagow and S. Suzuki, THIS JOURNAL, **77**, 6713 (1955).

[18] A. Streitwieser, Jr., and R. C. Fahey, unpublished results.

[19] A. Streitwieser, Jr., and L. Reif, unpublished results.

[20] Analysis by the Microanalytical Laboratory, Department of Chemistry, University of California.

had been preheated in the thermostat maintained at 114.4 ± 0.1°. After maintaining the solution at this temperature for 24 hr., the mixture was cooled in running water and was poured with stirring into a solution of 150 g. of sodium hydroxide dissolved in 700 ml. of ice and water. The alkaline mixture was then extracted three times with 60-ml. portions of pentane. The combined pentane extracts were dried with anhydrous sodium sulfate and were distilled through a small glass spiral column to yield 4.3 ml. of material, b. 120–125°. Redistillation through the same column gave 2.5 ml. of 1-butyl-1-*d* acetate, b. 124–125°, which had α^{25}D −0.171 ± 0.003° (*l* 2). The infrared spectrum of this acetolysis product was identical with that of a sample of 1-butyl-1-*d* acetate, having α^{25}D +0.200 ± 0.004° (*l* 2)[14] which was prepared from the starting 1-butanol-1-*d* with acetyl chloride and pyridine.

In 90% Nitrobenzene–10% Acetic Acid at 114.4°.—A solution of 20 g. (0.077 mole) of II in 200 ml. of preheated 90% nitrobenzene–10% acetic acid (by volume) was maintained in a thermostat at 114.4 ± 0.1° for 24 hr. The mixture was cooled and distilled at reduced pressure through a 24-inch Vigreux column collecting material b. 32–37° (30 mm.). The distillate was poured into 200 ml. of ice-cold 10% sodium hydroxide solution and was extracted three times with pentane. The combined pentane extracts were washed with aqueous sodium hydroxide and water and were dried with anhydrous sodium sulfate. After removal of the pentane by distillation, the residue was distilled through a small glass spiral column to give 5.0 ml. of material, b. 120–125°. Redistillation through the same column gave 3.0 ml. of III, b. 123–125°, having α^{25}D −0.102 ± 0.003° (*l* 2).

The residue from the initial reduced pressure distillation above was treated with 20 ml. of acetic acid and 12.5 g. of fused sodium acetate. The mixture was maintained at 114.4° for 24 hr. After cooling, the precipitated sodium *p*-nitrobenzenesulfonate was filtered, and the filtrate was again distilled under vacuum, collecting the product b. 31–36° (25 mm.). This distillate was treated with 100 ml. of cold 10% sodium hydroxide solution and extracted with pentane as above. Distillation gave 0.7 ml. of product, b. 115–130°. This material was too small for polarimetry and was diluted with 2.5 ml. of *n*-butyl acetate and redistilled through a small glass spiral column, yielding 2.4 ml. of product, b. 124–125°, having α^{25}D −0.040 ± 0.003° (*l* 2). Infrared analysis using the C–D band showed this product to contain 24% of 1-butyl-1-*d* acetate; hence, the rotation corresponds to α^{25}D −0.167 ± 0.013° (*l* 2) or 84 ± 12% inversion of configuration for the deuterated acetate.

In 90% Nitrobenzene–10% Acetic Acid at 90.8°.—A solution of 22.8 g. (0.088 mole) of II in 200 ml. of 90% nitrobenzene–10% acetic acid was maintained in a thermostat at 90.8 ± 0.1° for 259 hr. The reaction mixture was worked up as above, yielding 5.2 ml. of product, b. 120–125°. Redistillation of this material through the glass spiral column gave 2.5 ml. of III, b. 124–125°, having α^{25}D −0.118 ± 0.005° (*l* 2).

In 75% Dioxane–25% Acetic Acid at 97.1°.—A solution of 28.0 g. (0.089 mole) of 1-butyl-1-*d* *p*-nitrobenzenesulfonate (prepared from partially deuterated butanol described below) in 200 ml. of a mixture of 75% dioxane[21] was maintained at 97.1 ± 0.1° for 113.5 hr. The reaction mixture was cooled, diluted with 200 ml. of water and was placed in an ice-box. The 7.0 g. of unreacted II which crystallized from the solution was filtered. The filtrate was extracted four times with pentane. The pentane solution was washed with aqueous sodium hydroxide and water and was immersed in a Dry Ice–acetone-bath for 1 hr. The precipitated solid (mostly dioxane) was filtered in the cold. The filtrate was lyophilized at room temperature for several hours with the pressure gradually reduced to 2 mm., collecting the product in a Dry Ice–acetone trap. The pentane solution in the trap was distilled through the glass spiral column to give 2.5 ml. of 1-butyl-1-*d* acetate, b. 124–125°, having α^{25}D 0.099 ± 0.004° (*l* 2).

The II recovered from this reaction was added to a hot solution of 8.0 g. (0.098 mole) of fused sodium acetate in 70 ml. of dry methanol. After refluxing for 5 hr., the mixture was cooled to room temperature and was diluted with 100 ml. of water. The aqueous mixture was extracted three times with pentane, and the combined pentane extracts were dried with sodium sulfate. Distillation through the glass spiral column gave 1.2 ml. of material, b. 115–125°. Redistillation through a micro-distilling apparatus gave 0.5 ml. of 1-butyl-1-*d* acetate, b. 120–125°, having α^{25}D 0.098 ± 0.005° (*l* 1), corresponding to 92 ± 5% inversion of configuration.

In 75% *o*-Dichlorobenzene–25% Acetic Acid at 97.1°.—A solution of 15.0 g. (0.058 mole) of II (prepared from partially deuterated butanol below) in a mixture of 105 ml. of freshly distilled *o*-dichlorobenzene and 35 ml. of dry acetic acid was maintained at 97.1 ± 0.1° for 96 hr. After cooling to room temperature, the mixture was distilled under reduced pressure through a 24-inch Vigreux column, collecting material b. 32–38° (27 mm.). The distillate was diluted with 100 ml. of pentane, and the mixture was washed with water. The aqueous wash was re-extracted twice with pentane, and the combined pentane phases were washed with aqueous sodium hydroxide and water and were dried with anhydrous sodium sulfate. Distillation through a small glass spiral column gave 1.8 ml. of III, b. 123–125°, having α^{25}D 0.100 ± 0.004° (*l* 1), corresponding to 94 ± 6% inversion of configuration.

Optical Stability of 1-Butyl-1-*d* Acetate toward Solvolysis Conditions.—A solution of 16.1 g. (0.085 mole) of *p*-toluenesulfonic acid monohydrate and 8.65 g. (0.085 mole) of acetic anhydride in 190 ml. of the solvent mixture was brought to the required temperature; 5 ml. of optically active 1-butyl-1-*d* acetate was added to the mixture and the solution was maintained at the desired temperature for the appropriate length of time. After cooling, the mixtures were worked up in manners similar to those described in the corresponding solvolysis reactions. After removing the bulk of the solvent, the butyl acetate was extracted into pentane, washed, dried and distilled. The distillation through the glass spiral column gave 2.5–3.0 ml. of 1-butyl-1-*d* acetate, b. 123–125°. The solvents, temperatures, times of reactions and rotations are summarized in Table II.

Optically Active Partially Deuterated 1-Butanol-1-*d*.—A solution of 122 g. (0.80 mole) of (+)-camphor dissolved in 300 ml. of dry ethyl ether was added to a stirred suspension of 8.0 g. (0.19 mole) of lithium aluminum deuteride in 500 ml. of dry ethyl ether at a rate sufficient to maintain gentle reflux. After refluxing for 2 hr., dilute hydrochloric acid was added. The organic phase was separated and was dried with anhydrous sodium sulfate. Evaporation of the ether left 119 g. of solid having $[\alpha]^{25}$D +0.96° (*c* 10.4, benzene). The infrared spectrum of the product showed the presence of a considerable amount of unreacted camphor by the presence of a fairly intense carbonyl band.

The deuterated isoborneol–borneol–camphor mixture prepared above in 300 ml. of dry ether was added to a solution of the Grignard reagent prepared from 98.5 g. (0.80 mole) of *n*-propyl bromide and 500 ml. of dry ether. Because the alkoxymagnesium bromide salts are insoluble in ether, 800 ml. of dry benzene was added as the ether was removed by a 2-foot Vigreux column. The resulting solution was cooled in an ice-bath, and 50.0 g. (0.695 mole) of freshly distilled butyraldehyde was added. After stirring for 1 hr. at room temperature, an additional 20.0 g. (0.278 mole) of butyraldehyde was added, and stirring was continued for an additional 1.5 hr. After the reaction was stopped by the addition of excess dilute hydrochloric acid, the organic phase was separated, and the aqueous phase was extracted three times with benzene. The combined organic layers were dried with anhydrous sodium sulfate and were distilled through a 16-plate Oldershaw column to remove the benzene. Distillation of the residue yielded 16.0 g. of crude deutero-butanol, b. 110–119°.

The crude deutero-butanol was heated with 45.0 g. (0.304 mole) of phthalic anhydride for 15 hr. at 105–110°. The crude hydrogen phthalate ester was dissolved in 1200 ml. of water containing 55 g. of potassium carbonate. The clear solution was acidified with hydrochloric acid, and the precipitated oil which solidified on standing was filtered and dried. After two crystallizations from benzene–cyclohexane, the 40.5 g. of ester had $[\alpha]^{25}$D −0.238 ± 0.008° (*c* 29.3, benzene). After a third crystallization, the 37.0 g. of ester had $[\alpha]^{25}$D −0.229 ± 0.010° (*c* 25.6, benzene).

The thrice recrystallized hydrogen phthalate was reduced with 20.0 g. of lithium aluminum hydride in the usual way. Distillation of the product through a small glass spiral

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[21] Dioxane was purified by the method of L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 368.

column yielded 14.0 ml. of deutero-butanol having $\alpha^{25}D$ 0.154 ± 0.004° (*l* 2), d^{25}_4 0.8118. The intensity of the C–D band at 2200 cm.$^{-1}$ was compared with that of authentic 1-butanol-1-*d* and indicated the presence of 0.56 deuterium atom per molecule. The density measurement corresponds to 0.54 deuterium atom per molecule, assuming constancy of molecular volume. The 14.0 ml. of this deutero-butanol was diluted with *n*-butyl alcohol to a final volume of 30.0 ml., having $\alpha^{25}D$ 0.145 ± 0.005° (*l* 4). The deutero-butyl acetate prepared from this alcohol and acetyl chloride and pyridine had $\alpha^{25}D$ −0.213 ± 0.004° (*l* 2).

BERKELEY, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Decomposition of Peroxycarbamates and their Efficiency as Initiators in Vinyl Polymerization[1,2]

BY EUGENE L. O'BRIEN, F. MARSHALL BERINGER AND ROBERT B. MESROBIAN[3]

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t-Butyl and cumyl N-phenylperoxycarbamates have been prepared by the reaction of *t*-butyl and cumyl hydroperoxides with phenyl isocyanate, and *t*-butyl N-α-naphthylperoxycarbamate was prepared by the reaction of *t*-butyl hydroperoxide with α-naphthyl isocyanate. The decompositions of the first two N-phenylperoxycarbamates have been measured in several solvents between 50 and 90° and found to be first-order reactions governed by the specific rate constants $k_d = 1.52 \times 10^{16} \exp(32{,}500/RT)$ and $k_d = 1.26 \times 10^{14} \exp(28{,}100/RT)$, sec.$^{-1}$, respectively. In the case of *t*-butyl N-α-naphthylperoxycarbamate the tendency for induced decomposition is too great to enable an accurate determination of the decomposition rate expression. From polymerization studies of styrene monomer the initiation efficiencies of the N-phenyl derivatives are calculated to be 0.95 and 0.73, respectively, while the N-α-naphthyl derivative shows a wide variation of efficiency with catalyst concentration. Measurements of carbon dioxide evolution in several solvents indicate that nearly one mole of gas is evolved per mole of peroxycarbamate decomposed. Thus, it is concluded that both the *t*-butoxy and the phenylamino radicals from *t*-butyl N-phenylperoxycarbamate efficiently initiate chains while the radicals from the other two peroxycarbamates are less efficient.

It is well known that organic isocyanates react with compounds having active hydrogens to produce addition products. However, not until recent years has the preparation of peroxycarbamates from organic hydroperoxides and isocyanates been reported.[4] This study describes the preparation of three peroxycarbamates and their decomposition in various solvents including styrene monomer. By determination of the efficiency of initiation of styrene polymerization, it is possible to investigate the reactivity of radical intermediates obtained during decomposition.

Experimental[5]

Reagents.—*t*-Butyl hydroperoxide (Lucidol Div., Novadel–Agene Corp.) of 67% purity was added to a 25% solution of sodium hydroxide below 30°. Crystals of the sodium salt of the hydroperoxide were collected and washed twice with benzene. The crystals were then dissolved in distilled water, and the *p*H was adjusted to 7.5. The peroxide was extracted from solution with petroleum ether. *t*-Butyl hydroperoxide of 98% purity was obtained by distilling the petroleum ether under reduced pressure at room temperature. Cumene hydroperoxide was purified by an essentially similar procedure.

Phenyl isocyanate, b.p. 78° at 40 mm., and α-naphthyl isocyanate, b.p. 140° at 12 mm., were obtained by distillation under nitrogen and used immediately. Styrene (Dow Chemical Co.) was washed with 5% aqueous sodium hydroxide, dried over anhydrous magnesium sulfate and distilled under nitrogen; b.p. 40–42° (20 mm.). All other reagents were of highest available purity and were used as received.

t-Butyl **N-Phenylperoxycarbamate.**—One-tenth mole each of *t*-butyl hydroperoxide and phenyl isocyanate and a few drops of pyridine were dissolved in benzene, and the temperature was maintained at 30°. After 15 minutes the solution became yellow, and the benzene was removed under reduced pressure at room temperature. The product was twice recrystallized from petroleum ether, b.p. 28–38°, to give colorless crystals, m.p. 83° dec., which turned yellow if allowed to stand at room temperature. The peroxycarbamate was stored at Dry Ice temperature.

Alternatively, the hydroperoxide was added to phenyl isocyanate in the presence of pyridine catalyst. After 15 minutes there were formed crystals of the peroxycarbamate, which could be extracted with cold benzene, leaving a residue of *sym*-diphenylurea. The benzene was removed, and the peroxide was recrystallized from petroleum ether.

Iodometric analysis of various samples of the peroxycarbamate indicated 95–97% purity.

Anal. Calcd. for $C_{11}H_{15}NO_3$: N, 6.69. Found: N, 6.64.

Cumyl N-Phenylperoxycarbamate.—Equimolar amounts of phenyl isocyanate and cumene hydroperoxide were placed in a beaker containing 100 ml. of benzene and several drops of pyridine. After 15 minutes, the benzene was removed under reduced pressure at room temperature. The residue was crystallized twice from petroleum ether, b.p. 28–30°, to give a product of m.p. 72°, decomposing at 82°. Iodometric analysis of the compound gave a purity of 95%.

Anal. Calcd. for $C_{16}H_{17}NO_3$: N, 5.16. Found: N, 5.35.

t-Butyl **N-α-Naphthylperoxycarbonate.**—A solution of one-tenth mole each of *t*-butyl hydroperoxide and α-naphthyl isocyanate, 5 ml. of benzene and a drop of pyridine deposited a solid after 15 minutes. The solid was collected and extracted with petroleum ether, b.p. 28–30°. The insoluble residue was di-α-naphthylurea, m.p. 297–298°. After the extract was cooled to −50° and allowed to warm to 0°, the petroleum ether was removed by decantation from an oily solid, impure *t*-butyl N-α-naphthylperoxycarbonate. The procedure was repeated several times with fresh petroleum ether. The peroxycarbonate as recovered was of 98% purity, as determined iodimetrically.

Anal. Calcd. for $C_{15}H_{17}NO_3$: N, 5.41. Found: N, 5.68.

Procedures.—Solutions of the peroxycarbamates were sealed in ampules that had been deoxygenated by flushing with prepurified nitrogen (Matheson Co.) bubbled through xylene and a solution of benzophenone containing suspended potassium metal. After specified time intervals in a waterbath, aliquots of each ampule were pipetted into 20–30 ml. of glacial acetic acid. After aqueous potassium iodide had

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(2) This paper is taken from a doctoral dissertation of Eugene L. O'Brien.

(3) To whom inquiries about this paper should be sent. Central Research and Engineering Division, Continental Can Co., Inc., 7622 South Racine Ave., Chicago 20, Ill.

(4) A. G. David and K. J. Hunter, *J. Chem. Soc.*, 1808 (1953).

(5) Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.