(13c).—The methylation of 0.2 g of 13c,[2] carried out as described for 5-bromoindole-3-carboxaldehyde (13a), gave 0.185 g (88.5%) of 12c.

Registry No.—Bromine, 7726-95-6; **3**, 25055-54-3; **4a**, 25055-55-4; **5**, 25055-56-5; **6a**, 25055-57-6; **7**, 25055-58-7; **7** (phenylhydrazone), 25055-59-8; **8b**, 25055-60-1; **9a**, 25055-61-2; **10a**, 25055-62-3; **10b**, 25055-63-4; **10b** (phenylhydrazone), 25055-64-5; **12b**, 25055-65-6; **12c**, 25055-66-7; **14a**, 25055-67-8; **14b**, 25055-68-9; **14c**, 25055-50-9; **15a**, 25055-51-0; **15b**, 25055-52-1; **15c**, 25055-53-2.

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Alkyl Nitrate Nitration of Active Methylene Compounds. VIII. Synthesis of α-Nitrosulfonate Esters

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The alkyl nitrate nitration of neopentyl sulfonate esters gives the corresponding neopentyl α-nitrosulfonate esters in good yield. On the other hand, the nitration of ethyl sulfonate esters such as ethyl 1-butanesulfonate (**1a**) leads not only to ethyl 1-nitro-1-butanesulfonate (**2a**) but also to potassium 1-nitro-1-butanesulfonate (**3**). Compound **3** arises from a β-elimination reaction on the ester portion of the molecule which occurs during the nitration step and not during anion formation or during the acidification step.

In continuation of our studies of the alkyl nitrate nitration,[1] we are now reporting on its application to the preparation of α-nitrosulfonate esters which constitute a new class of compounds.

In preliminary experiments it was established that nitration of ethyl 1-butanesulfonate (**1a**) gave best results in the potassium amide–liquid ammonia system, affording a 54.8% yield of ethyl 1-nitro-1-butanesulfonate (**2a**). The yield of **2a** was only 35.5 and 37.0%, respectively, when nitrations were performed in sodium amide–liquid ammonia and potassium *t*-butoxide–THF. In addition to **2a**, potassium 1-nitro-1-butanesulfonate (**3**) was also obtained in each of the base-solvent systems employed (eq 1). However, only neopentyl α-nitrobutanesulfonate (**2b**) was obtained from the nitration of neopentyl butanesulfonate (**1b**).

$$\underset{\mathbf{1}}{H_3C(CH_2)_3SO_3R} \xrightarrow[2.\ H^+]{1.\ KNH_2\text{–liquid } NH_3\text{–}R^1ONO_2}$$

$$\underset{\mathbf{2}}{H_3C(CH_2)_2CH(NO_2)SO_3R} + \underset{\mathbf{3}}{H_3C(CH_2)_2CH(NO_2)SO_3^-K^+} + \underset{\mathbf{12}}{CH_2{=}CH(CH_2)_5CH_3} \quad (1)$$

a, R = CH_2CH_3; b, R = $CH_2C(CH_3)_3$; c, R = $(CH_2)_7CH_3$; $R^1 = C_2H_5$ or n-C_3H_7

The acid salt rather than the nitronate structure was assigned to compound **3** on the basis of its nmr spectrum which showed the characteristic methine proton absorption at 5.48–5.72 ppm.

The results of the nitration of various neopentyl sulfonate estera are summarized in Table I. It is noteworthy that in order to obtain optimum yields of α-nitrosulfonate esters containing 8–12 carbons in the side chain, more concentrated reaction mixtures had to be employed, (instead of 250 ml, only 100 ml of liquid ammonia was used). In the case of neopentyl 1-hexadecanesulfonate (**4**), no nitrated product was obtained. Even though anion formation was carried out with potassium amide in THF at 65°, 95% of the ester **4** was recovered. The failure of **4** to undergo nitration was due to the fact that it was not converted to its anion. This was ascertained from a deuterium-exchange experiment, for nmr and mass spectral data showed that no deuterium was incorporated into **4** after treatment with potassium amide in liquid ammonia and subsequent acidification with deuterium oxide in anhydrous ether.[2] Under similar reaction conditions, deuterium was incorporated into **1b** and neopentyl 1-dodecanesulfonate to the extent of 100 and 75%, respectively.

The nitration was also successful with a disulfonate ester.

The nitration was also successful with a disulfonate ester. Thus dineopentyl 1,4-butanedisulfonate was converted into dineopentyl 1,4-dinitro-1,4-butanedisulfonate in 68.9% yield.

The neopentyl α-nitrosulfonate esters were identified by infrared and nmr spectra and by conversion to the corresponding bromo derivatives (eq 2).

$$\underset{\mathrm{NO_2}}{\mathrm{RCHSO_3R^1}} \xrightarrow[2.\ Br_2;\ CCl_4]{1.\ KOH\text{–}C_2H_5OH} \underset{\mathrm{NO_2}}{\overset{\mathrm{Br}}{\mathrm{RCSO_3R^1}}} \quad (2)$$

In contrast to the results in the nitration of *t*-butyl α-methylbutyrate which led with decarboxylation to 2-nitrobutane,[1a] neopentyl 2-butanesulfonate was converted to neopentyl 2-nitro-2-butanesulfonate (**5**) in 34.7% yield. The lower yield of **5** as compared with **2b** could be caused by the methyl group in the α position, which lowers the acidity of the α hydrogen[3] and hinders the approach of base in forming the carbanion.

The nitration of ethyl 2-butanesulfonate (**6**) led in 53.1% yield to potassium 2-nitro-2-butanesulfonate (**7**) instead of the expected α-nitrosulfonate ester. In addition to **7**, 35.1% ethyl 3-methyl-3-pentanesulfonate (**8**) was also isolated (eq 3).

(1) For previous publications, see (a) H. Feuer and R. P. Monter, *J. Org. Chem.*, **34**, 991 (1969); (b) H. Feuer and J. P. Lawrence, *J. Amer. Chem. Soc.*, **91**, 1856 (1969); (c) W. E. Truce, T. C. Klinger, J. E. Paar, and by H. Feuer, and D. K. Wu, *J. Org. Chem.*, **34**, 3104 (1969).

(2) A steric factor might be responsible for preventing conversion of compound **4** to its anion. Models indicate that coiling back of the alkyl chain could hinder approach to the α hydrogen.

(3) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1959.

TABLE I

ALKYL NITRATE NITRATION OF NEOPENTYL SULFONATE ESTERS

$RSO_3CH_2C(CH_3)_3$, R	Neopentyl 1-nitrosulfonate ester— Yield, %[a]	Yield, %[b]
CH_3CH_2-	73.8 (22.2)[c]	
n-C_4H_9-	75.5 (22.2)	75.6 (20.2)
n-$C_6H_{13}-$	55.8 (36.7)	75.2 (20.8)
n-$C_8H_{17}-$	32.8 (61.6)	75.6 (21.7)
n-$C_{10}H_{21}-$	16.9 (78.1)	55.7 (39.7)
n-$C_{12}H_{25}-$	3.0 (93.4)	33.9[d] (62.7)
n-$C_{16}H_{33}-$	0 (95.7)	0 (95.5)
$CH_3CH_2CH(CH_3)-$		34.7 (59.8)

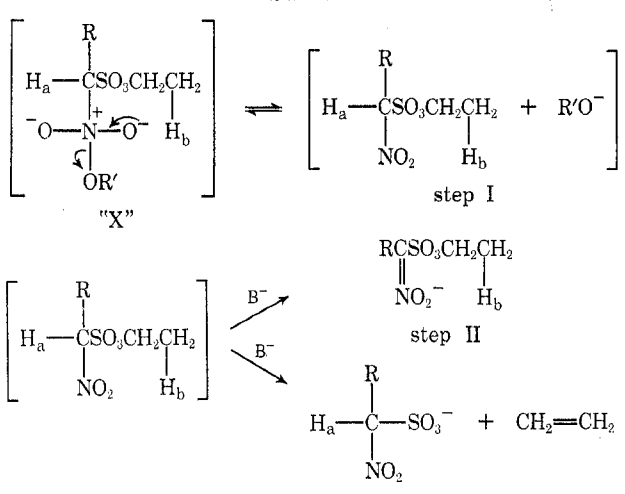
[a] Reactions were carried out with potassium amide in 250 ml of liquid ammonia at −33°. The nitration time was 5 min. [b] Reactions were carried out with potassium amide in 100 ml of liquid ammonia at −33°. The nitration time was 1 hr. [c] The numbers in parenthesis represent recovered starting material. [d] The yield was 47.0% when anion formation was carried out with potassium amide in THF at 65°, and the nitration at −33°.

$$\underset{\mathbf{6}}{H_3CCH_2CH(CH_3)SO_3CH_2CH_3} \xrightarrow[2.\ NH_4Cl]{1.\ KNH_2\text{–liquid } NH_3\text{–}R^1ONO_2} H_3CCH_2\underset{NO_2}{\overset{CH_3}{C}}SO_3^-K^+ + (H_3CCH_2)_2\overset{CH_3}{C}SO_3CH_2CH_3 \quad (3)$$

7 **8**

It is possible that ethyl 2-nitro-2-butanesulfonate (**9**) is an intermediate in the reaction, and that it is converted by a nucleophilic attack of the anion of **6** on the ester portion of **9** to compounds **7** and **8**. However, salt **7** could also form *via* a β-elimination reaction as shown in step III of Scheme I (*vide infra*).

SCHEME I



That an intermediate such as **9** is involved in the formation of **8** was indicated by the fact that **6** was recovered unchanged in 93.4% yield when treated with potassium amide in liquid ammonia. However, it should be emphasized that the nitro group is not essential for the alkylation reaction since the reaction of **8** with neopentyl 2-butanesulfonate (**10**) in the potassium amide–liquid ammonia system led to neopentyl 3-methyl-3-pentanesulfonate (**11**) in 21.1% yield (eq 4).

$$\underset{\mathbf{10}}{CH_3CH_2CH(CH_3)SO_3CH_2C(CH_3)_3} + \mathbf{8} \xrightarrow[2.\ NH_4Cl]{1.\ KNH_2\text{–liquid } NH_3} (CH_3CH_2)_2\overset{CH_3}{C}\text{—}SO_3CH_2C(CH_3)_3 + (CH_3CH_2)_2\overset{H_3C}{C}SO_3^-K^+ \quad (4)$$

11

Study of the Elimination Reaction.—It has been suggested[4] that the alkyl nitrate nitration of an active methylene compound proceeds *via* collapse of an intermediate which is formed by nucleophilic attack of a carbanion on the alkyl nitrate. The results from the nitration of neopentyl sulfonate esters are consistent with this suggested mechanism. However, the formation of potassium 1-nitrobutanesulfonate (**3**) in the nitration of compound **1a** (eq 1) requires additional clarification. It involves a β-elimination reaction in the ester part of **1**, for the nitration of octyl 1-butanesulfonate (**1c**) gave 1-octene (**12**) in addition to **3** and octyl 1-nitro-1-butanesulfonate (**2c**). That the reaction takes place during the nitration step and not during anion formation or the acidification step is based on the results from the following control experiments. (a) Compound **1a** was recovered in 92% yield on treatment with potassium amide in liquid ammonia, followed by acidification with ammonium chloride. (b) Potassium 1-ethoxysulfonyl-1-butanenitronate was converted in 96.4% yield to ethyl 1-nitro-1-butanesulfonate (**2a**) on treatment with potassium amide in liquid ammonia and subsequent acidification with ammonium chloride. (c) Treatment of **2a** with potassium amide in liquid ammonia followed by acidification with ammonium chloride gave a mixture consisting of **3** (26.3%) and **2a** (67.3%) (eq 5). A mechanism consistent with these observations is proposed in Scheme I.

$$\underset{\mathbf{2a}}{CH_3(CH_2)_2\underset{NO_2}{CH}SO_3CH_2CH_3} \xrightarrow[2.\ NH_4Cl]{1.\ KNH_2\text{–liquid } NH_3} CH_3(CH_2)_2\underset{NO_2}{CH}SO_3^-K^+ + \mathbf{2a} \quad (5)$$

3

In step I intermediate "X" collapses into α-nitrosulfonate ester and alkoxide. According to the results of control experiment c, a competitive reaction can occur in which the base can then attack the α proton (H_a) to give the nitronate salt as shown in step II, or alternately attack the β proton (H_b) in the ester portion to give the α-nitrosulfonic acid salt and olefin (step III).

It is of interest that the nitration of carboxylic esters[1a] gave nitroalkanes which arose *via* a decarboxylation rather than an elimination reaction.

Experimental Section

All melting points are uncorrected. All infrared spectra were taken with a Perkin-Elmer recording spectrophotometer, Models 21 and 421. Nuclear magnetic resonance spectra were determined in a Varian Model A-60 analytical nmr spectrometer using tetramethylsilane as an internal standard. Gas chromatographic analyses were performed on an Aerograph A-700 using a 4-ft SF-96 on Chromosorb W column and a 6-ft SE-30 on Chromosorb P column. Solvents were evaporated on a Buchler flash evaporator.

(4) H. Feuer and C. Savides, *J. Amer. Chem. Soc.*, **91**, 5826 (1959).

Reagents.—Ethyl and propyl nitrate and ethane and 1-butanesulfonyl chloride of Eastman White Label grade were used as received. All alkyl halides used for the preparation of the corresponding sulfonyl chlorides by methods described in the literature[5,6] were from commercial sources.

Neopentyl 1-Butanesulfonate (1b).—The following experiment is typical of the procedure employed for preparing sulfonate esters.[7] To a mixture consisting of neopentyl alcohol (30.36 g, 0.3 mol), triethylamine (30.36 g, 0.3 mol), and benzene (150 ml) was added dropwise in 1 hr 1-butanesulfonyl chloride (26.45 g, 0.3 mol) at 0–10°. Stirring for 12 hr more at 20°, filtering, and washing the filtrate with four 60-ml portions of 4% hydrochloric acid and then with three 80-ml portions of water was followed by drying (Na_2SO_4) and concentrating the benzene extract. Distillation of the residue afforded 49.55 g (79.5%) of **neopentyl 1-butanesulfonate (1b)**: bp 78–80° (0.6 mm); $n^{20}D$ 1.4339; nmr (CCl_4) δ 0.86–1.10 (t, 3, CH_3), 1.0 [s, 9 $C(CH_3)_3$], 1.32–2.08 [m, 4, $(CH_2)_2$], 2.96–3.22 (t, 2, CH_2SO_3), and 3.87 (s, 2, OCH_2).

Anal. Calcd for $C_9H_{20}O_3S$: C, 51.89; H, 9.68; S, 15.39. Found: C, 51.73; H, 9.60; S, 15.50.

By the same procedure, the following alkyl sulfonates were prepared [satisfactory analytical data (± 0.35% for C, H, and S) were reported for each product (Editor)]: octyl 1-butanesulfonate (1c), 76.3%, bp 108° (0.2 mm), $n^{20}D$ 1.4438; neopentyl 2-butanesulfonate (10), 70.5%, bp 59° (0.15 mm), $n^{20}D$ 1.4346; ethyl 2-butanesulfonate (6), 81%, bp 65° (0.2 mm), $n^{20}D$ 1.4311; neopentyl ethanesulfonate, 79.4%, bp 55° (0.12 mm), $n^{20}D$ 1.4290; neopentyl 1-hexanesulfonate, 81%, bp 86° (0.25 mm), $n^{20}D$ 1.4378; neopentyl 1-octanesulfonate, 80.9%, bp 110–112° (0.38 mm), $n^{20}D$ 1.4420; neopentyl 1-decanesulfonate, 82.2%, bp 140–141° (<0.001 mm), $n^{20}D$ 1.4458; neopentyl 1-dodecanesulfonate, 70.5%, bp 147° (<0.001 mm), $n^{20}D$ 1.4484; neopentyl 1-hexadecanesulfonate (4), 59.2%, mp 47–48° (isopropyl alcohol); dineopentyl 1,4-butanedisulfonate, 57.3%, mp 125–127° (CCl_4).

Neopentyl 1-Nitro-1-butanesulfonate (2b).—The following is typical of the procedure employed for preparing α-nitrosulfonate esters. Into an oven-dried, nitrogen-flushed, 200-ml round-bottom four-necked flask equipped with a Dry Ice condenser, thermometer, mechanical stirrer, and dropping funnel were placed freshly cut potassium (3.91 g, 0.10 g-atom) and a catalytic amount of ferric nitrate in 100 ml of anhydrous ammonia at −33°. After the potassium amide had formed, neopentyl 1-butanesulfonate (1b) (10.42 g, 0.05 mol) was added in 2 min. After stirring for 3 min longer, propyl nitrate (15.77 g, 0.15 mol) was added in 5 min[8] at −35° and stirring was continued for 55 min. The reaction mixture was then acidified with ammonium chloride (5.89 g, 0.11 mol) at −50° and the ammonia replaced with anhydrous ether. Filtering off the potassium chloride, extracting the ethereal filtrate with 10% aqueous potassium hydroxide (1b remained in the ethereal layer), reacidifying the basic extract with glacial acetic acid, extracting the aqueous acidic layer with ether, drying the combined extracts (Na_2SO_4), and concentrating *in vacuo* gave 9.6 g (75.6%) of analytically pure **2b**:[9] $n^{20}D$ 1.4451; ir (neat) 1384 and 1183 (SO_2), and 1575 and 1372 cm^{-1} (NO_2); nmr (CCl_4) δ 0.92–1.16 (t, 3, CH_3), 1.02 [s, 9, $C(CH_3)_3$], 1.25–1.70 (m, 2, CH_3CH_2), 2.2–2.62 (m, 2, CH_2CH), 4.08 (s, 2, OCH_2), and 5.52–5.77 (q, 1, CH).

Anal. Calcd for $C_9H_{19}NO_5S$: C, 42.67; H, 7.56; N, 5.53; S, 12.66. Found: C, 42.96; H, 7.54; N, 5.29; S, 12.78.

Neopentyl 1-nitro-1-ethanesulfonate (73.8%): $n^{20}D$ 1.4441; ir (neat) 1375 and 1180 (SO_2), and 1578 and 1348 cm^{-1} (NO_2); nmr (CCl_4) δ 1.03 [s, 9, $C(CH_3)_3$], 1.92–2.04 (d, 3, CH_3), 4.06 (s, 2, OCH_2), and 5.53–5.88 (q, 1, CH).

Anal. Calcd for $C_7H_{15}NO_5S$: C, 37.32; H, 6.71; N, 6.22; S, 14.24. Found: C, 37.25; H, 6.56; N, 6.22; S, 14.24.

Neopentyl 1-nitro-1-hexanesulfonate (75.2%): $n^{20}D$ 1.4470; ir (neat) 1373 and 1180 (SO_2), and 1570 and 1348 cm^{-1} (NO_2); nmr (CCl_4) δ 0.9–1.05 (t, 3, CH_3), 1.02 [s, 9, $C(CH_3)_3$], 1.3–1.5 [m, 6, $CH_3(CH_2)_3$], 2.12–2.55 (m, 2, CH_2CH), 4.07 (s, 2, OCH_2), and 5.48–5.71 (q, 1, CH).

Anal. Calcd for $C_{11}H_{23}NO_5S$: C, 46.95; H, 8.24; N, 4.98; S, 11.40. Found: C, 47.12; H, 8.13; N, 5.19; S, 11.56.

Neopentyl 1-nitro-1-octanesulfonate (75.6%): $n^{20}D$ 1.4502; ir (neat) 1378 and 1181 (SO_2), and 1572 and 1351 cm^{-1} (NO_2); nmr (CCl_4) δ 0.88–1.05 (t, 3, CH_3), 1.0 [s, 9, $C(CH_3)_3$], 1.32 [s, 10, $CH_3(CH_2)_5$], 2.18–2.46 (m, 2, CH_2CH), 3.97 (s, 2, OCH_2), and 5.36–5.60 (q, 1, CH).

Anal. Calcd for $C_{13}H_{27}NO_5S$: C, 50.46; H, 8.80; N, 4.53; S, 10.36. Found: C, 50.69; H, 8.78; N, 4.69; S, 10.35.

Neopentyl 1-nitro-1-decanesulfonate (55.7%): $n^{20}D$ 1.4552; ir (neat) 1384 and 1180 (SO_2), and 1575 and 1368 cm^{-1} (NO_2); nmr (CCl_4) δ 0.88–1.05 (t, 3, CH_3), 0.99 [s, 9, $C(CH_3)_3$], 1.28 [s, 14, $CH_3(CH_2)_7$], 2.0–2.4 (m, 2, CH_2CH), 3.98 (s, 2, OCH_2), and 5.34–5.58 (q, 1, CH).

Anal. Calcd for $C_{15}H_{31}NO_5S$: C, 53.38; H, 9.26; N, 4.15; S, 9.50. Found: C, 53.47; H, 9.55; N, 3.91; S, 9.69.

Neopentyl 1-Nitro-1-dodecanesulfonate.—The general procedure was followed except anion formation was performed at 65° in THF for 1 hr after the ammonia was evaporated, followed by nitration at −33° and acidification with glacial acetic acid at −50°. Neopentyl 1-dodecanesulfonate (8.01 g, 0.025 mol) gave 4.3 g (47.0%) of **neopentyl 1-nitro-1-dodecanesulfonate**: $n^{20}D$ 1.4560; ir (neat) 1370 and 1178 (SO_2), and 1568 and 1358 cm^{-1} (NO_2); nmr (CCl_4) δ 0.89–1.05 (t, 3, CH_3), 1.0 [s, 9, $C(CH_3)_3$], 1.27 [s, 18, $CH_3(CH_2)_9$], 2.1–2.5 (m, 2, CH_2CH), 3.98 (s, 2, OCH_2), and 5.35–5.60 (q, 1, CH).

Anal. Calcd for $C_{17}H_{35}NO_5S$: C, 55.86; H, 9.65; N, 3.83; S, 8.77. Found: C, 55.92; H, 9.49; N, 3.88; S, 8.50.

Dineopentyl 1,4-dinitro-1,4-butanedisulfonate (68.9%): mp 92° dec ($CHCl_3$); ir (KBr) 1382 and 1181 (SO_2), and 1575 and 1369 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 1.01 [s, 18 $C(CH_3)_3$], 2.45–2.70 (m, 4, CH_2), 4.08 (s, 4, OCH_2), and 5.45–5.71 (m, 2, CH).

Anal. Calcd for $C_{14}H_{28}N_2O_{10}S_2$: C, 37.49; H, 6.29; N, 6.25; S, 14.30. Found: C, 37.27; H, 6.44; N, 6.35; S, 14.34.

Neopentyl 2-Nitro-2-butanesulfonate (5)—The general procedure was followed except that neopentyl 2-butanesulfonate (10.42 g, 0.05 mol) was used. Filtering off potassium chloride, concentrating the ethereal filtrate *in vacuo*, and eluting the oily residue with benzene on an aluminum oxide (alumina, acid washed) column gave 4.4 g (34.7%) of **5**: mp 37.5–38.5°; ir (melt) 1360 1183 (SO_2), and 1568 and 1330 cm^{-1} (NO_2); nmr (CCl_4) δ 0.90–1.16 (t, 3, CH_3CH_2), 0.99 [s, 9, $C(CH_3)_3$], 1.95 [s, 3, $C(NO_2)CH_3$], 2.0–2.8 (m, 2, CH_3CH_2), and 3.94 (s, 2, OCH_2).

Anal. Calcd for $C_9H_{19}NO_5S$: C, 42.67; H, 7.56; N, 5.53; S, 12.66. Found: C, 42.95; H, 7.83; N, 5.61; S, 12.64.

Octyl 1-Nitro-1-butanesulfonate (2c), Potassium 1-Nitrobutanesulfonate (3), and 1-Octene (12).—The general procedure was followed except that octyl 1-butylsulfonate (1c) (12.52 g, 0.05 mol) and 250 ml of ammonia were used, and that the nitration time was 5 min at −33°.

After acidification with ammonium chloride (5.89 g, 0.11 mol) and replacement of ammonia with absolute ether, precipitate A was filtered off. The ethereal filtrate (B) was extracted with 10% aqueous potassium hydroxide and the basic extract reacidified with glacial acetic acid and extracted with ether. Drying the combined extracts (Na_2SO_4) and concentrating *in vacuo* gave 3.5 g (23.8%) of **octyl 1-nitro-1-butanesulfonate (2c)**: $n^{20}D$ 1.4451; ir (neat) 1378 and 1180 (SO_2), and 1572 and 1358 cm^{-1} (NO_2); nmr (CCl_4) δ 0.85–1.19 [m, 6, CH_3 and $(CH_2)_6CH_3$], 1.40–2.0 [m, 14, CH_3CH_2 and $(CH_2)_6CH_3$], 2.2–2.75 (m, 2, CH_2CH), 4.32–4.53 (t, 2, OCH_2), and 5.42–5.67 (q, 1, CH).

Anal. Calcd for $C_{12}H_{25}NO_5S$: C, 48.79; H, 8.53; N, 4.74; S, 10.86. Found: C, 48.67; H, 8.59; N, 4.72; S, 10.79.

Concentration of filtrate B *in vacuo* and glpc analysis of the residue showed it to contain **1-octene** (0.22 g, 4,0%), $n^{20}D$ 1.4080 (lit.[10] $n^{20}D$ 1.4087), and 1c (8.2 g, 65.6% recovery).

Continuous extraction of precipitate A with acetone and concentration of the extract *in vacuo* gave **potassium 1-nitrobutanesulfonate (3)** (0.9 g, 8.1%): mp 234° dec (95% ethanol); ir (KBr) 1210 and 1052 (SO_2), and 1552 and 1360 cm^{-1} (NO_2); nmr ($DMSOd_6$) δ 0.78–1.01 (t, 3, CH_3), 1.08–1.65 (m, 2, CH_3CH_2), 1.92–2.4 (m, 2, CH_2CH), and 5.26–5.51 (q, 1, CH).

Anal. Calcd for $C_4H_8KNO_5S$: C, 21.71; H, 3.64; K, 17.67; N, 6.33; S, 14.49. Found: C, 21.71; H, 3.86; K, 17.45; N, 6.26; S, 14.37.

Ethyl 1-Nitro-1-butanesulfonate (2a) and Compound 3.—By following the procedure for preparing compound **2c**, there were obtained 10.8% potassium salt **3** and 54.8% **ethyl 1-nitro-1-butanesulfonate**: bp 80–82° (0.025 mm); $n^{20}D$ 1.4450; ir (neat)

(5) T. B. Johnson and J. M. Sprague, *J. Amer. Chem. Soc.*, **58**, 1348 (1936).

(6) J. M. Sprague and T. B. Johnson, *ibid.*, **59**, 1837 (1937).

(7) W. E. Truce and L. W. Christensen, *J. Org. Chem.*, **33**, 2261 (1968).

(8) *Caution!* The first drops of alkyl nitrate should be added slowly because a considerable exotherm develops.

(9) Attempted vacuum distillation at < 0.001 mm resulted in decomposition.

(10) A. F. Forziati, D. L. Camin, and F. D. Rossini, *J. Res. Nat. Bur. Stand. A*, **45**, 406 (1950).

1380 and 1180 (SO_2), and 1572 and 1365 cm^{-1} (NO_2); nmr (CCl_4) δ 0.91–1.13 (t, 3, CH_3CH_2), 1.32–1.58 (t, 3, OCH_2CH_3), 1.58–2.0 (m, 2, CH_3CH_2), 2.18–2.70 (m, 2, CH_2CH), 4.28–4.65 (q, 2, OCH_2), and 5.48–5.72 (q, 1, CH).

Anal. Calcd for $C_6H_{13}NO_5S$: C, 34.12; H, 6.20; N, 6.63; S, 15.18. Found: C, 34.39; H, 6.27; N, 6.56; S, 15.40.

Ethyl 3-Methyl-3-pentanesulfonate (8) and Potassium 2-Nitro-2-butanesulfonate (7).—The procedure was similar to the preparation of **2b** except that ethyl 2-butanesulfonate (8.31 g, 0.05 mol) was used. Filtering off the potassium chloride precipitate and concentrating the filtrate *in vacuo* gave 3.4 g (35.1%) of compound **8** as determined by glpc analysis: $n^{20}D$ 1.4438; ir (neat) 1344 and 1183 cm^{-1} (SO_2); nmr (CCl_4) δ 0.86–1.09 [t, 6, (CH_3CH_2)$_2$C], 1.25–1.49 (t, 3, OCH_2CH_3), 1.28 [s, 3, $C(CH_3)$], 1.61–2.0 [m, 4, $(CH_3CH_2)_2C$ and 4.0–4.35 (q, 2, OCH_2).

Anal. Calcd for $C_8H_{18}O_3S$: C, 9.45; H, 9.34; S, 16.51. Found: C, 49.73; H, 9.53; S, 16.68.

Extracting the precipitate continuously with acetone, concentrating the extract *in vacuo*, and recrystallizing the residue three times with 95% ethanol gave 5.9 g (53.1%) of **7**: mp 244° dec; ir (KBr) 1205, and 1038 (SO_2), and 1538 and 1338 cm^{-1} (NO_2); nmr (D_2O) δ 0.88–1.13 (t, 3, CH_3CH_2), 1.96 [s, 3, $C(NO_2)CH_3$], and 2.0–3.0 (m, 2, CH_3CH_2).

Anal. Calcd for $C_4H_8KNO_5S$: C, 21.71; H, 3.64; K, 17.67; N, 6.33; S, 14.49. Found: C, 21.51; H, 3.82; K, 17.90; N, 6.51; S, 14.76.

Treatment of Ethyl 1-Butanesulfonate (1a) with Potassium Amide at Alkyl Nitrate Nitration Conditions.—To 11.03 g (0.2 mol) of potassium amide in 250 ml of anhydrous ammonia was added at −33° compound **1a** (16.62 g, 0.10 mol). After the reaction mixture stirred for 5 min, ammonium chloride (11.24 g, 0.21 mol) was added at −50° and the ammonia replaced by anhydrous ether. Filtering off potassium chloride, concentrating the filtrate *in vacuo*, and distilling the residue gave 15.3 g (92.2% recovery) of **1a**: bp 70–73° (0.7 mm); $n^{20}D$ 1.4348.

Treatment of Ethyl 2-Butanesulfonate (6) with Potassium Amide at Alkyl Nitrate Nitration Conditions.—The procedure was similar to the treatment of compound **1a** with potassium amide. Ethyl 2-butanesulfonate (**6**) (8.31 g, 0.05 mol) was recovered in 93.4% yield: bp 65° (0.2 mm); $n^{20}D$ 1.4310.

Conversion of Ethyl 1-Nitro-1-butanesulfonate (2a) to Potassium 1-Nitro-1-butanesulfonate (3).—The procedure was similar to the treatment of **1a** with potassium amide except that ethyl 1-nitro-1-butanesulfonate (**2a**) (10.56 g, 0.05 mol) was used. After replacing the ammonia with anhydrous ether, the precipitate was filtered. Extracting the precipitate with acetone and concentrating the extract *in vacuo* gave 2.91 g (26.3%) of **3**: mp 234° dec.

Concentrating the ethereal filtrate *in vacuo* and distilling the residue gave 7.1 g (67.3% recovery) of **2a**: bp 80–82° (0.25 mm); $n^{20}D$ 1.4450.

Conversion of Potassium 1-Ethoxysulfonyl-1-butanenitronate to Ethyl 1-Nitro-1-butanesulfonate (2a).—The procedure was similar to the treatment of **1a** with potassium amide. Potassium 1-ethoxysulfonyl-1-butanenitronate (4.4 g, 0.0177 mol) gave 3.6 g (96.2%) of **2a**: bp 80–82° (0.25 mm); $n^{20}D$ 1.4447.

Deuteration of Neopentyl 1-Dodecanesulfonate.—To 0.36 g (0.0066 mol) of potassium amide in 100 ml of liquid ammonia was added at −33° neopentyl 1-dodecanesulfonate (1.06 g, 0.0033 mol). After 5 min the ammonia was replaced with anhydrous ether and the last traces of ammonia were removed by refluxing for 30 min. The reaction mixture was then cooled to −50° and deuterium oxide (0.30 g, 0.0149 mol) was added. Warming the reaction mixture to room temperature, decanting the clear ethereal layer, and concentrating *in vacuo* gave a mixture of **neopentyl 1-dodecanesulfonate** and **neopentyl 1-dodecanesulfonate-d_1**: nmr (CCl_4) δ 2.85–3.15 [t, 1.25, $CH_3(CH_2)_{10}CHD$] (75% of deuterium was incorporated).

Neopentyl 3-Methyl-3-pentanesulfonate (11).—To a solution of potassium amide (3.44 g, 0.0624 mol) in 250 ml of ammonia was added at −33° neopentyl 2-butanesulfonate (**10**) (6.50 g, 0.0312 mol). After stirring the reaction mixture for 5 min, ethyl 3-methyl-3-pentanesulfonate (**8**) (6.04 g, 0.0312 mol) was added in 5 min at −35°. Then acidifying the reaction mixture with ammonium chloride (3.67 g, 0.0686 mol) at −50°, replacing the ammonia with anhydrous ether, filtering the potassium chloride, concentrating the filtrate *in vacuo*, and distilling the residue gave a mixture of compounds **10** and **11**: bp 64° (0.15 mm). Analysis by glpc gave 4.74 g (72.9% recovery) of **10** and 1.55 g (21.1%) of **11**: $n^{20}D$ 1.4450; ir (neat) 1344 and 1184 cm^{-1} (SO_2); nmr (CCl_4) δ 0.86–1.10 [t, 6, (CH_3CH_2)$_2$C], 0.97 [s, 9, $C(CH_3)_3$], 1.28 [s, 3, $C(CH_3)$], 1.62–2.01 [m, 4, (CH_3CH_2)$_2$C], and 3.75 (s, 2, OCH_2).

Anal. Calcd for $C_{11}H_{24}O_3S$: C, 55.89; H, 10.23; S, 13.57). Found: C, 55.79; H, 10.36; S, 13.35.

Neopentyl 1-Bromo-1-nitroethanesulfonate.—The following experiment is typical of the method used for the bromination of α-nitroalkylsulfonates. To a solution of 0.66 g (0.01 mol) 85% potassium hydroxide in 50 ml of absolute ethanol was added with stirring at 0–5° neopentyl 1-nitro-1-ethanesulfonate (2.37 g, 0.106 mol). Allowing the reaction mixture to warm to room temperature, concentrating the clear solution *in vacuo*, slurrying the solid residue in ether, and filtering gave 2.63 g (100%) of crude potassium 1-neopentoxysulfonyl-1-ethanenitronate.

To a slurry of the crude salt (2.63 g, 0.01 mol) in 50 ml of carbon tetrachloride was added in 15 min at 0–5° bromine (1.60 g, 0.01 mol), and then stirring was continued for 1 hr at room temperature. Filtering off potassium bromide, concentrating the filtrate *in vacuo*, dissolving the residue in ether, and washing the ethereal solution successively with 0.5% sodium bisulfite, 1% potassium hydroxide, and water, followed by drying (sodium sulfate), and concentrating *in vacuo* gave 2.87 g (94.2%) of analytically pure **neopentyl 1-bromo-1-nitroethanesulfonate**: mp 33–35°; ir (melt) 1372 and 1186 (SO_2), and 1570 and 1375 cm^{-1} (NO_2); nmr (CCl_4) δ 1.05 [s, 9, $C(CH_3)_3$], 2.62 (s, 3, CH_3), and 4.20 (s, 2, OCH_2).

Anal. Calcd for $C_7H_{14}BrNO_5S$: C, 27.64; H, 4.64; Br, 26.27; N, 4.61; S, 10.54. Found: C, 27.62; H, 4.74; Br, 26.42; N, 4.67; S, 10.51.

Neopentyl 1-bromo-1-nitrobutanesulfonate (85%) was analyzed as follows: $n^{20}D$ 1.4759; ir (neat) 1385 and 1183 (SO_2), and 1575 and 1368 cm^{-1} (NO_2); nmr (CCl_4) δ 0.95–1.15 (t, 3, CH_3), 1.03 [s, 9, $C(CH_3)_3$], 1.36–1.88 (m, 2, CH_3CH_2), 2.5–2.9 (m, 2, CH_2C), and 4.12 (s, 2, OCH_2).

Anal. Calcd for $C_9H_{18}BrNO_5S$: C, 32.54; H, 5.46; Br, 24.05; N, 4.22; S, 9.65. Found: C, 32.68; H, 5.38; Br, 24.07; N, 4.18; S, 9.78.

Ethyl 1-bromo-1-nitrobutanesulfonate (47.1%) was analyzed as follows: bp 78–80° (0.3 mm); $n^{20}D$ 1.4822; ir (neat) 1390 and 1182 (SO_2), and 1575 and 1380 cm^{-1} (NO_2); nmr (CCl_4) δ 0.98–1.18 (t, 3, CH_3), 1.4–1.65 (t, 3, OCH_2CH_3), 1.70–2.1 (m, 2, CH_3CH_2), 2.3–3.1 (m, 2, CH_2C), and 4.5–4.83 (q, 2, OCH_2).

Anal. Calcd for $C_6H_{12}BrNO_5S$: C, 24.84; H, 4.17; Br, 27.54; N, 4.83; S, 11.05. Found: C, 24.78; H, 4.18; Br, 27.25; N, 5.02; S, 10.99.

Dineopentyl 1,4-dibromo-1,4-dinitro-1,4-butanedisulfonate (74.0%) was analyzed as follows: mp 77° dec (CCl_4); ir (KBr) 1388 and 1180 (SO_2), and 1575 and 1370 cm^{-1} (NO_2); nmr ($CDCl_3$) δ 1.02 [s, 18, $C(CH_3)_3$], 3.10 (s, 4, CH_2), and 4.18 (s, 4, OCH_2).

Anal. Calcd for $C_{14}H_{26}Br_2N_2O_{10}S_2$: C, 27.73; H, 4.32; Br, 26.36; N, 4.26; S, 10.58. Found: C, 27.50; H, 4.50; Br, 26.20; N, 4.47; S, 10.57.

Neopentyl 1-bromo-1-nitrohexanesulfonate (76.8%) was analyzed as follows: $n^{20}D$ 1.4710; ir (neat) 1388 and 1184 (SO_2), and 1582 and 1374 cm^{-1} (NO_2); nmr (CCl_4) δ 0.92–1.02 (t, 3, CH_3), 1.02 [s, 9, $C(CH_3)_3$], 1.2–1.5 [s, 6, $CH_3(CH_2)_3$], 2.5–3.0 (m, 2, CH_2C), and 4.12 (s, 2, OCH_2).

Anal. Calcd for $C_{11}H_{22}BrNO_5S$: C, 36.67; H, 6.16; Br, 22.18; N, 3.89; S, 8.90. Found: C, 36.75; H, 5.94; Br, 22.23; N, 3.87; S, 8.86.

Registry No.—**1b**, 25056-20-6; **1c**, 25056-18-2; **2b**, 25056-19-3; **2c**, 25056-21-7; **3**, 25056-22-8; **4**, 25056-23-9; **5**, 25056-41-1; **6**, 25056-24-0; **7**, 25056-25-1; **8**, 25056-26-2; **10**, 25056-27-3; **11**, 25056-28-4; neopentyl ethenesulfonate, 25056-29-5; neopentyl 1-hexanesulfonate, 25056-30-8; neopentyl 1-octanesulfonate, 25056-31-9; neopentyl 1-decanesulfonate, 25056-32-0; neopentyl 1-dodecanesulfonate, 25056-33-1; dineopentyl 1,4-butanedisulfonate, 25056-34-2; neopentyl 1-nitro-1-ethanesulfonate, 25056-35-3; neopentyl 1-nitro-1-hexanesulfonate, 25056-36-4; neopentyl 1-nitro-1-octanesulfonate, 25056-37-5; neopentyl 1-nitro-1-decanesulfonate, 25056-38-6; neopentyl 1-nitro-1-dodecanesulfonate, 25056-39-7; dineopentyl 1,4-dinitro-

1,4-butanedisulfonate, 25056-40-0; ethyl 1-nitro-1-butanesulfonate, 25056-42-2; neopentyl 1-bromo-1-nitroethanesulfonate, 25056-43-3; neopentyl 1-bromo-1-nitrobutanesulfonate, 25056-44-4; ethyl 1-bromo-1-nitrobutanesulfonate, 25056-45-5; dineopentyl 1,4-dibromo-1,4-dinitro-1,4-butanedisulfonate, 25056-46-6; neopentyl 1-bromo-1-nitrohexanesulfonate, 25056-47-7.

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Formation, Proof of Structure, and Thermal Decomposition of Peroxide from Benzyl Mesityl Ketone[1]

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Experimental conditions for autoxidation of benzyl mesityl ketone to a peroxide were investigated. The peroxide was characterized as 2-hydroperoxy-2-phenyl-2′,4′,6′-trimethylacetophenone (III) by ir and ^{1}H nmr spectra, and iodide reduction to the known 2,4,6-trimethylbenzoin (IV). Solid-state thermal decomposition of III forms mesitoic acid and benzaldehyde in equal amounts by one pathway and mesityl phenyl diketone (V) and water by another. The latter is a new mode of thermal decomposition for α-keto hydroperoxides. Decomposition also takes place slowly by both pathways at room temperature on standing in contact with a glass surface. Differential thermal analysis and differential scanning calorimetry studies under various conditions show that decomposition of III occurs in the solid phase without prior melting. A mechanism is proposed for the two modes of decomposition.

In a previous paper[4] on the autoxidative cleavage of isopropyl mesityl ketone to mesitoic acid and acetone,[5] an intermediate peroxide was detected but could not be isolated for characterization. A study of time sequential infrared spectra of oxidation mixtures indicated the α-keto hydroperoxide structure (Ia) in preference to an isomeric oxaoxetane formulation (Ib) (Scheme I). Kohler who was the first to report[6] a stable keto peroxide formulated structures analogous to Ib.[7] Rigaudy observed[8] ultraviolet absorption in the carbonyl region for Kohler's keto peroxides and formulated their structures as keto hydroperoxides analogous to Ia; carbonyl bands in the infrared spectra were reported by Fuson and Jackson[9] in confirmation of Rigaudy's formulation. The present paper reports the formation, characterization by infrared and ^{1}H nmr spectra and chemical methods, and thermal decomposition of a stable peroxide isolated from autoxidation of benzyl mesityl ketone (II)[10] which was originally prepared for use in studies of structures of Grignard compounds derived from hindered ketones.[13]

Results and Discussion

Autoxidation.—The samples of benzyl mesityl ketone (II) were obtained as liquids[14] which solidified or precipitated peroxides after standing in stoppered or unstoppered vessels for varying lengths of time (15 days to 6 months). A number of qualitative observations were made on autoxidative behavior of II in order to ascertain conditions under which oxidation could be accelerated or minimized. The random nature of the autoxidations was evident from 15 experiments[15] which were carried out. The following observations can be made. Autoxidation proceeded as readily (1) when apparatus was flushed with nitrogen as when allowed to stand in contact with air, (2) when oxygen was bubbled through the liquid or a solution or allowed to stand, and (3) whether exposed to light or shielded from it. Traces of oxygen appeared to be sufficient to result in autoxidation. In one experiment no peroxide precipitate was observed[16] when the sample was allowed to stand undisturbed exposed to air for 11 months. The recommended procedure for conducting the autoxidation is simply to allow the liquid ketone to stand in a vessel with maximum surface area exposed to the atmosphere and to agitate the sample occasionally. The best conditions found for minimizing autoxidation of II were to carry out preparation and handling of the compound in a rigorously deoxygenated nitrogen atmosphere and to store the compound at low temperature.

Spectral and Chemical Proof of Structure of Peroxide III.—Ir and ^{1}H nmr spectra are consistent with an α-keto hydroperoxide structure (III). The ir spectrum

(1) A. G. Pinkus, M. Z. Haq, and J. G. Lindberg, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, ORGN-59.

(2) Robert A. Welch Foundation postdoctoral fellow.

(3) Robert A. Welch Foundation predoctoral fellow.

(4) A. G. Pinkus, W. C. Servoss, and K. K. Lum, *J. Org. Chem.*, **32**, 2649 (1967).

(5) Water was also found to be a product.

(6) E. P. Kohler, *Amer. Chem. J.* **36**, 177, 529 (1906).

(7) E. P. Kohler and R. B. Thompson, *J. Amer. Chem. Soc.*, **59**, 887 (1937).

(8) J. Rigaudy, *C. R. Acad. Sci., Paris*, **226**, 1993 (1948)

(9) R. C. Fuson and H. L. Jackson, *J. Amer. Chem. Soc.*, **72**, 1637 (1950).

(10) Two recent papers on α-keto hydroperoxides have appeared. One paper[11] mainly concerned with hydrogen-bonding aspects of two keto hydroperoxides was published when the present work was well under way. When this paper appeared we discontinued our ir and ^{1}H nmr studies on hydrogen bonding of the hydroperoxides but completed other aspects of the problem. A second paper[12] which appeared after the present work was complete, deals with preparation and properties of aliphatic α-keto hydroperoxides.

(11) W. H. Richardson and R. F. Steed, *J. Org. Chem.*, **32**, 771 (1967).

(12) R. C. P. Cubbon and C. Hewlett, *J. Chem. Soc., C*, 2978 (1968).

(13) A. G. Pinkus, J. G. Lindberg, and A. B. Wu, *ibid., D*, 1351 (1969).

(14) H. H. Weinstock, Jr., and R. C. Fuson, *J. Amer. Chem. Soc.*, **58**, 1233 (1936), report mp 32.0–32.5°.

(15) A table summarizing the results of these experiments was eliminated from the original paper to save space.

(16) An ir spectrum of the mother liquor from one of the experiments showed no detectable amount of peroxide; this would indicate solubility of peroxide to be low in this mixture. Although peroxide was not tested for in this sample, it is possible that it could have been present in solution in small amount.