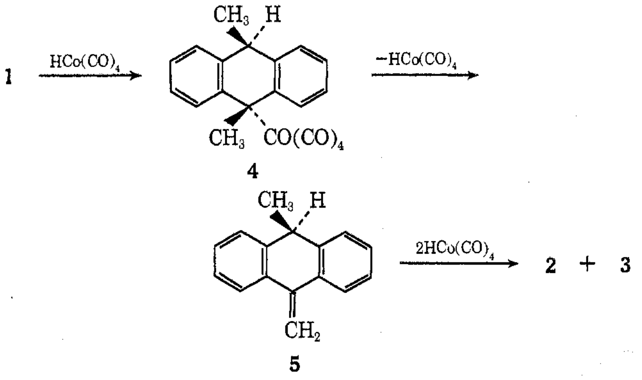
SCHEME I

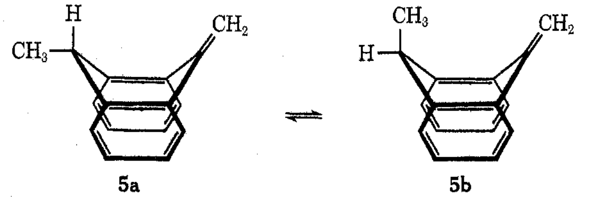


Markovnikov addition is also possible. In an experiment with the structurally related 1,1-diphenylethene, it was shown that the reaction proceeds smoothly and relatively rapidly with $HCo(CO)_4$ to give 1,1-diphenylethane. It is likely that this reaction proceeds by anti-Markovnikov addition

$$Ph_2C{=}CH_2 \longrightarrow Ph_2CHCH_2Co(CO)_4 \longrightarrow Ph_2CHCH_3$$

The reaction with **5** may proceed similarly. Preliminary results with $DCo(CO)_4$ showed, as expected, the presence of $D_3$ in both **2** and **3**. However, in addition to $D_3$ (~10%), there was substantial $D_1$ and $D_2$ present; the deuterium experiments are not clear-cut and need further investigation.

At this time we have no firm explanation for the differences in cis/trans ratio found under the different conditions shown in Table I. The intermediate **5**, if indeed it does exist, may be present in isomeric[6] form



**5a** **5b**

The equilibrium concentration of these isomers may change with temperature and the ratio of exo/endo attack by $HCo(CO)_4$ may be different for each isomer and also be affected by temperature.

**Registry No.**—**1**, 781-43-1; **2**, 13417-34-0; **3**, 13417-35-1; cobalt hydrocarbonyl, 16842-03-8.

**Acknowledgment.**—The authors are grateful to the Houdry Process and Chemical Division of Air Products and Chemicals, Inc., for generous support of this research in the form of a fellowship to Paul D. Taylor. Compound **2** was kindly furnished by Dr. David Morgan.

[6] S. J. Cristol, *Accounts Chem. Res.*, **4**, 393 (1971).

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# The Polar and Steric Substituent Constants for an Alkylperoxy Group and Related Ether Groups

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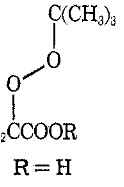
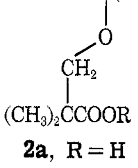
*Received May 3, 1972*

Rates of acid-catalyzed esterification were measured for 2-*tert*-butylperoxy-2-methylpropanoic acid (**1a**), 2,2-dimethyl-3-*tert*-butoxypropanoic acid (**2a**), and 2-methyl-2-neopentoxypropanoic acid (**3a**). Rates of the basic hydrolysis of the methyl esters of these acids were obtained and from the kinetic data from these two types of reactions $\sigma^*$ and $E_s$ values were calculated. The $\sigma^*$ and $E_s$ values for the substituents $(CH_3)_3COOC(CH_3)_2$, $(CH_3)_3COCH_2C(CH_3)_2$, and $(CH_3)_3CCH_2OC(CH_3)_2$ are +0.520 and −1.96, −0.166 and −1.57, and +0.178 and −1.43, respectively. These values are discussed with relationship to each other and to analogous groups that are reported in the literature. The basic hydrolysis of methyl 2-*tert*-butylperoxy-2-methylpropanoate (**1b**) yields *tert*-butyl alcohol and acetone. The origin of these fragmentation products is discussed by considering the rate of *tert*-butyl alcohol formation from **1b**, the rate of disappearance of **1b**, and the rate of disappearance of ethyl 2-*tert*-butylperoxy-2-methylpropanoate (**5**) in 85% ethanol. The basic hydrolysis of **1b** was considered as a possible source of excited-state carbonyl products. However, the lack of light emission from an acceptor (fluorescein) added to the reaction mixture indicates that excited-state carbonyl species are not produced.

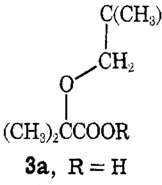
As part of a program to evaluate neighboring peroxide group reactions[2] it was necessary to determine the polar substituent constant[3,4] $\sigma^*$ for an alkylperoxy group. To our knowledge there are no previous reports of such a substituent constant. Polar substituent constants for stereochemically similar ether groups were required as well and they are reported here. The $\sigma^*$ values were obtained from the rates of acid-catalyzed esterification of 2-*tert*-butylperoxy-2-methylpropanoic acid (**1a**), 2,2-dimethyl-3-*tert*-butoxypropanoic acid (**2a**), and 2-methyl-2-neopentoxypropa-


$(CH_3)_3C{-}O{-}O{-}C(CH_3)_2COOR$

**1a**, R = H
**b**, R = $CH_3$


$(CH_3)_3C{-}O{-}CH_2{-}C(CH_3)_2COOR$

**2a**, R = H
**b**, R = $CH_3$


$(CH_3)_3C{-}CH_2{-}O{-}C(CH_3)_2COOR$

**3a**, R = H
**b**, R = $CH_3$

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[1] National Science Foundation Undergraduate Research Participant, summer, 1969.

[2] (a) W. H. Richardson and V. F. Hodge, *J. Amer. Chem. Soc.*, **93**, 3996 (1971); (b) W. H. Richardson, J. W. Peters, and W. P. Konopka, *Tetrahedron Lett.*, 5531 (1966).

[3] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

[4] We have retained the $\sigma^*$ symbol for convenience in estimating our neighboring peroxide group rate data, which will be reported later. It has been suggested that the $\sigma^*$ constant should be replaced by other substituent constants such as $\sigma_I$[5] and field and resonance constants.[6]

[5] C. D. Ritchie and W. F. Sager, "Progress in Physical Organic Chemistry," Vol. 2, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Jr., Ed., Interscience, New York, N. Y., 1964, p 323.

[6] C. G. Swain and E. C. Lupton, *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

noic acid (**3a**) in methanol and from the rates of the basic hydrolysis of the corresponding methyl esters (**1b**, **2b**, **3b**) in 85% ethanol. Since fragmentation products result from the basic hydrolysis of **1b**, our interest in these reactions[7] led to a study of the mechanism of this reaction.

The rates of esterification of the acids were measured by the same procedures that were employed previously.[8] The kinetic data must be treated to account for the formation of water in the esterification reaction. For hydrogen chloride catalyzed esterification (as used here), the derived rate coefficient is given in eq 1, where $a$ =

$$k = \frac{(r + a)\ln\left(\frac{a}{a - x}\right) - x}{[\mathrm{HCl}]rt} \qquad (1)$$

initial carboxylic acid concentration, $x$ = concentration of ester formed at time $t$, and $r$ = a constant which is defined by eq 2. For esterification in methanol R in eq 2

$$r = \frac{[\mathrm{ROH_2^+}][\mathrm{H_2O}]}{[\mathrm{H_3O^+}]} \qquad (2)$$

is $CH_3$ and values of $r$ are temperature dependent and they are reported[8a,b] to be 0.11 at 0°, 0.20 at 20°, 0.25 at 30°, 0.32 at 40°, and 0.42 at 50°. We have used the reported $r$ value at 30° and processed the data with a least-squares computer program to give the rate coefficients that are shown in Table I. Acetic acid was included in our measurements in order to ensure a self-consistent set of data and it is in reasonable agreement with the value of 81.4 × $10^{-3}$ l. $mol^{-1}$ $sec^{-1}$ reported by Smith.[8b] Since relative rate coefficients will be used to calculate substituent constants, this small discrepancy will not be troublesome. Data for the basic hydrolysis of esters **1b**, **2b**, **3b**, and methyl acetate are given in Table II. Since the peroxy-substituted ester **1b** yields the fragmentation products *tert*-butyl alcohol, acetone, and carbon dioxide (as carbonate), the titrimetric method that was used for the other esters could not be employed. For this reason, the overall rate of hydrolysis of **1b** was determined by following the appearance of *tert*-butyl alcohol by gas–liquid chromatography (glc).

TABLE I

KINETIC DATA FOR THE HYDROGEN CHLORIDE[a] CATALYZED ESTERIFICATION OF CARBOXYLIC ACIDS IN METHANOL AT 30.00°

| Acid | [Acid], *M* | | $10^3k$,[b] l. $mol^{-1}$ $sec^{-1}$ |
|---|---|---|---|
| $CH_3COOH$ | 0.486 | | 71.6 ± 0.6 |
| | 0.510 | | 72.3 ± 0.9 |
| | | Av | 72.0 ± 0.4 |
| **1a** | 0.505 | | 0.799 ± 0.005 |
| **2a** | 0.505 | | 1.91 ± 0.02 |
| | 0.452 | | 1.95 % 0.03 |
| | | Av | 1.93 ± 0.02 |
| **3a** | 0.448 | | 2.77 ± 0.03 |
| | 0.448 | | 2.65 ± 0.02 |
| | | Av | 2.71 ± 0.06 |

[a] [HCl] = 0.00706 *M*. [b] Individual rate coefficients are given with probable error and average values with average error.

TABLE II

KINETIC DATA FOR THE BASIC HYDROLYSIS OF ESTERS IN 85% AQUEOUS ETHANOL AT 25.00°

| Ester | $10^2$[Ester], *M* | $10^2[OH^-]$, *M* | | $10^3k$,[a] l. $mol^{-1}$ $sec^{-1}$ |
|---|---|---|---|---|
| $CH_3COOCH_3$[b] | 2.30 | 4.65 | | 8.46 ± 0.08 |
| | 2.72 | 4.65 | | 8.67 ± 0.08 |
| | 2.81 | 4.65 | | 8.26 ± 0.05 |
| | | | Av | 8.46 ± 0.14 |
| **1b**[c] | 4.52 | 41.5 | | 1.86 ± 0.06 |
| | 4.58 | 48.2 | | 1.82 ± 0.09 |
| | | | Av | 1.84 ± 0.02 |
| **2b**[b] | 1.49 | 6.07 | | 0.0907 ± 0.0022 |
| | 1.55 | 6.07 | | 0.0853 ± 0.0029 |
| | | | Av | 0.0880 ± 0.0027 |
| **3b**[b] | 1.39 | 6.08 | | 0.890 ± 0.012 |
| | 1.45 | 6.08 | | 0.887 ± 0.016 |
| | 1.85 | 6.08 | | 0.873 ± 0.021 |
| | | | Av | 0.883 ± 0.007 |

[a] Individual and average rate coefficients are given with probable and average error, respectively. [b] Titrimetric data. [c] Glc data by following the appearance of *tert*-butyl alcohol. Calculated from the pseudo-first-order rate coefficient by $k = k_\psi/[\mathrm{OH^-}]$.

Polar substituent constants were calculated from the data in Tables I and II with the well-known equation (eq 3)[3] for $\sigma^*$. These values, along with the steric

$$\sigma^* = \frac{1}{2.48}\,[\log (k/k_0)_\mathrm{B} - \log (k/k_0)_\mathrm{A}] \qquad (3)$$

substituent constants $[E_s \equiv \log (k/k_0)_\mathrm{A}]$, are given in Table III. The $\sigma^*$ values given in Table III are not directly comparable to reported values for similar groups. In order to make more direct comparisons, we have used the additivity principle[9] to convert the $C(CH_3)_2$ terminus of the groups in Table III to a $CH_2$ terminus. Thus, by the additivity principle, $\sigma^*$ $[(CH_3)_3CCH_2OCH_2]$ = $\sigma^*$ $[(CH_3)_3CCH_2OC(CH_3)_2]$ − $2\sigma^*$ $(CH_3CH_2)$ = 0.378. The smaller value of $\sigma^*$ $[(CH_3)_3CCH_2OCH_2]$, compared to $\sigma^*$ $(CH_3OCH_2)$ (0.520),[3] is not unreasonable considering the approximate calculation and the observation that substituent effects are transmitted through oxygen as seen by $\sigma^*$ $(C_6H_5OCH_2)$ = 0.850[3] *vs.* $\sigma^*$ $(CH_3OCH_2)$ = 0.520. This latter effect can be seen again in the comparison of the $\sigma^*$ values of $(CH_3)_3CCH_2OC(CH_3)_2$ and $(CH_3)_2COCH_2C(CH_3)_2$ in Table III. For convenience of comparison, the *gem*-dimethyl terminus is converted to a methylene terminus by the additivity principle, where $\sigma^*$ $[(CH_3)_3CCH_2OCH_2]$ = 0.378 and $\sigma^*$ $[(CH_3)_3COCH_2CH_2]$ = 0.034. If a fall-off factor of 0.34[9,10] is

TABLE III

POLAR AND STERIC SUBSTITUENT CONSTANTS CALCULATED FROM ACID-CATALYZED ESTERIFICATION OF CARBOXYLIC ACIDS AND BASIC HYDROLYSIS OF ESTERS

| Substituent | $\sigma^*$ | $E_s$ |
|---|---|---|
| $(CH_3)_3COOC(CH_3)_2$ | +0.520 | −1.96 |
| $(CH_3)_3COCH_2C(CH_3)_2$ | −0.166 | −1.57 |
| $(CH_3)_3CCH_2OC(CH_3)_2$ | +0.178 | −1.43 |

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(7) (a) W. H. Richardson and R. S. Smith, *J. Amer. Chem. Soc.*, **89**, 2230 (1967); (b) *ibid.*, **91**, 3610 (1969); (c) W. H. Richardson and T. C. Heesen, *J. Org. Chem.*, **37**, 3416 (1972).

(8) (a) K. L. Loening, A. B. Garrett, and M. S. Newman, *J. Amer. Chem. Soc.*, **74**, 3929 (1952); (b) H. A. Smith, *ibid.*, **61**, 254 (1939); (c) H. Goldschmidt, H. Haaland, and R. S. Melbye, *Z. Phys. Chem. (Leipzig)*, **143**, 278 (1929); (d) H. Goldschmidt and R. S. Melbye, *ibid.*, **143**, 139 (1929); (e) H. Goldschmidt and A. Thuesen, *ibid.*, **81**, 30 (1912); (f) H. Goldschmidt and O. Udby, *ibid.*, **60**, 728 (1907).

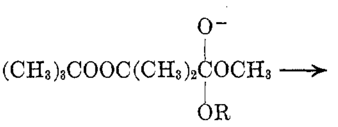
(9) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 224.

(10) This is the most common value for the fall-off factor, but other values have been suggested.[11]

(11) J. C. McGowan, *J. Appl. Chem.*, **10**, 312 (1960).

used, one predicts $\sigma^*$ $[(CH_3)_3CCH_2OCH_2CH_2] = 0.13$ $(0.34 \times 0.378)$, which is significantly larger than the estimated 0.034 value for $\sigma^*$ $[(CH_3)_3COCH_2CH_2]$, which differs by replacement of *tert*-butyl for neopentyl in the R portion of the alkoxy group (RO). Since polar effects of the R portion of the RO group are transmitted through oxygen and since *tert*-butyl is more electron-releasing than neopentyl,[12] a decrease in $\sigma^*$ from 0.13 for $(CH_3)_3CCH_2OCH_2CH_2$ to 0.034 for $(CH_3)_3COCH_2CH_2$ is not unreasonable. By the same reasoning, the values of $\sigma^*$ for $(CH_3)_3COOC(CH_3)_2$ (0.520) and $(CH_3)_3CCH_2OC(CH_3)_2$ (0.178) are in qualitative accord, since an electron-withdrawing R group in $ROC(CH_3)_2$ should cause $\sigma^*$ to be more positive. The values for the steric parameters ($E_s$) of $(CH_3)_3COCH_2C(CH_3)_2$ and $(CH_3)_3CCH_2OC(CH_3)_2$ appear reasonable compared to the $E_s$ value of $-1.54$ for $CH_3C(CH_3)_2$.[3] A formal interpretation of $E_s$ would suggest that the *tert*-butylperoxy group is larger than either the $(CH_3)_3COCH_2$ or $(CH_3)_3CCH_2O$ groups. However, such formal interpretation of $E_s$ values for groups, other than for hydrocarbon groups, may be unwarranted.[13,14]

Previously we found that the peroxy-substituted acid **1a** undergoes a fragmentation reaction with base to give quantitative yields of *tert*-butyl alcohol and acetone.[7a,b] The basic hydrolysis of the methyl ester of this acid (**1b**) also yields these products. Although basic hydrolysis of **1b** to the acid **1a** followed by fragmentation of **1a** would explain the products, it is possible that fragmentation could occur entirely from the tetrahedral intermediate **4** formed in the ester solvolysis.



$$(CH_3)_3COOC(CH_3)_2\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle OR}{|}}{C}}OCH_3 \longrightarrow (CH_3)_3CO^- + CH_3COCH_3 + ROCOOCH_3 \quad (4)$$

**4a,** R = H
**b,** R = $C_2H_5$

Analogous mechanisms were considered for the basic decomposition of $\alpha$-hydroperoxy esters, but it was not determined which mechanism was operative.[15] Our data do not allow an unequivocal answer to this question, but we can state that eq 4 is not the exclusive reaction path for **4**. It is seen from Table II that the rate of *tert*-butyl alcohol formation ($k = 1.84 \times 10^{-3}$ l. mol$^{-1}$ sec$^{-1}$) is slower than the rate of methyl ester disappearance (Table IV) in the basic hydrolysis of **1b** in 85% ethanol. This can be explained by transesterification of **1b** to give the ethyl ester **5** in which **4b** is an intermediate, as shown in Scheme I. A steady-state treatment of this scheme gives $k_{1b} = k_B(1 + k_t/k_5R) - k_tR$ and $k_t = (k_5/k_B)k_{Me}(1/R + 1) - k_5 \cdot (1/R)$, where $R = [C_2H_5O^-]/[OH^-]$, $k_5 = 0.996 \times 10^{-3}$ l. mol$^{-1}$ sec$^{-1}$ (the rate coefficient for disappearance of **5**), $k_B = 1.84 \times 10^{-3}$ l. mol$^{-1}$ sec$^{-1}$ (the rate coefficient for appearance of *tert*-butyl alcohol), and $k_{Me} = 3.58 \times 10^{-3}$ l. mol$^{-1}$ sec$^{-1}$ (the rate coefficient for the overall disappearance of **1b**). With $R \cong 2$ (calculated from the ionization constants of ethanol and water and accounting for the composition of the solvent),[16] the above two equations yield $k_{1b} = 5.93 \times 10^{-3}$ l. mol$^{-1}$ sec$^{-1}$ and $k_t = 2.41 \times 10^{-3}$ l. mol$^{-1}$ sec$^{-1}$ so that the relative velocities, $v_{1b}/v_t = (k_{1b}/k_t)(1/R) = 1.2$. The transesterification process is further verified by the glc observation that the ethyl ester **5** appears during the course of the basic hydrolysis of **1b**. Since transesterification proceeds through intermediate **4b**, it is clear that this intermediate does not undergo exclusively fragmentation by eq 4. This suggests that the intermediate in the basic hydrolysis of **1b** (*i.e.*, **4a**) does not undergo exclusively fragmentation either and thus *tert*-butyl alcohol and acetone arise in part from the basic fragmentation of the acid **1a**.

Scheme I

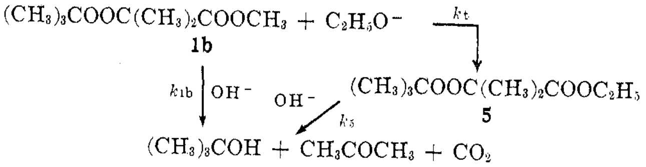


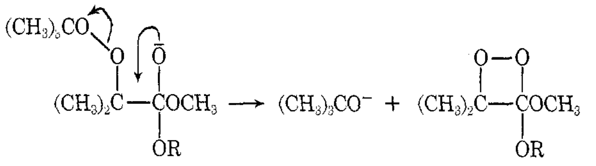
Table IV

Kinetic Data for the Rate of Disappearance of Methyl and Ethyl 2-*tert*-Butylperoxy-2-methylpropanoate during the Basic Hydrolysis in 85% Aqueous Ethanol at 25.00°

| Ester | $10^2$[Ester], *M* | [OH⁻], *M* | $10^3k$,[a] l. mol$^{-1}$ sec$^{-1}$ |
|---|---|---|---|
| **1b** | 5.12 | 0.451 | 3.64 ± 0.11 |
| | 5.12 | 0.452 | 3.52 ± 0.07 |
| | | | Av 3.58 ± 0.06 |
| **5** | 5.13 | 0.457 | 0.996 ± 0.022 |

[a] Individual rate coefficients are given with probable error. The average rate coefficient is given with average error. Glc data are used to obtain the rate coefficients.

The possibility of generating excited-state carbonyl products from the basic hydrolysis of **1b** was pursued.[18] Providing that the intermediates are of sufficiently high energy, the resulting carbonyl products from **1b** could be produced in an excited state. Intermediates to consider are the carboxylate anion of **1a** and **4a** or **4b**. All of these intermediates can give carbonyl products, although this reaction was shown above not to be exclusive reaction path of the latter two species. Rather than directly producing carbonyl species from **4a** or **4b**, these intermediates could produce 1,2-dioxetanes (eq 5), which are known to undergo decomposition to produce excited-state carbonyl species.[19] To detect the presence of excited-state carbonyl species, fluorescein was used as an acceptor from which light emission can be detected.[2a] Under conditions where



**4** (R = H or $C_2H_5$) **6** (5)

$$\mathbf{6} \longrightarrow [CH_3COCH_3 + ROCOOCH_3]^* \quad (6)$$

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[12] $\sigma^*$ $(t\text{-}C_4H_9) = -0.300$, $\sigma^*$ $(t\text{-}C_4H_9CH_2) = -0.165$.[3]

[13] P. R. Wells, "Linear Free Energy Relationships," Academic Press, New York, N. Y., 1968, p 42.

[14] K. Bowden, *Can. J. Chem.*, **44**, 661 (1966).

[15] M. Avramoff and Y. Sprinzak, *J. Amer. Chem. Soc.*, **85**, 1655 (1963).

[16] $R = (K_a^{C_2H_5OH}/K_a^{H_2O})([EtOH]/[H_2O]) = (\sim 1)$[17]$(2) = 2$.

[17] P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, **82**, 795 (1960).

[18] See ref 7c for a similar consideration in the basic fragmentation of 2-*tert*-butylperoxy-2-methyl-1-propanol.

[19] See W. H. Richardson, M. B. Yelvington, and H. E. O'Neal, *J. Amer. Chem. Soc.*, **94**, 1619 (1972), and references cited therein.

light emission was detected from the basic decomposition of chloro-*tert*-butyl hydroperoxide (where 3,3-dimethyl-1,2-dioxetane is an intermediate) no light emission was detected from the basic hydrolysis of **1b** It may be concluded that **6** is not produced to a significant extent in this reaction and that other intermediates in the reaction are not of sufficiently high energy to give excited-state carbonyl products.

## Experimental Section[20]

**Materials.**—Methanol (ACS, reagent) was purified by refluxing over magnesium turnings with a catalytic amount of iodine followed by distillation.[21] The methanolic hydrogen chloride solution, used for acid-catalyzed esterification of the carboxylic acids, was prepared by bubbling anhydrous hydrogen chloride gas (Matheson) into methanol. The resulting solution was titrated with standard sodium hydroxide solution and the hydrogen chloride concentration was adjusted by adding the appropriate amount of methanol. The 85% ethanol was prepared by mixing 743.54 g of absolute ethanol (U.S. Industrial Chemicals, reagent grade) and 131.3 g of boiled distilled water. The stock base solution in 85% ethanol was prepared by mixing 1085 g of absolute ethanol, 185 g of boiled distilled water, and 8.00 g of carbonate-free 18 *M* sodium hydroxide solution. The resulting solution was stored in polyethylene bottles and periodically standardized against potassium acid phthalate to a phenolphthalein end point. The preparations of 2-*tert*-butylperoxy-2-methylpropanoic acid (**1a**) and 2-methyl-2-neopentoxypropanoic acid (**3a**) were described previously.[7b]

**Methyl 2-*tert*-Butylperoxy-2-methylpropanoate (1b).**—The acid **1a** (9.50 g, 54.0 mmol) was dissolved in 10 ml of ice-cold ether and treated with freshly generated diazomethane until the persistence of the yellow color of diazomethane indicated that all of the acid had undergone reaction. Diazomethane was prepared by adding dropwise a solution of 15.0 g (70.0 mmol) of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald, Aldrich Chemical Co.) in 100 ml of ether to 3.00 g of potassium hydroxide in a solution of 3.3 ml of water and 15 ml of 95% ethanol contained in the pot of a distilling apparatus, which was heated to 65°. The diazomethane distilled over with the ether into the receiver, which contained **1a**. After the reaction was completed, the ether was distilled at atmospheric pressure and then the product **1b** was distilled at 40° (1 mm), 6.48 g, 63% yield. The ir ($CCl_4$ solution) of **1b** showed the following significant absorptions: 2930, 1725, 1465, 1280, 1190, 1140, and 875 $cm^{-1}$. The nmr ($CCl_4$ solution) spectrum consisted of the following absorptions: $(CH_3)_3C$, 1.18, s, 9; $(CH_3)_2C$, 1.37, s, 6; and $COOCH_3$, 3.57, s, 3.

*Anal.* Calcd for $C_9H_{18}O_4$: C, 56.82; H, 9.53. Found: C, 57.02; H, 9.66.

**3-*tert*-Butoxy-2,2-dimethylpropanoic Acid (2a).**—3-*tert*-Butoxy-2,2-dimethylpropyl alcohol[22] (10.0 g, 63.0 mmol) was added dropwise to a stirred solution of chromium trioxide (20.0 g, 200 mmol) in 180 ml of acetic acid and 20 ml of water at room temperature. The solution was stirred for 12 hr, then diluted with 120 ml of water and extracted with five 20-ml portions of carbon disulfide. After drying over sodium sulfate, the carbon disulfide was allowed to evaporate, leaving 5.90 g (54% yield) of white crystals, mp 60.8–64.0°. These crystals of **2a** were sublimed three times at 70° (1 mm) and then dried under vacuum with phosphorus pentoxide for 2 days, mp 64.5–65.5° (5.30 g, 44% yield). The ir ($CCl_4$ solution) showed bands at 3400–3050 (broad), 2970–2860, 1700, 1475, 1250, 1200, 1090, 900, and 865 $cm^{-1}$. Absorptions in the nmr ($CCl_4$ solution) spectrum were observed at $(CH_3)_3C$ and $(CH_3)_2C$, 1.165 and 1.173, two singlets, 17; $CH_2$, 3.32, s, 2; and COOH, 12.0, s, 1.

*Anal.* Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 62.22; H, 10.26.

**Methyl 3-*tert*-Butoxy-2,2-dimethylpropanoate (2b).**—This ester was prepared by the same procedure that was used for **1b**. The ir ($CCl_4$ solution) of the product, bp 69° (9 mm), showed the following absorptions: 2975, 1730, 1470, 1230, 1190, 1145, 1085, 965, and 895 $cm^{-1}$. The nmr ($CCl_4$ solution) spectrum was consistent with **2b**: $(CH_3)_3C$ and $(CH_3)_2$ 0.95, s, 15; $CH_2$, 3.26, s, 2; and $COOCH_3$, 3.62, s, 3.

*Anal.* Calcd for $C_{10}H_{20}O_3$: C, 63.79; H, 10.70. Found: C, 63.70; H, 10.93.

**Methyl 2-Methyl-2-neopentoxypropanoate (3b).**—The diazomethane procedure described for **1b** was used to prepare **3b**, bp 30° (1 mm), in 92.5% yield. The ir ($CCl_4$ solution) spectrum showed absorptions at 2955, 1730, 1475, 1275, 1185, 1140, and 1080 $cm^{-1}$. The nmr ($CCl_4$ solution) assignments are $(CH_3)_3C$, 0.87, s, 9; $(CH_3)_2C$, 1.33, s, 6; $CH_2$, 2.95, s, 2; and $COOCH_3$, 3.67, s, 3.

*Anal.* Calcd for $C_{10}H_{20}O_3$: C, 63.79; H, 10.70. Found: C, 63.48; H, 11.07.

**Ethyl 2-*tert*-Butylperoxy-2-methylpropanoate (5).**—A solution of 0.433 g (2.46 mmol) of **1a**, 0.1 ml of concentrated sulfuric acid, and 3 ml of absolute ethanol was allowed to reflux for 2.5 hr. The reaction mixture was neutralized with a 10% sodium bicarbonate solution and then 3 ml of water was added, followed by three 5-ml ether extractions. The combined ether extract was washed with 10% sodium bicarbonate solution and dried over magnesium sulfate, and the ether was removed by a rotevaporator. Distillation of the residue gave 0.331 g, bp 69–70° (6 mm), of **5**, 66% yield, which showed only one peak by glc analysis on a 5 ft × 0.125 in. 3% SE-30 on Varaport column at 60° with a nitrogen flow rate of 28 ml/min. The ir ($CCl_4$ solution) spectrum of **5** showed absorptions at 3055–2785, 1735, 1460, and 1360 $cm^{-1}$. The nmr ($CCl_4$ solution) spectrum was consistent with the structure of **5**: $(CH_3)_3C$, 1.24, s, 8.7; $(CH_3)_2C$, 1.40, s. 6.7; $COOCH_2CH_3$, 1.31, t, 3.1; and $COOCH_2CH_3$, 4.17, q, 2.0. The mass spectrum of **5** showed *m/e* 204 (M), 131 (M − $COOC_2H_5$), 57 [$(CH_3)_3C^+$].

**Kinetic Methods.**—The method of Smith[8b] was used to determine the rate of esterification of the acids with a catalytic amount of hydrogen chloride. A titrimetric method was used to determine the rates of the basic hydrolysis of all esters, except for the peroxy-substituted esters **1b** and **5**. The titrimetric method consisted of thermally equilibrating the ester solution and the base solution, followed by mixing into a flask under a nitrogen atmosphere, which was contained in a thermostated bath. Aliquots were periodically removed, quenched with a given volume of standardized hydrochloric acid solution, and then titrated with standardized sodium hydroxide solution to a phenolphthalein end point. The rates of basic hydrolysis of the peroxy-substituted esters **1b** and **5** were determined by glc analysis. The reaction procedure and quenching were the same as used in the titrimetric measurements. For the rate of appearance of *tert*-butyl alcohol, *n*-butyl alcohol was added to the stock ester solution as an internal standard. Anisole was added to stock solutions of **1b** and **5** as an internal standard to follow the rate of disappearance of the esters. The glc analysis of *tert*-butyl alcohol was performed on a 5 ft × 0.125 in. Porapak N (Waters Associates, Inc.) column at 120° with a nitrogen flow rate of 28 ml/min. Glc analyses for **1b** and **5** were carried out on a 5 ft × 0.125 in. 3% SE-30 on Varaport column at 60° with a nitrogen flow rate of 28 ml/min. A quantitative yield of *tert*-butyl alcohol was observed from the basic decomposition of **1b** by glc analysis with reference to an authentic mixture of *tert*-butyl alcohol and *n*-butyl alcohol. The glc data were processed by a first-order least squares program, where the input was time and relative areas of *tert*-butyl alcohol/*n*-butyl alcohol or ester/anisole. The kinetic data was usually gathered over 3 half-lives in both the glc and titrimetric measurements.

**Light Emission.**—A Hamamatsu R374 heat-on photomultiplier tube (PMT) supplied with 900 V was used to detect light emission *via* a Keithley 610A electrometer. The PMT was mounted at one window of a Bausch and Lomb 250-mm grating monochromator and a thermostated silicon oil bath was mounted at the other window. The thermostated compartment was machined from brass and contained a thermistor for temperature

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(20) All melting points are corrected and boiling points are uncorrected. Nuclear magnetic resonance (nmr) spectra were obtained with a Varian A-60 spectrometer. Chemical shifts are expressed in parts per million (ppm) relative to the internal tetramethylsilane standard as 0 ppm (δ scale). The nmr absorptions are given as parts per million, coupling, relative area. Infrared (ir) spectra were determined with a Perkin-Elmer 621 or 337 spectrometer and mass spectra were obtained with a Hitachi RMU-6E instrument. Glc analyses were performed on a Varian Aerograph Hy-Fi III (FID) instrument. Elemental analyses were performed by C. F. Geiger, Ontario, Calif.

(21) L. F. Feiser, "Experiments in Organic Chemistry," D. C. Heath, Boston, Mass., 1941, p 359.

(22) W. H. Richardson and R. S. Smith, *J. Org. Chem.*, **33**, 3882 (1968).

control, a heating element, a stirrer, a thermometer, a 1-cm cell mount, and quartz windows for absorption or fluorescence measurements. These windows could be capped on the exterior of the compartment so that chemiluminescence measurements could be made. The compartment was used in this mode for the light emission measurements and the monochromator was set at the "zero-order" position so that all wavelengths of light were detected. A basic 60% aqueous methanol solution, containing fluorescein, was placed in a 1-cm quartz cell, which was contained in the thermostated bath at 29°. The peroxide was then introduced into the solution with a 250-$\mu$l Hamilton syringe and the solution was mixed. The final sodium hydroxide and fluorescein concentrations were 0.50 and 0.008 $M$, respectively. The initial chloro-*tert*-butyl hydroperoxide and **1b** concentrations were $2.0 \times 10^{-2}$ and $4.0 \times 10^{-2} M$, respectively. Light emission increased to a maximum of 0.53 na and then began to decrease in the former solution. With **1b**, no light was detected within experimental error (±0.02 na).

**Registry No.**—**1a**, 16424-69-4; **1b**, 27492-18-8; **2a**, 35889-98-6; **2b**, 35889-99-7; **3a**, 35890-00-7; **3b**, 35890-01-8; **5**, 35890-02-9.

**Acknowledgment.**—We thank the U. S. Army Research Office (Durham) and the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank William Koskinen and Mary Yelvington for the light-emission studies, and Dr. M. McElroy for an informative discussion of luciferin-AMP chemiluminescence.

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# Base-Induced Rearrangement of Epoxides. V. Phenyl-Substituted Epoxides[1]

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*Received June 8, 1972*

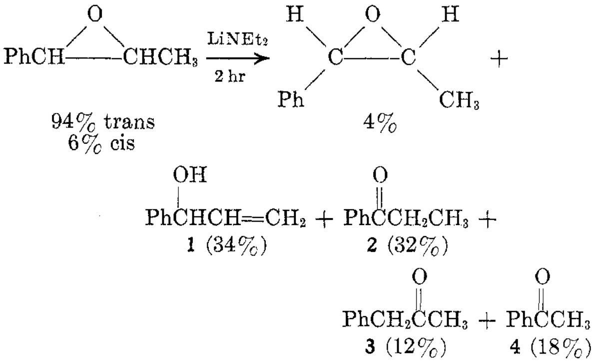
A number of $\alpha$- and $\beta$-phenyl substituted epoxides have been subjected to lithium diethylamide treatment. The trans and cis isomers of $\beta$-methylstyrene oxide give different product distributions, but in both cases the $\beta$-elimination pathway is preferred over $\alpha$-proton abstraction. The trans isomer leads to the formation of some acetophenone. Indene oxide gives a low yield of 1-indanone as the only isolable product. $\beta$-Phenyl substitution strongly affects the course of the epoxide to allylic alcohol rearrangement. For the first time in these reactions, some cis olefinic product is observed, formed preferentially from the trans isomer of 1-phenyl-2-butene oxide. The reactions of *trans*- and *cis*-3-phenylcyclohexene oxide substantiate a syn elimination mechanism.

Earlier work has established the strongly regioselective abstraction from the least substituted carbon in various alkyl-substituted epoxides,[2,3] the highly stereospecific formation of trans olefin[2,4] in these systems, and also the preferred syn elimination mechanism[5,6] in the reaction with lithium diethylamide. We have subsequently examined the base-induced reactions of various epoxides bearing substituents other than simple alkyl groups. This paper describes the results obtained with a number of $\alpha$- and $\beta$-phenyl-substituted epoxides.

Cope and his coworkers[7] examined the reaction of some diarylethylene oxides with lithium diethylamide, and discovered some interesting stereochemical features. For example, *cis*-stilbene oxide gave 70% of deoxybenzoin, while *trans*-stilbene oxide gave 66% of diphenylacetaldehyde, both reactions occurring with high specificity. These illustrate the $\alpha$-proton abstraction reaction pathway, various aspects of which have subsequently been explored in detail by Crandall, *et al.*[8]

## Results and Discussion

Epoxidation of commercial $\beta$-methylstyrene gave a distilled epoxide mixture which contained 94% trans and 6% cis isomer. This material was treated with a twofold molar excess of lithium diethylamide in refluxing ether–hexane for 2 hr to give the product mixture shown in eq 1.



Several interesting conclusions can be drawn from these data. First, the recovered epoxide proved to be essentially pure cis material (by vpc and ir), suggesting a considerable difference in rates of reaction for the isomeric epoxides;[9] this was substantiated by examining the reaction of isolated cis material, as discussed below. Second, examination of points taken during the course of eq 1 established that the allylic alcohol **1** was being converted fairly rapidly to the ketone **2** under the reaction conditions. In fact, extrapolation of these data suggests that no **2** is formed directly by an $\alpha$-proton abstraction mechanism, but rather is generated exclusively by rearrangement of **1**. Similar allylic alcohol to ketone base-induced rearrangements have been previously observed[2,3,10] with terminal methylene allylic alcohols, and in the present system a more rapid reaction is anticipated because of the benzylic proton in **1**.

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[1] (a) This work was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society (5744-AC4). (b) Part IV: C. K. Kissel and B. Rickborn, *J. Org. Chem.*, **37**, 2060 (1972).

[2] B. Rickborn and R. P. Thummel, *ibid.*, **34**, 3583 (1969).

[3] J. K. Crandall and L. C. Lin, *ibid.*, **33**, 2375 (1968).

[4] A. C. Cope and J. K. Heeren, *J. Amer. Chem. Soc.*, **87**, 3125 (1965).

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[6] R. P. Thummel and B. Rickborn, *J. Org. Chem.*, **36**, 1365 (1971).

[7] A. C. Cope, P. A. Trumbull, and E. R. Trumbull, *J. Amer. Chem. Soc.*, **80**, 2844 (1958).

[8] J. K. Crandall, L. C. Crawley, D. B. Banks, and L. C. Lin, *J. Org. Chem.*, **36**, 510 (1971).

[9] This behavior stands in contrast to the reaction of *cis*- and *trans*-2-pentene oxide, where no significant difference in rates is observed.[2]

[10] C. K. Kissel and B. Rickborn, unpublished work.