was heated on a steam bath for 15 min. Dilution with water gave a solid which was recrystallized from toluene. The yield of light yellow solid,[8] mp >300°, mass spectrum m/e 506, was 73 mg or 45%. Benzene solutions gave strong blue fluorescence. The absorption spectrum of **9** in benzene had peaks at 403 mμ (log ε 4.47), 380 (4.36), and 360 (4.06).

Anal. Calcd for $C_{40}H_{26}$: C, 94.87; H, 5.13. Found: C, 94.63; H, 4.95.

Irradiation of 10,10′-Diphenyl-9,9′-bianthranyl (9).—The absorption spectrum of a solution of 43 mg of **9** and 2 mg of iodine in 400 ml of benzene, which has been irradiated for 6 hr, showed that only 1% of **9** had been destroyed.

3,10-Diphenyl-1,2,11,12-dibenzoperylene (4) from Diol 3.—Nitrogen was bubbled into a solution of 324 mg of **3** and 168 mg of iodine in 600 ml of benzene for 20 min. The bubbling of nitrogen was continued while the solution was irradiated for 6 hr. The solvent was evaporated and the solid was stirred in 30 ml of ethanol. Filtration gave 196 mg of red-purple solid: mp 366–369° (lit.[2] mp 371°); visible absorption at 582 mμ (log ε 4.45) and 452 (4.24) [lit.[2] 580 mμ (log ε 4.99) and 548 (4.80)]. The absorption spectrum indicated that 5% diphenylbisanthene was aso present.

Anal. Calcd for $C_{40}H_{24}$: C, 95.23; H, 4.77. Found: C, 94.62; H, 4.31.

Photooxidation of 4.—A blue-green solution with bright blue fluorescence developed when a red-purple solution of 50 mg of **4** in 100 ml of benzene was irradiated for 30 min. Evaporation of the solvent gave 48 mg of a green solid, mp 295–299°. Recrystallization from toluene gave light yellow crystals: mp 302–304°; visible absorption in benzene at 427, 430, and 382 mμ (log ε 4.28, 4.26, and 4.00).

Registry No.—**6**, 23102-61-1; **9**, 23102-67-2.

Acknowledgments.—The author gratefully acknowledges the financial support of the work reported here by the Pyrotechnics Laboratory, Picatinny Arsenal, Dover, N. J., and the helpful suggestions contributed by Dr. W. A. Henderson.

Thermal Decomposition of Some *t*-Alkyl Peroxyoxalates

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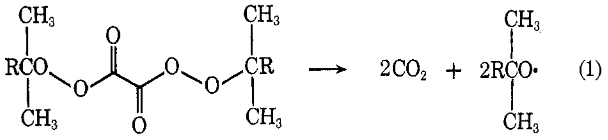
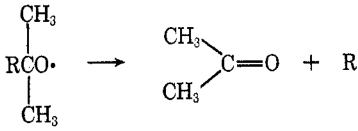
The thermal decomposition of di-*t*-butyl peroxyoxalate has previously been investigated by Bartlett,[1] Traylor,[2] and coworkers. It was shown that decomposition is quite facile at room temperature, and there is negligible cage recombination of the *t*-butoxy radicals formed.

A variety of *t*-alkoxy radicals is known to undergo β scission to afford a ketone and an alkyl radical.[3] The efficiency with which this fragmentation occurs is markedly dependent on both the structure of the *t*-alkoxy radical and on the solvent.

We sought *t*-alkyl peroxyoxalates as useful precursors for alkyl radicals at low temperatures in a process uncomplicated by cage reactions (eq 1, 2).[4] In this paper we wish to report the preparation of a series of *t*-alkyl peroxyoxalates I and the investigation of the rates and products of their thermal decomposition.


(1)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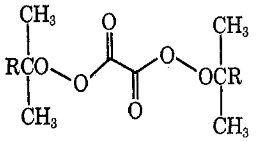

Ia, R = CH_3 c, R = $(CH_3)_2CH$
b, R = CH_3CH_2 d, R = $PhCH_2$

The peroxyoxalates were prepared by the method of Bartlett, *et al.*,[1] from the corresponding *t*-alkyl hydroperoxide and oxalyl chloride. *t*-Butyl peroxyoxalate is a white, crystalline solid which is stable at room temperature for short periods of time but explodes on pounding or scratching.[1] Compounds Ib[5] and Id were also obtained as white needles by crystallization from pentane at −30° or below. Compound Ic was an oil which we were unable to crystallize. All three of these compounds were unstable at room temperature. Compounds Ic and Id decomposed spontaneously with vigorous evolution of gas when allowed to warm to room temperature. All of these compounds were more stable in dilute pentane solutions and could be stored at −30° for days without appreciable decomposition.

The purities of the peroxyoxalates were determined by examination of their infrared spectra and by the yields of the carbon dioxide liberated in the thermal decomposition. Compounds Ia and Ib could also be analyzed by iodometric titration in acetic acid.[6] However, Ic and Id gave very low titres by this method owing to the rapid ionic decomposition in acetic acid solutions.

The rates of thermal decomposition of the four peroxyoxalates were measured in pentane solution at 25° by following the appearance of carbon dioxide. These results are shown in Table I. The reaction was first

TABLE I

RATES OF DECOMPOSITION OF *t*-ALKYL PEROXYOXALATES IN PENTANE AT 25°[a]

Compd	R	k, sec^{-1}	$t_{1/2}$, min
Ia	Methyl[b]	1.7×10^{-5}	700
Ib	Ethyl	2.6×10^{-5}	450
Ic	Isopropyl	6.0×10^{-5}	190
Id	Benzyl	6.7×10^{-5}	173

[a] Average of at least two determinations. [b] Literature[1] $k = 7.9 \times 10^{-6}$ sec^{-1} at 20° in benzene.

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[1] P. Bartlett, E. Benzing, and R. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960).

[2] (a) H. Kiefer and T. Traylor, *ibid.*, **89**, 6667 (1967); (b) R. Hiatt and T. G. Traylor, *ibid.*, **87**, 3766 (1965).

[3] (a) F. D. Greene, M. L. Savitz, F. D. Osterholz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963); (b) C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, **85**, 1593 (1963); (c) C. Walling and P. Wagner, *ibid.*, **85**, 2333 (1963); (d) J. Bacha and J. Kochi, *J. Org. Chem.*, **30**, 3272 (1965).

[4] A source of free alkyl radicals uncomplicated by cage reactions would be useful for measuring rates of bimolecular reactions of alkyl radicals in solution, *e.g.*, disproportionation–combination ratios which have been unambiguously measured heretofore only in the gas phase.

[5] C. Walling and J. A. McGuinness [*J. Amer. Chem. Soc.*, **91**, 2053 (1969)] have also recently prepared Ib.

[6] L. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

order in peroxyoxalate over at least one half-life. There was a slight increase in rate in the order R = $CH_3 < CH_3CH_2 < (CH_3)_2CH < PhCH_2$.[7]

The presence of excess galvinoxyl had no effect on the rate of decomposition of Ic, although galvinoxyl was consumed throughout the reaction. Galvinoxyl is an efficient scavenger for both alkoxy and alkyl radicals.[8] The insensitivity of the rate of thermolysis in the presence of galvinoxyl showed that induced decomposition of the peroxyoxalate was unimportant under these conditions.[8] The products of the thermal decomposition of the peroxyoxalates were studied in three different solvents (Table II). Pentane represented a nonpolar solvent in which heterolytic processes would be minimized, whereas acetic acid and acetonitrile were chosen because β scission of *t*-alkoxy radicals is facile in these solvents.[3c,d]

Table II

Thermal Decomposition of Peroxyoxalates[a]

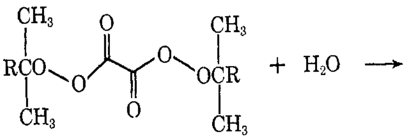
				Products						
Compd	Solvent	Temp, °C	Reaction[b] time, hr	CO_2, mmol	RH, mmol	R(–H), mmol	R–R, mmol	$(CH_3)_2CO$, mmol	$RC(CH_3)_2$-OH, mmol	R–OH, mmol
Ia	Pentane	25	48	0.44	Trace[c]			Trace[c]	0.47[d]	None
Ib	Pentane	25	24	0.45	0.03	Trace[c]	Trace[c]	0.04	0.43	None
Ic	Pentane	25	18	0.45	0.10	0.075	0.07	0.35	0.12	Trace[c]
Ic	Pentane[e]	25	18	0.47	None	~0.01	None			
Id	Pentane	25	18	0.47	None		0.07	0.25	0.20	0.07[f]
Ia	CH_3CN	40	6	0.46	0.20		None	0.24	0.25[g]	None
Ib	CH_3CN	40	1	0.46	0.04	Trace[c]	Trace[c]	0.19	0.20	0.15
Ic	CH_3CN	25	1	0.48	Trace[c]	Trace[c]	None	0.25	0.21	0.25
Id	CH_3CN	25	1	0.47	None		Trace[c]	0.23	0.26	0.20[g]
Ia	HOAc	40	6	0.48	0.33		None	0.40	0.08	None
Ib	HOAc	40	1	0.45	Trace[c]	Trace[c]	None	0.24	0.21	0.21
Ic	HOAc	25	1	0.45	Trace[c]	Trace[c]	None	0.22	0.23	0.19[h]

[a] 0.25 mmol of peroxyoxalate in 5 cc of solvent (0.05 *M*). [b] Indicates the time the reaction mixture was left in the bath for complete reaction. Unrelated to rate studies. [c] Less than 0.01 mmol. [d] Trace of $(CH_3)_3COOC(CH_3)_3$ found, no $(CH_3)_3COCH_3$ detected. At 45°, Traylor, *et al.*,[2] found 4% di-*t*-butyl peroxide. [e] 0.5 mmol of galvinoxyl added. [f] 0.07 mmol of PhCHO found. [g] 0.03 mmol of PhCHO found. [h] ~0.01 mmol of $(CH_3)_2CHOAc$ also found.

Good yields of the expected products of homolytic decomposition were obtained in pentane solutions from all of these peroxyoxalates with the exception of Id (see Table II). The β scission of the *t*-alkoxy radicals into alkyl radicals and acetone was the major reaction only with Ic. It gave substantial amounts of products derived from the isopropyl radical (propane, propylene, 2,3-dimethylbutane).[9] In the presence of excess galvinoxyl, no propane or 2,3-dimethylbutane was formed from Ic. Only a small amount of propylene was detected. These results show that 96% of the isopropyl products was generated *via* free isopropyl radicals. The small amount of propylene formed in the presence of galvinoxyl may have arisen *via* a molecular rearrangement or *via* disproportionation of an isopropyl and a 2,3-dimethyl-2-butoxy radical. The latter is less likely than the former, since no 2,3-dimethyl-2-butyl isopropyl ether was found.[10]

In addition to bibenzyl, the decomposition of Id in pentane afforded benzyl alcohol and benzaldehyde. The formation of these products indicated that the homolytic decomposition of Id was complicated by a competing heterolytic decomposition (*vide infra*). A small amount of induced decomposition *via* the hydroxybenzyl radical (formed by hydrogen transfer from benzyl alcohol) could account for the benzaldehyde.

t-Butyl peroxyoxalate also gave products expected from the radical intermediates in both acetonitrile and acetic acid. Thus the marked increase in the yields of methane and acetone paralleled the importance of β scission of the *t*-butoxy radicals in these solvents (compared with pentane). However, Ib, Ic, and Id produced carbon dioxide, acetone, and the two alcohols, ROH and $RC(CH_3)_2OH$, in these solvents, according to the stoichiometry given by eq 3. A molecule of water is needed to balance the reaction as written. The solvent contained enough water (*ca.* 0.1%) to react with all the peroxyoxalate.[11] We interpret the decomposition of Ib, Ic, and Id in acetonitrile and acetic acid as occurring *via* a Criegee rearrangement.[12] Such a process is represented *schematically* by eq 4–6. Alkyl peroxyoxalate ion is known to lose carbon dioxide spon-



$$ROH + (CH_3)_2CO + 2CO_2 + RC(CH_3)_2OH \quad (3)$$

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[7] These rate differences are too small to warrant further studies of temperature dependence. Steric and electronic effects or the multibond fragmentation of these peroxyoxalates are, no doubt, minor. (b) *Cf.* R. Hiatt and W. M. J. Strachan, *J. Org. Chem.*, **28**, 1893 (1963).

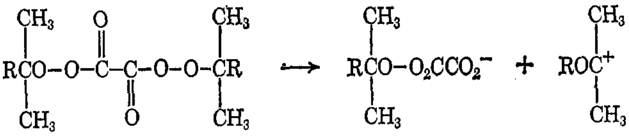
[8] P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc.*, **84**, 2596 (1962).

[9] The ratio of the rates of disproportionation and combination of isopropyl radicals is 1.1 (*cf.* Table II). This ratio compares favorably with values obtained in the gas phase [Trotman-Dickenson, *Progr. React. Kinet.*, **1**, 107 (1961)] and in solution from diacyl peroxides (R. A. Sheldon, unpublished results).

[10] It has been shown that the cage reaction of isopropyl and 2,3-dimethyl-2-butoxy radicals gives this ether by combination as well as propylene from disproportionation: R. A. Sheldon, unpublished observation.

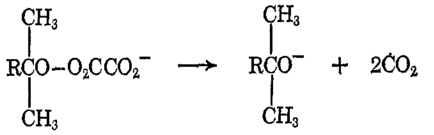
[11] The amount of water in these systems was not determined directly. It is possible that other protic sources would effect similar transformations.

[12] (a) R. Criegee, *Justus Liebigs Ann. Chem.*, **560**, 127 (1948); (b) Y. K. Syrkin and I. I. Moiseev, *Russ. Chem. Rev.*, 193 (1960).



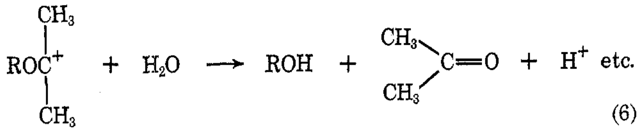
$$R\overset{CH_3}{\underset{CH_3}{C}}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}\underset{\underset{O}{\|}}{C}{-}O{-}O{-}\overset{CH_3}{\underset{CH_3}{C}}R \longrightarrow R\overset{CH_3}{\underset{CH_3}{C}}O{-}O_2CCO_2^- + RO\overset{CH_3}{\underset{CH_3}{C}}{}^+$$

(4)



$$R\overset{CH_3}{\underset{CH_3}{C}}O{-}O_2CCO_2^- \longrightarrow R\overset{CH_3}{\underset{CH_3}{C}}O^- + 2CO_2$$

(5)

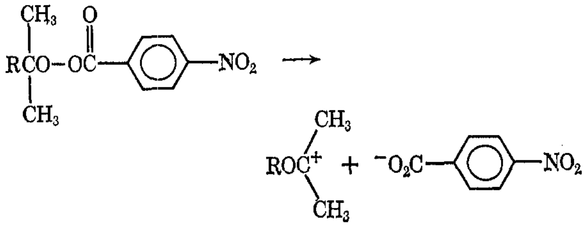


$$RO\overset{CH_3}{\underset{CH_3}{C}}{}^+ + H_2O \longrightarrow ROH + (CH_3)_2C{=}O + H^+ \text{ etc.}$$

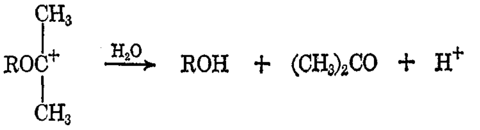
(6)

taneously.[1] The rate of decomposition of Ic and Id in acetic acid and acetonitrile was very fast. Although accurate measurements were not made, these peroxyoxalates had half-lives of *ca.* 5 min in acetonitrile at 25°.

Hedaya and Winstein[13] showed that the rate of heterolytic decomposition (*via* a Criegee rearrangement) of a series of alkyl *p*-nitroperbenzoates in methanol increased in the order (R) Me < Et < $PhCH_2$ < *i*-Pr. The products were the alcohol (ROH), acetone, and *p*-nitrobenzoic acid. The results were interpreted according to eq 7–8.



(7)



$$RO\overset{CH_3}{\underset{CH_3}{C}}{}^+ \xrightarrow{H_2O} ROH + (CH_3)_2CO + H^+$$

(8)

The ease of the Criegee rearrangement is also influenced by the anion. When the anion is a good leaving group, the Criegee rearrangement is facile. Thus *t*-butyl pertosylate[14] and *t*-butyl N-succinimidepercarboxylate[15] decompose heterolytically even in nonpolar solvents at room temperature. We also expect the alkyl peroxyoxalate anion to be a good leaving group.

In conclusion, we find that *t*-alkyl peroxyoxalates are of limited utility as low-temperature precursors for alkyl radicals. In polar solvents they undergo facile heterolysis, whereas in hydrocarbon solvents many *t*-alkoxy radicals produced in the homolysis do not undergo β scission efficiently at low temperatures.

Isopropyl radicals, however, could be generated in good yields in pentane solutions. We feel that analogous alkyl peroxyoxalates should be useful for the production of a variety of secondary and tertiary alkyl radicals in nonpolar solvents.

Experimental Section

t-Butyl hydroperoxide (Lucidol Corp., 90%) was vacuum distilled and was 99% pure by iodometric titration. *t*-Amyl hydroperoxide was prepared from *t*-amyl alcohol and hydrogen peroxide by the Milas[16] procedure. 2,3-Dimethyl-2-butanol was prepared from isopropylmagnesium bromide and acetone, bp 115–116° (lit.[17] bp 117–122°). 2,3-Dimethyl-2-butyl hydroperoxide was prepared by the method of Criegee,[18] bp 37° (3 mm). α,α-Dimethylphenethyl hydroperoxide was prepared from α,α-dimethylphenethyl alcohol (Givaudan Co.) and hydrogen peroxide, mp 45–46° (lit.[19] mp 38–41°). Galvinoxyl was generously donated by Dr. Galvin Coppinger. Di-*t*-butylperoxy oxalate was prepared from oxalyl chloride and *t*-butyl hydroperoxide by the Bartlett procedure,[1] mp 49–51° dec (heating rate 2°/min, lit.[1] mp 50.5–51.5°). Iodometric titration in acetic acid required 1.85 equiv of sodium thiosulphate per 1 mol of peroxalate (lit.[1] 1.89 equiv).

The three peroxyoxalates Ib, Ic, and Id were similarly prepared in virtually quantitative yields (based on the carbon dioxide evolved from an aliquot of the reaction solution in pentane) from the corresponding hydroperoxide and oxalyl chloride. Compounds Ib and Id could be crystallized as white needles from pentane at −30°, but Ic was an oil which could not be crystallized. On warming to room temperature, Ib melted; it decomposed in a short time if kept at room temperature. Compounds Ic and Id, on warming to room temperature, spontaneously decomposed with vigorous evolution of gas. The compounds were more stable in dilute solution and were usually stored as 0.05 *M* solutions in pentane at −30°. Infrared spectra (in pentane) of all four peroxyoxalates showed no absorption owing to a hydroxyl group and showed a doublet in the carbonyl region (1820 and 1780 cm^{-1}) characteristic of peroxyoxalates. Iodometric titration of Ib in acetic acid required 1.83 equiv of sodium thiosulphate per 1 mol of peroxyoxalate. Compounds Ic and Id gave low and inconsistent titres under these conditions.

For the reactions in acetic acid and acetonitrile, aliquots of the 0.05 *M* solution of the peroxyoxalates in pentane were evaporated *in vacuo* while being cooled in a Dry Ice–acetone bath and then dissolved in the corresponding amount of acetic acid or acetonitrile. For the reactions of Ib, Ic, and Id in these solvents the solutions were not degassed with helium because of the rapidity of the decomposition under these conditions.

Kinetic runs were carried out using 3-ml aliquots of a 0.05 *M* solution of the peroxyoxalate in glass tubes capped with a gastight rubber serum cap. The solutions were degassed quickly with a stream of helium while cooled in ice. The log $[CO_{2\infty} - CO_2{}^t]$ value was plotted against time. Linearity was obtained in all cases over at least one half-life.

Gas chromatographic analyses of gaseous products were performed on instruments equipped with thermal conductivity detectors. Other analyses were performed on instruments with hydrogen flame ionization detectors: Varian Aerograph Model 1200 and Aerograph HiFy Model 600. The following are the conditions used in determining yields of products (product, marker, column, temperature): carbon dioxide, ethylene or methane, 2-ft Porapak Q, room temperature; methane, ethylene, 2-ft Porapak Q, room temperature; ethylene, methane, 2-ft Porapak Q, room temperature; ethane, methane or ethane, 2-ft Porapak Q, room temperature; propane, isobutane, 15-ft 30% Dowtherm on firebrick, room temperature; propylene, isobutane, 5-ft 30% Dowtherm on firebrick, room temperature; *n*-butane, isobutane, 15-ft 30% Dowtherm on firebrick, room temperature; 2,3-dimethylbutane, *n*-hexane, 15-ft SF-96 on firebrick, 90°; acetone, 2-propanol or *t*-butyl alcohol, 9-ft FFAP, 90°; *t*-butyl alcohol, 2-propanol, 9-ft FFAP, 90°; 2-propanol, *t*-butyl alcohol, 9-ft FFAP, 90°; *t*-amyl alcohol, 2-propanol, 9-ft FFAP, 90°; 2,3-dimethyl-2-butanol, *t*-amyl alcohol, 9-ft FFAP, 90°; ethanol, 2-propanol, 9-ft FFAP, 90°; di-*t*-butyl peroxide, 2-propanol, 9-ft FFAP, 90°; *t*-butyl methyl ether, 9-ft FFAP, 90°; benzyl alcohol, *n*-heptanol, 6-ft 15% Carbowax 20M on acid-washed Chromosorb P, 140°; benzaldehyde, *n*-heptanol, 6-ft 15% Carbowax 20M on acid-washed Chromosorb P, 140°; α,α-dimethylphenethyl alcohol, *n*-heptanol, 6-ft 15% Carbowax

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[13] E. Hedaya and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1661 (1967).

[14] P. Bartlett and T. Traylor, *ibid.*, **83**, 856 (1961).

[15] (a) E. Hedaya, R. L. Hinman, L. Kibler, and S. Theodoropulos, *ibid.*, **86**, 2727 (1964); (b) T. Koenig and W. Brewer, *ibid.*, **86**, 2729 (1964).

[16] N. Milas and D. Surgenor, *ibid.*, **68**, 205 (1946).

[17] M. Delacre, *Chem. Zentr.*, **77**, 1234 (1906).

[18] R. Criegee and H. Dietrich, *Justus Liebigs Ann. Chem.*, 135 (1948).

[19] J. K. Kochi and F. F. Rust, *J. Amer. Chem. Soc.*, **83**, 2007 (1961); **86**, 5264 (1964).

20M on acid-washed Chromosorb P; toluene, 9-ft FFAP, 90°; dibenzyl, diphenyl, 4-ft XF 1150, 130°.

Registry No.—Ia, 1876-22-8; Ib, 23042-72-0; Ic, 23042-73-1; Id, 23042-74-2.

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α Alkylation of Alkyl Alkanesulfonates

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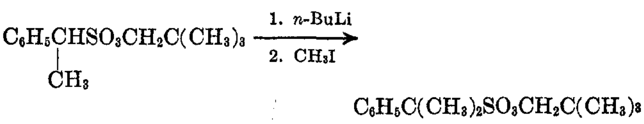
Received August 20, 1969

Recently, the facile α metalation (by *n*-butyllithium) and subsequent alkylation of alkyl α-toluenesulfonates were described.[1] Almost simultaneously, the α metalation and subsequent reactions of various sultones were reported.[2] The present work concerns the successful extension of our method of metalation and alkylation to simple alkyl alkanesulfonates.

The metalation of the starting sulfonates shown in Table I proceeds quantitatively and apparently instantaneously at Dry Ice bath temperatures. The time required for subsequent alkylation is a function of the alkylating agent. Contrary to what may have been implied earlier,[1] *n*-butyllithium is a superior metalating agent over potassium hydride, which requires a much longer time for metalation and a more complicated work-up procedure.

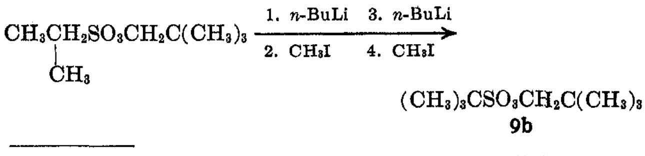
Using the method described herein, all of the α hydrogens of an alkyl alkanesulfonate can be replaced by alkyl groups. Thus a useful route to esters of tertiary sulfonic acids is at hand.[3] For example, a derivative (**1**) of α-cumenesulfonic acid is easily prepared by alkylation, while the acid itself has probably not been prepared.[4]



$$\underset{\displaystyle CH_3}{C_6H_5CHSO_3CH_2C(CH_3)_3} \xrightarrow[\text{2. } CH_3I]{\text{1. } n\text{-BuLi}} C_6H_5C(CH_3)_2SO_3CH_2C(CH_3)_3$$

1

Also, as shown in the preparation of neopentyl 2-methyl-2-propanesulfonate (**9b**), the metalation and alkylation can be repeated without isolation of the first-formed product (**9a**).



$$\underset{\displaystyle CH_3}{CH_3CH_2SO_3CH_2C(CH_3)_3} \xrightarrow[\text{2. } CH_3I \quad \text{4. } CH_3I]{\text{1. } n\text{-BuLi} \quad \text{3. } n\text{-BuLi}} (CH_3)_3CSO_3CH_2C(CH_3)_3$$

9b

From the examples given in Table I, it is evident that, regardless of the alcohol portion of the ester, at Dry Ice bath temperatures metalation α to the sulfonyl group is preferred over other possible reactions, *i.e.*, elimination or displacement. As reported by Durst,[2] however, if the solution of the metalated species is allowed to warm, to *ca.* −30°, rapid exothermic decomposition takes place. The decomposition products are unknown, but with α-lithio methyl methanesulfonate an intractable, syrupy oil that shows strong sulfonyl bands in the ir spectrum separates from the reaction mixture. Therefore, alkylations with 1-bromopropane, and presumably with others of the less reactive alkylating agents, cannot be speeded by simply allowing the reaction mixture to warm, but, rather, the time for alkylation must be greatly extended while the reaction mixture is kept well cooled.

Experimental Section[5]

Materials.—*n*-Butyllithium in hexane was purchased from the Foote Mineral Co. or from Alfa Inorganics, Inc. Tetrahydrofuran (Baker Analyzed Reagent) was used directly from freshly opened bottles, or after storage over Linde Molecular Sieves. The alkyl halides (Columbia), sulfonyl chlorides (Eastman), and neopentyl alcohol (Aldrich) were used as obtained. All reactions described herein were carried out in thoroughly dried equipment under a nitrogen atmosphere. Starting sulfonates, prepared as described below, were distilled shortly before use.

General Method for the Preparation of Starting Alkyl Alkanesulfonates.—To a benzene solution of 1.0 equiv of the alcohol and 1.03 equiv of triethylamine cooled in an ice bath, a benzene solution of 1.0 equiv of the sulfonyl chloride was added dropwise. After the addition was complete, triethylammonium chloride was filtered and washed with benzene. The combined filtrate and washings were extracted once with 10% HCl and thrice with distilled water, dried (Na_2SO_4), and evaporated *in vacuo*, yielding the crude ester. Vacuum distillation yielded the pure product.

Neopentyl methanesulfonate was prepared in 78.4% yield on a 0.50-mol scale according to the general procedure: bp 93.5–94.5° (9 mm); ir (neat) 2980 (CH) and 1360 and 1180 cm^{-1} (SO_3); nmr δ 0.98 [s, 9, $(CH_3)_3$], 2.98 (s, 3, CH_3), and 3.82 (s, 2, CH_2). The analytical sample was prepared by vpc.

Anal. Calcd for $C_6H_{14}O_3S$: C, 43.35; H, 8.49; S, 19.29. Found: C, 43.53; H, 8.58; S, 19.01.

Neopentyl ethanesulfonate was prepared in 90.0% yield on a 0.23-mol scale according to the general procedure: bp 58–60° (0.15 mm); ir (neat) 2970 (CH) and 1355 and 1175 cm^{-1} (SO_3); nmr δ 0.98 [s, 9, $(CH_3)_3$], 1.37 (t, 3, J = 8 Hz, CH_3), 3.12 (q, 2, J = 8 Hz, CH_2S), and 3.82 (s, 2, OCH_2), The analytical sample was prepared by vpc.

Anal. Calcd for $C_7H_{16}O_3S$: C, 46.69; H, 8.95; S, 17.79. Found: C, 46.57; H, 9.12; S, 17.61.

Methyl methanesulfonate was prepared in 60% yield on a 1.0-mol scale: bp 71–73° (5.0 mm) [lit.[6] bp 100.5–101.5° (25 mm)]; ir (neat) 1360 and 1185 cm^{-1} (SO_3); nmr δ 3.00 (s, 3, CH_3S) and 3.88 (s, 3, OCH_3).

Ethyl methanesulfonate was prepared in 65% yield on a 0.10-mol scale: by 78–79° (7.5 mm) [lit.[7] bp 85–86° (10 mm)]; ir (neat) 1350 and 1180 cm^{-1} (SO_3); nmr δ 1.39 (t, 3, J = 7 Hz, CH_2CH_3), 2.99 (s, 3, CH_3S), and 4.27 (q, 2, J = 7 Hz, OCH_2CH_3).

2-Propyl methanesulfonate was prepared in 68% yield on a 0.50-mol scale: bp 39–41° (0.15 mm) [lit.[8] bp 86–88° (12 mm)];

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(2) T. Durst and J. du Manoir, *ibid.*, **47**, 1230 (1969).

(3) The only other route to esters of this type is the reaction of a tertiary sulfonic acid with a diazo alkane, a method limited chiefly by the availability of the sulfonic acid: F. Asinger, B. Fell, and A. Commichau, *Chem. Ber.*, **98**, 2154 (1965); R. B. Scott, Jr., and W. S. Heller, *J Org. Chem.*, **31**, 1999 (1966).

(4) The preparation of α-cumenesulfonic acid has been claimed *via* treatment of cumene with the pyridine–sulfur trioxide complex. The product was characterized only by a nitrogen analysis of its S-benzylthiouronium derivative. See Y. S. Shabarov, R. Y. Levina, and V. K. Potapov, *Zh. Obshch. Khim.*, **32**, 3184 (1962); *J. Gen. Chem. USSR*, **32**, 3129 (1962).

(5) Melting and boiling points are uncorrected. Infrared spectra were recorded on an Infracord spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian Associates A-60A spectrometer in deuteriochloroform with tetramethylsilane as internal standard. Microanalyses were performed by Dr. C. S. Yeh and staff.

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