

## Positive Halogen Compounds

### VI. Preparation of Alkoxydimethylsulfonium Salts and their Role in the Kornblum Oxidation. Revision of the Structure for the Olefin-Bromotrinitromethane Adduct\*

KURT TORSSELL

*Institute of Organic Chemistry, University of Stockholm, Stockholm, Sweden*

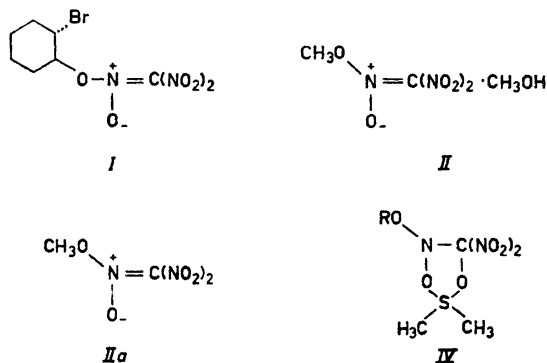
The mechanism of the Kornblum oxidation is elucidated. It has been proved that sulfonium salts are intermediates and that the final step proceeds *via* a cyclic mechanism (5) or according to (4) if the  $\alpha$ -proton is activated. The Pfitzner-Moffat oxidation proceeds *via* the complex XV. New routes to alkoxydimethylsulfonium salts have been worked out. The salts are preferably isolated as tetraphenylborates. The structure of the nitronate esters<sup>1,2</sup> is revised. Carbonium exchange in dimethylsulfoxide is observed. A new case of magnetic nonequivalence has been found.

It was recently reported that bromotrinitromethane formed unstable, oily or low melting adducts with olefins in dimethylsulfoxide solution.<sup>1,2</sup> The crystalline cyclohexene adduct was given the nitronate structure I on the following grounds. Hydrolysis afforded *trans*-2-bromocyclohexanol, and trinitromethane was isolated as its potassium salt. Methanolysis gave a nitronate ester II, which on heating in an inert medium rearranged to 1,1,1-trinitroethane III. Analytical data proved difficult to obtain because of the low decomposition point of the adducts but the "best" data fitted the structures I and II. However, a very recent publication by Novikov *et al.*<sup>3</sup> reported the preparation of IIa by quite another route and throws doubts on the previously proposed structures. The properties of their product differed from our compound II and therefore a reinvestigation was undertaken.

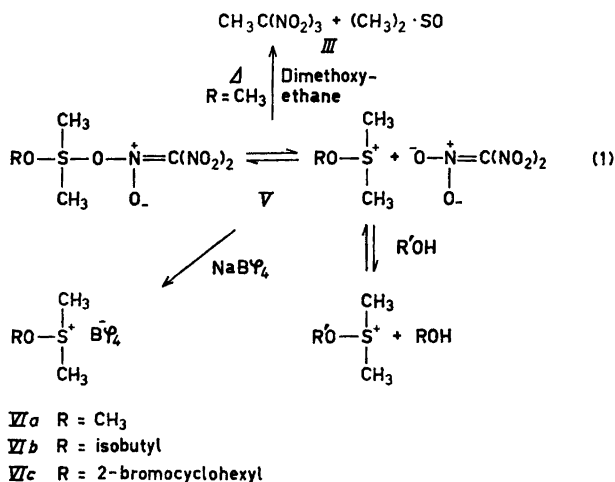
\* A preliminary account of the mechanism of the Kornblum oxidation was given in *Tetrahedron Letters* 1966 4445.

## REVISION OF THE NITRONATE STRUCTURE

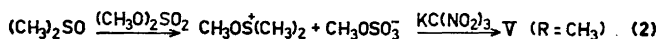
The NMR spectra of the nitronates immediately revealed the presence of one mole of dimethylsulfoxide, which could not be removed by reprecipitation. Of the two structures considered, the 1,3-dipolar adduct IV could be disproved since Novikov's compound IIa failed to react with dimethylsulfoxide. Therefore it remained to prove the correctness of the sulfonium structure V.



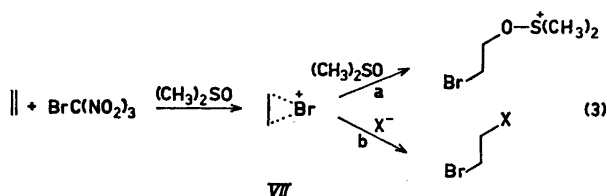
The methyl derivative V exhibits two sharp peaks in its NMR spectrum with the intensity 1:2, Table 1. Addition of another alcohol, *e.g.* ethyl alcohol, demonstrates clearly that the alkoxy groups are interchangeable. Methanol is liberated with formation of the ethoxydimethylsulfonium ion;  $\text{CH}_2\text{OS}$  at  $\delta = 4.38$  ppm and  $\text{CH}_3\text{C}$  at  $\delta = 1.33$  ppm. The latter reaction explains why the adducts afford bromohydrins on hydrolysis. With sodium tetraphenylborate a crystalline product is obtained, which analyzes correctly for VIa. The observed reactions can be rationalized by the following scheme (1):



Finally, the structure was proved unambiguously by synthesis of the methyl derivative according to the following route. It was found that dimethyl sulfate slowly methylated dimethylsulfoxide at room temperature and by addition of the potassium salt of trinitromethane V ( $R = CH_3$ ) could be isolated from the reaction mixture, eqn. (2).



These new findings therefore completely invalidate the discussion and conclusions of the preceding paper.<sup>2</sup> The adducts are still in a sense nitronate esters but at the instant of dissociation they are more correctly named alkoxydimethylsulfonium salts of trinitromethane. Hence, the reaction of bromotrinitromethane with olefins proceeds ionically with participation of the solvent according to (3a). Dimethylsulfoxide is in excess and competes favourably with the trinitromethyl ion for the intermediary carbonium ion VII. The ionic mechanism is supported by the observation



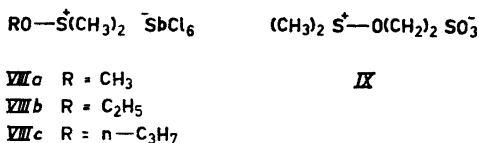
that the presence of other inorganic ions leads to an addition of these ions ( $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $CH_3COO^-$ , path 3b). The yields of these derivatives are generally low and they are always obtained together with the bromohydrin. Minor amounts of I are certainly formed in the reaction mixture but the instability<sup>3</sup> of the nitronate esters hampers the isolation.

An intermediary carbonium ion VII is most easily created by direct bromination with bromine. By performing this reaction in dimethylsulfoxide one would anticipate that the solvent should trap VII and afford the sulfonium ion. This is verified experimentally by the isolation of considerable amounts of *trans*-2-bromocyclohexanol from the bromination of cyclohexene in dimethylsulfoxide. Dimethylsulfoxide reacts violently with bromine at room temperature but the bromination can be run smoothly at  $-10^\circ C$  using a mixed solvent (dimethoxyethane or acetonitrile as diluents). By adding lithium bromide to the reaction mixture the formation of bromohydrins is repressed.

#### MECHANISM OF THE KORNBLUM OXIDATION

Until recently, very few works have dealt with the chemistry of alkoxydimethylsulfonium salts. Mehrwein *et al.*<sup>4,5</sup> have prepared the methoxy, ethoxy, and propoxy derivatives VIIIa—c, Smith *et al.*<sup>6</sup> have reported on the preparation of some other salts of VIIIa and VIIIb, and the betain structure IX has

been synthesized by Natus *et al.*<sup>7</sup> Alkoxysulfonium ions have been postulated as intermediates<sup>8-12</sup> in the



Kornblum oxidation method and very recent works<sup>13-17</sup> lend further support to this view. With the actual derivatives accessible we set out to test the suggested mechanistic paths experimentally. VIb is most suited for the purpose and this salt was therefore exposed to the various oxidation conditions given in the literature.

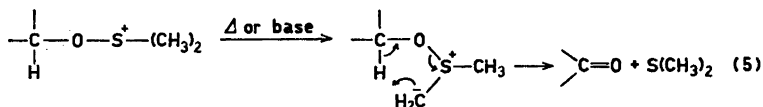
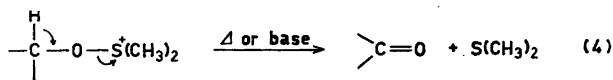
The original Kornblum method<sup>8</sup> recommends heating of a tosylate or a halogenide at 150° for some minutes whereas the novel mild procedures<sup>11,15-17</sup> are complete at room temperature within 24 h or in some cases within a few hours.

Pyrolysis of VIb at 140–150° for 8 min on a small preparative scale gave *ca.* 25 % of isobutyraldehyde (as crude DNP-derivative). The salt is stable for several days in dimethylsulfoxide at room temperature but the decomposition is complete in less than 3 min at 130°. The yield rises to about 50 % as determined spectroscopically by infrared technique. The decomposition was also studied by NMR (DMSO, D<sub>6</sub>) at 100°. The characteristic peak of the aldehyde proton at  $\delta = 9.66$  ppm develops rapidly and the integrated curve indicates a yield of *ca.* 60 % after 15 min. The sulfonium salt had then completely vanished. An equivalent amount of dimethyl sulfide is formed, which is shown by the appearance of a sharp peak at  $\delta = 2.10$  ppm. After 2 h at 65° only *ca.* 20 % of the salt had decomposed. The liberation of dimethylsulfoxide (*ca.* 25 % of the intensity of the dimethyl sulfide peak) is due to the formation of olefin (traces) and some hydrolysis but mostly to carbonium ion exchange with the solvent. This reaction is discussed in connection with the NMR studies of the methyl derivative (see below).

Barton *et al.* modified the oxidation by treatment of the intermediary sulfonium ion with base. Under these conditions the oxidation is complete within 15 min.<sup>11</sup> This is verified by our NMR studies; in fact the oxidation of VIb was almost instantaneous upon addition of triethyl amine. The spectroscopically measured yield of isobutyraldehyde was *ca.* 60 %.

We are now able to present full evidence that Barton's modification proceeds *via* a sulfonium ion by precipitation of this intermediate as its tetraphenylborate in a good yield. Thus, the experiments prove unequivocally that the Kornblum oxidation and Barton's modification proceeds *via* an intermediary sulfonium ion, which collapses to a carbonyl compound and dimethylsulfide either by the concerted (or stepwise) reaction (4) or by a cyclic mechanism<sup>17</sup> (5).

In order to reach a decision between these possibilities the deuterated compound X was prepared. Provided that only a negligible hydrogen scrambling occurs in the sulfonium ion before decomposition, the mechanism (4)



gives rise to unchanged dimethylsulfide whereas (5) affords a labelled dimethylsulfide XI which can be detected by NMR measurements. The absorption of the single proton of XI is split by the two deuterons to a quintet (1:2:3:2:1). Fig. 1 shows the NMR spectrum of X. A small peak at  $\delta = 3.3$  ppm comes

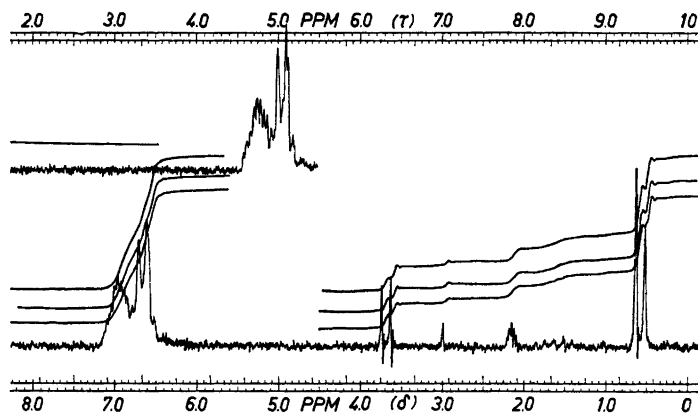


Fig. 1. NMR spectrum of  $(\text{CH}_3)_2\text{CHCH}_2\text{OS}^+(\text{CD}_3)_2 \text{---B}\phi_4$ .

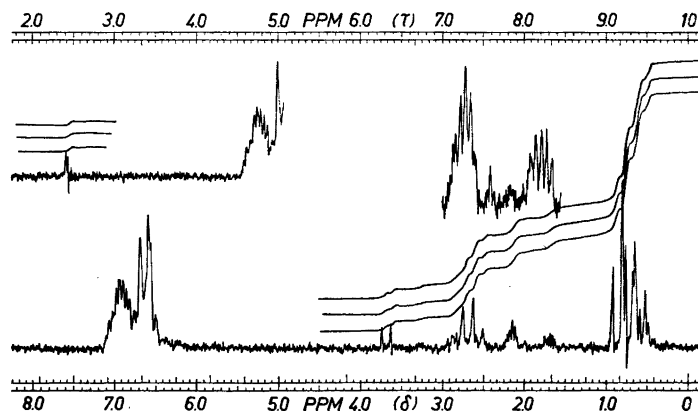
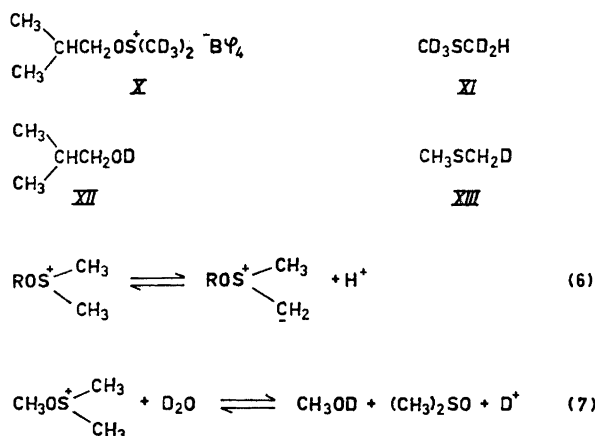


Fig. 2. NMR spectrum of  $(\text{CH}_3)_2\text{CHCH}_2\text{OS}^+(\text{CD}_3)_2 \text{---B}\phi_4$ , triethylamine added.

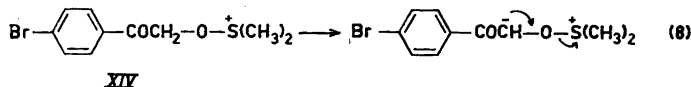
from water. Addition of two drops of triethylamine causes an immediate change of the spectrum, Fig. 2. The aldehyde proton is visible at  $\delta = 9.66$  ppm and the quintet of XI is located at  $\delta = 2.10$  ppm, proving that one of the methylene protons of X must have been incorporated in dimethylsulfide *via* the cyclic mechanism (5). The actual part of the spectrum is enlarged in the



upper part of Fig. 2. The quintet at  $\delta = 2.57$  ppm, coincidentally of about the same intensity, comes from dimethylsulfoxide,  $\text{D}_6$  (solvent). The triplet at  $\delta = 1.21$  ppm and the quartet at  $\delta = 3.11$  ppm are due to triethylamine. XI was also formed on direct pyrolysis of X at  $100^\circ$  in DMSO,  $\text{D}_6$ .

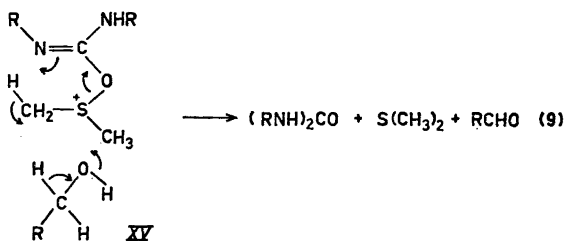
A labelled dimethylsulfoxide can of course arise *via* the concerted reaction (4) combined with a rapid hydrogen exchange (6). An early indication that this route is not the prevailing one was obtained from the observation that VIa with a ten molar excess of deuterium oxide on addition of triethylamine afforded no (or possibly traces of) deuterium labelled dimethylsulfoxide XIII, *i.e.* hydrolysis (7) proceeds faster than (6). Finally it was found that oxidation of VIb in the presence of a ten molar excess of deuterium labelled isobutanol XII afforded no detectable amounts of XIII in the NMR spectrum. Alkoxy exchange according to scheme (1) has no influence on reactions (4) – (6) in this system.

It should be pointed out in this connection that this investigation concerns the oxidation mechanism of inactivated alcohols. In their first paper on dimethylsulfoxide oxidations Kornblum *et al.*<sup>18</sup> describe the facile dicarbonyl formation from  $\alpha$ -bromoketones, which proceeds at room temperature. The intermediate sulfonium salt XIV from phenacyl bromide contains enolizable protons and in this case it is conceivable that mechanism (4) = (8) is working. In fact, when we dissolved *p*-bromophenacyl bromide in DMSO,  $\text{D}_6$  and heated the solution for 2 h at  $70^\circ$  all of the starting material had disappeared. The glyoxal was formed but no labeled dimethylsulfide XI could be detected by the NMR spectrum proving that the cyclic mechanism is not working in this case. *We can conclude therefore that the oxidation mechanism follows eqn. (5), but if the  $\alpha$ -proton is activated as in XIV mechanism (4) is working.*



We then investigated the action of the novel mild oxidation media according to Pfitzner and Moffat<sup>16,17</sup> and Albright and Goldman<sup>15</sup> on the alkoxyulfonium salts. We found unexpectedly that the yield of the carbonyl compounds was very low. One mmole of VIb or VIc oxidized according to the first method afforded *ca.* 10 % of a crude DNP derivative, whereas the latter method gave only traces of carbonyl compounds. The experiments were repeated and the products analyzed by gas chromatography with the same result. Oxidation of isobutyl alcohol, *trans*-2-bromocyclohexanol, and cyclohexanol according to the acetic anhydride method<sup>15</sup> met with little success. Some carbonyl compounds were obtained but the main product was the acetate and the starting material. Addition of triethylamine to the reaction mixture increased the yield of the acetate. The authors point out that this method is particularly suited for the oxidation of sterically hindered hydroxyl groups. A gas chromatogram of the products from the oxidation<sup>15</sup> of VIb revealed the presence of isobutanol but only small amounts of aldehyde and no isobutyl acetate. This does not necessarily mean that alkoxyulfonium salts are not intermediates in the oxidation but rather that these simple unhindered alcohols and salts are stable in the medium.

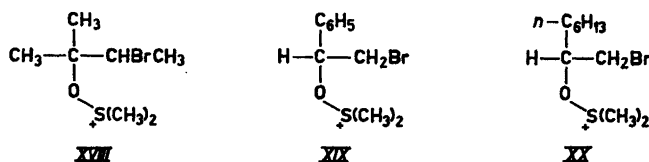
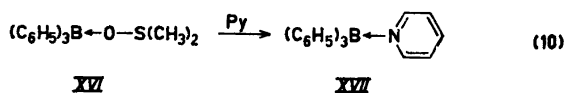
Oxidation of isobutanol and *trans*-2-bromocyclohexanol by the dicyclo-carbodiimide method<sup>16,17</sup> proceeded with good yield (41 and 63 %). The yield of isobutyraldehyde from VIb in the same reaction was distinctly lower and considerable amounts of isobutanol in the workup were detected by gas chromatography. As a consequence we cannot accept a free alkoxyulfonium ion as an intermediate here as suggested by Pfitzner and Moffat.<sup>16,17,17a</sup> This can be circumvented by the following three-body mechanistic scheme (9).



At the very moment the alcohol displaces the urea, a strong base is formed, which abstracts a proton from the S-methyl group as in XV and thus creates the cyclic intermediate. This explains why the oxidation proceeds in a weak acid medium in which the sulfonium ion is stable, and also why the DCC method is sensitive to changes of pH. We were not successful in trapping the ionic carbodiimide-DMSO intermediate of XV with sodium tetraphenylborate. In their latest paper Fenselau and Moffat<sup>17a</sup> studied the mechanism by <sup>18</sup>O

labelling and NMR techniques. They also proved the cyclic mechanism (5), in general agreement with our results but with the reservation above for scheme (9).

Pyrolysis of VIc afforded very small amounts of carbonyl compounds as determined by infrared spectroscopy; somewhat better results were obtained by heating the salt in dimethylsulfoxide but the yield was far from satisfactory. Benzene was identified as one of the products together with a solid, which also was isolated from VIa and VIb. Analysis, spectral data and an independent synthesis showed that the structure of the compound was XVI. It gave XVII on treatment with pyridine. The latter compound was also formed as a by-product in the Pfitzner-Moffat oxidation of VIb and VIc.



#### MAGNETIC NONEQUIVALENCE \* OF THE S-METHYL GROUPS

The S-methyl resonance peak of VIc appears as a doublet with a separation of 1.7 cps, Table 1. Since *cis-trans* isomerism and long-range coupling are excluded (there is no coupling in VIa and VIb) the origin of this nonequivalence must be a restricted rotation of the sulfoxonium group. An intrinsic effect of the asymmetric center might also contribute to the nonequivalence (VIb and XVIII do not show doubling of the S-methyl peaks). The rotational barrier is surprisingly high because the separation was not affected by running the spectrum at 90° in DMSO, D<sub>6</sub>. The NMR spectrum of XIX shows a still larger separation of the peaks (12.8 cps with no change at 80° in DMSO, D<sub>6</sub>). However, changing the solvent to 60 % CDCl<sub>3</sub> and 40 % DMSO, D<sub>6</sub> causes an increased separation (17.7 cps at -10° and 15.3 cps at 60°). This is indicative of a changing population of the conformers. No doubling of the S-methyl peak was observed for XX.

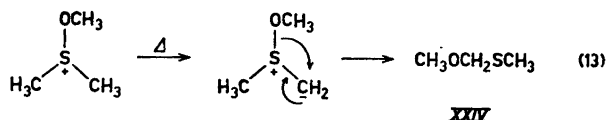
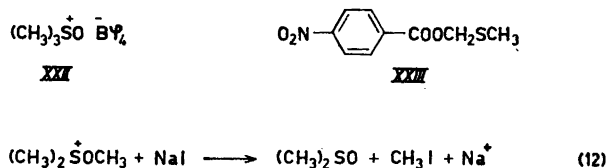
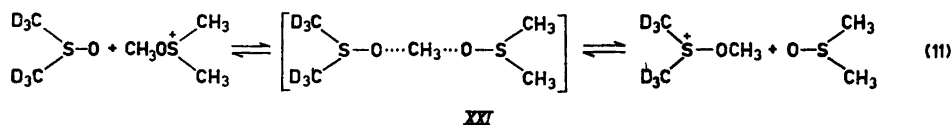
#### CARBONIUM ION EXCHANGE IN DIMETHYLSULFOXIDE

The NMR spectrum of VIa or V (R = CH<sub>3</sub>) underwent a drastic change when the compounds were heated in DMSO, D<sub>6</sub> at 65°. After 1 h the absorption of SCH<sub>3</sub> at δ = 3.29 ppm had vanished and a new peak had arisen at δ =

\* For references pertinent to the subject see, e.g., Bowman, N. S., Rice, D. E. and Switzer, B. R. *J. Am. Chem. Soc.* **87** (1965) 4477.



2.57 ppm, which emanated from liberated dimethylsulfoxide. The peak at  $\delta = 3.97$  ppm had the same intensity as before and only traces of dimethyl sulfide were detected. These observations are explicable assuming a carbonium exchange with the deuterated solvent (11), a reaction comparable with the proton exchange in water. The reaction is completely reversible because when XXI is dissolved in dimethylsulfoxide VIa is regenerated. There is no tendency for VIa to rearrange to XXII,  $S(CH_3)_3$  at  $\delta = 3.85$  ppm. However, addition of sodium iodide to VIa caused a very rapid change of the spectrum. The  $OCH_3$  group vanished completely after a few minutes and peaks developed



originating from the dimethylsulfoxide and methyl iodide formed in quantitative yield (reaction 12). The formation of III from V on heating in an inert medium is now understandable in the light of the reactions above. We tried to trap the methyl carbonium ion by adding *p*-nitrobenzoic acid with the aim of isolating the methyl ester. The product was not the expected compound but *p*-nitrobenzoyloxymethyl methyl sulfide XXIII the structure of which was determined from its NMR spectrum ( $CDCl_3$ );  $\delta = 8.28$  ppm (s, ArH),  $\delta = 5.46$  ppm (s,  $SCH_2O$ ) and  $\delta = 2.33$  ppm (s,  $SCH_3$ ). Onodera *et al.*<sup>19</sup> have recently prepared this compound by another route. Pyrolysis of VIa led to XXIV as one of the products (reaction 13). The latter two reactions resemble the Pummerer rearrangement.

#### PREPARATIVE METHODS FOR ALKOXYDIMETHYLSULFONIUM SALTS

As has been shown the addition of bromotrinitromethane to olefins in dimethylsulfoxide leads to the formation of alkoxydimethylsulfonium salts of trinitromethane, which in a few cases have been isolated in a pure state. The sulfonium ions are preferably isolated as tetraphenylborates, which are more

Table 1. Physical data for alkoxydimethylsulfonium salts,  $\text{ROS}(\text{CH}_3)_2^+ \text{X}^-$ .

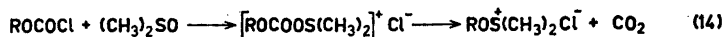
No.	R	$\text{X}^-$	Decomp. °C	Analysis				NMR data, $\delta$ ppm, <sup>c</sup> multiplicity ( ), <i>J</i> cps.
				Found		Calculated		
				C	H	C	H	
V	$\text{CH}_3-$ $\text{CH}_3-$	$\text{O}_2\text{N}=\text{C}(\text{NO}_2)_2$ B $\phi_4$	55–56 ~190 <sup>a</sup>	78.83	7.19	78.61	7.08	$\text{CH}_3\text{O}$ 4.00(s); $\text{CH}_3\text{S}$ 3.31(s) $\text{CH}_3\text{O}$ 3.98(s); $\text{CH}_3\text{S}$ 3.29(s); ArH 6.8–7.5(m) $\text{CH}_3\text{S}$ 3.30(s), 3.28(s); CH ~4.3 (m); $\text{CH}_2$ ~1.5(m)
VIa	$\text{C}_6\text{H}_{10}\text{Br}$	$\text{O}_2\text{N}=\text{C}(\text{NO}_2)_2$	70–71	27.69	4.10	27.84	4.30	$\text{CH}_3\text{S}$ 3.35(s), 3.33(s); CH ~4.3(m); $\text{CH}_3$ ~1.5(m).
VIc	$\text{C}_6\text{H}_{10}\text{Br}$	B $\phi_4$	138–140	68.79	6.21	68.70	6.49	$\text{CH}_3\text{S}$ 3.26(s); $\text{CCH}_3$ 0.97(d) <i>J</i> = 6.5; $\text{CH}_2$ 4.08(d) <i>J</i> = 6.5; CH ~1.9(m)
VIb	$(\text{CH}_3)_2\text{CHCH}_2-$	B $\phi_4$	141–143	79.52	7.76	79.30	7.77	$\text{CH}_3\text{S}$ 3.37(s); <i>gem</i> - $\text{CH}_3$ 1.64(s); $\text{CCH}_3$ 1.70(d) <i>J</i> = 6.9; CH 4.62 (q)
XVIII	$\text{CH}_3\text{CHBrC}(\text{CH}_3)_2-$	B $\phi_4$	112–114	68.31	6.59	68.01	6.63	$\text{CH}_3\text{S}$ 3.20(s), 3.42(s); $\text{CH}_2$ 4.08(d) <i>J</i> = 6.4; CH 5.88(t)
XIX	$\text{CH}_2\text{BrC}(\text{C}_6\text{H}_5)\text{H}-$	B $\phi_4$	118–120	70.09	5.96	70.25	5.90	$\text{CCH}_3$ 0.97(d) <i>J</i> = 6.5; $\text{CH}_2$ 4.08(d) <i>J</i> = 6.5; CH ~1.9(m)
X	$(\text{CH}_3)_2\text{CHCH}_2-$ <sup>b</sup>	B $\phi_4$	143–145					$\text{CH}_3\text{O}$ 3.98(s) <i>gem</i> - $\text{CH}_3$ 1.64(s); $\text{CCH}_3$ 1.70(d) <i>J</i> = 6.9; CH 4.62(q)
XXI	$\text{CH}_3-$ <sup>b</sup>	B $\phi_4$	~190					
XVIII	$\text{CH}_3\text{CHBrC}(\text{CH}_3)_2-$ <sup>b</sup>	B $\phi_4$	112–114					

<sup>a</sup> Solidifies and melts again at ca. 290°.<sup>b</sup> Deuterated dimethylsulfoxide.<sup>c</sup> The  $\delta$ -values refer to  $(\text{CH}_3)_2\text{SO}$ .

stable and easier to handle. They can be stored for many months in the refrigerator without any decomposition.

Alkoxy exchange can be used preparatively for the preparation of other simple derivatives. This is demonstrated for the preparation of the methyl (VIa) and isobutyl (VIb) derivatives from V (R = 2-*trans*-bromocyclohexyl) and methanol and isobutanol, respectively. The method is less suitable for secondary alcohols.

Decarboxylation<sup>11</sup> of chloroformic esters in dimethylsulfoxide opens a new route to the alkoxyulfonium salts (14). When isobutanol is reacted with phosgene and then treated with excess of dimethylsulfoxide the sulfonium ion of VIb is obtained. It is precipitated with sodium tetraphenylborate and the product is in every respect identical with the compound obtained by the other route. The method is not suitable for alcohols easily convertible to chlorides.



Dimethylsulfoxide is O-alkylated by alkylsulfates and tosylates.<sup>6</sup> The best method for the preparation of the O-methyl derivative is the reaction of dimethylsulfate with dimethylsulfoxide in equimolecular amounts for 24 h. Only one of the methyl groups of dimethylsulfate is reactive enough for this purpose. Precipitation with sodium tetraphenylborate affords VIa in a good yield. Physical data on the prepared alkoxyulfonium salts together with data from the NMR measurements are collected in Table 1.

## EXPERIMENTAL

The IR spectra were recorded with a Perkin-Elmer Infracord, M 137, and the NMR spectra (DMSO, D<sub>6</sub>) with a Varian A-60 instrument. The analyses were carried out by Mrs. Ilse Beetz, Mikroanal. Laboratorium, Kronach, West-Germany.

*Preparation of alkoxydimethylsulfonium salts V, VIc, XVIII and XIX by the bromotrinitromethane method.* The general procedure for the preparation of the supposed nitronate esters<sup>2</sup> was followed. The tetraphenylborates were prepared by adding an equimolecular amount of sodium tetraphenylborate in cold dimethoxyethane:water, 1:1 (0.1 mole salt in 400 ml solvent) to the crude reaction mixture with external cooling. The precipitate was filtered, washed with cold methanol and ether and then dried in a desiccator. VIc, XVIII, and XIX were obtained in yields of 56, 67, and 42 % (crude material) from cyclohexene, 2-methylbutene-2, and styrene, respectively. The crystalline, white precipitate of XIX contained minor amounts of isomers, which were removed by recrystallization (ethyl acetate:acetonitrile, 2:1; heating for a long period of time was avoided).

The preparation of V (R = 2-*trans*-bromocyclohexyl) is described in Ref. 2. VIc was obtained in a yield of 82 % by starting from a pure preparation of V (0.20 g) dissolved in ethyl acetate (1 ml). Sodium tetraphenylborate (0.20 g) in ethyl acetate was added with cooling and crystals of VIc precipitated immediately, m.p. 138–140° (decomp.). The compounds should be stored in a refrigerator.

*Preparation of the isobutoxy derivative VIb. Method a.* (alkoxy exchange). V (R = 2-*trans*-bromocyclohexyl, 0.20 g) was dissolved and heated in isobutanol (1 ml) at 55–66° for 45 min. Sodium tetraphenylborate (0.20 g) in ethyl acetate (1 ml) was added with cooling. The precipitate (0.19 g) was filtered off and crystallized from ethyl acetate, m.p. 141–143° (decomp.).

*Method b.* Isobutyl chloroformate was prepared from isobutanol (0.16 g) and a slight excess of phosgene (10% in ether). The ether was evaporated and dimethylsulfoxide (1 ml) was added. After half an hour, when the gas evolution had stopped, sodium tetraphenylborate (0.7 g in ice cold water:methanol, 1:1, 6 ml) was added and the precipitate (0.4 g) filtered off, washed with a little cold methanol and ether and dried in a desiccator; m.p. 143–146° (decomp.) (from ethyl acetate). It was identical in all respects to the product from method a.

The *ethoxy*-derivative was prepared from ethyl chloroformate by the same method. It decomposes at 150–160°, solidifies and melts again at ~260°.

*Preparation of the methyl derivatives V and VIa. Method a.* V (R = *trans*-2-bromocyclohexyl, 1.0 g) was dissolved in methanol (4 ml) and kept at 40–50° for 20 min. Half of the methanol was evaporated in vacuum and carbon tetrachloride (10 ml) was added to the remainder. V (R = CH<sub>3</sub>) precipitated as oily crystals (0.55 g) and was purified by reprecipitation from a little methanol with carbon tetrachloride. VIa was prepared from the trinitromethane salt V (0.25 g) dissolved in methanol (1 ml) by adding sodium tetraphenylborate (0.40 g) in methanol (1 ml). The precipitate (0.38 g) was crystallized from acetonitrile.

*Method b.* Dimethylsulfoxide (0.30 g) was mixed with dimethyl sulfate (0.50 g) and set aside for 24 h at room temperature. Potassium trinitromethane (0.75 g) dissolved in dimethoxyethane (5 ml) was added. The precipitated potassium salt of monomethyl sulfate was filtered off and half of the solvent evaporated in vacuum. Carbon tetrachloride (10 ml) was added, the yellow oil separated and crystallized from a small amount of methanol. Yellow crystals were obtained (0.3 g), m.p. 51–52° (decomp.), identical to the compound from method a. The tetraphenylborate VIa was also prepared from this material and the IR spectra were found to be identical.

VIa was prepared directly from the reaction mixture of dimethyl sulfate (0.50 g) and dimethylsulfoxide (0.30 g) by addition of sodium tetraphenylborate (1.4 g) in methanol (10 ml). The precipitate (1.6 g) was crystallized from acetonitrile; yield 0.9 g. Addition of methanol to the mother liquor afforded 0.2 g more.

*Synthesis of deuterated derivatives. XXI.* Dimethylsulfoxide, D<sub>6</sub> (0.4 g, Merck, Darmstadt) was methylated with dimethyl sulfate (0.7 g) for 24 h at room temperature. The product was precipitated with sodium tetraphenylborate (1.7 g in 5 ml ethyl acetate). The precipitate (1.9 g) was crystallized from acetonitrile.

X. The isobutyl chloroformate prepared from isobutanol (0.16 g) and phosgene in ether (see above) was added to dimethylsulfoxide, D<sub>6</sub> (0.5 ml). After one hour sodium tetraphenylborate (0.7 g, in ice cold water-methanol, 1:1, 6 ml) was added and the precipitate (0.4 g) was filtered off, washed once with a little cold methanol and then with ether. It was dried in vacuum and crystallized from ethyl acetate-acetonitrile (5:1).

*S-Methyl deuterated XVIII.* 2-Methylbutene-2 (0.16 g) was dissolved in dimethylsulfoxide, D<sub>6</sub> (1 ml) and bromotrinitromethane (0.5 g) was added with cooling by tap water. After one hour sodium tetraphenylborate was added with cooling (0.7 g in water-methanol, 1:1, 6 ml). The precipitate (0.5 g) was crystallized from acetonitrile-ethyl acetate, 1:1. Yield 0.26 g.

*p-Nitrobenzoylhydroxymethyl methyl sulfide XXIII.* V (R = CH<sub>3</sub>, 0.5 g) and *p*-nitrobenzoic acid (0.30 g) in diglyme (4 ml) were heated to 75° for 60 min and then poured into ice water. The precipitate was dissolved in chloroform and extracted with sodium bicarbonate. Evaporation of the solvent yielded an oil (0.13 g) which afforded crystals of XXIII from benzene-cyclohexane, 1:1, m.p. 53–55°; 0.14 g of the acid was recovered.

*Pyrolysis of VIa, preparation of XVI and XVII.* VIa (0.2 g) was heated to 170° in a small "Kugelrohr" until the evolution of gas stopped (ca. 10 min). The condensate (40 mg) was analyzed by IR and NMR and was found to contain benzene and XXIV ( $\delta$  = 4.49, 3.27, and 2.07 ppm; CH<sub>2</sub>, OCH<sub>3</sub>, and SCH<sub>3</sub>; 2:3:3). The remainder was partly crystalline and afforded XVI on crystallization from chloroform, m.p. 160–163°. (Found: C 74.64; H 6.44. Calc. for C<sub>20</sub>H<sub>24</sub>OSB: C 75.00; H 6.61).

This compound was identical to the product obtained by adding conc. hydrochloric acid (0.1 ml) to sodium tetraphenylborate (0.2 g) in water (2 ml) and dimethylsulfoxide (0.3 ml). The precipitate was crystallized from chloroform, m.p. 160–162°. The IR spectrum was identical to the spectrum of the compound above.

XVI (50 mg) was dissolved in warm ethyl acetate (3 ml) and pyridine (50 mg) was added. A crystalline precipitate of XVII was formed, m.p. 210° (decomp.) (lit.<sup>20</sup> 214°).

*Pyrolysis of VIb.* VIb (0.21 g) was heated at 140–150° for 8 min in a "Kugelrohr". The condensate (60 mg) contained benzene and isobutyraldehyde in a yield of ca. 25 %. A partly crystalline oil remained in the bulb from which XVI was isolated in low yield. When a small amount of VIb was heated in dimethylsulfoxide at 110° for 10 min and analyzed by IR a strong absorption at 1725 cm<sup>-1</sup> was observed indicating the presence of isobutyraldehyde in a yield of approximately 50 %.

*Pyrolysis of VIc.* VIc (0.20 g) was pyrolyzed at 130–140° for 5 min. The condensate (0.30 g, consisting mostly of benzene) and the partly crystalline remainder showed very little absorption in the carbonyl region (DNP test negative). XVI was isolated in low yield. When VIc was decomposed in dimethylsulfoxide at 130° for 5 min the IR spectrum indicated a somewhat higher yield of carbonyl compounds; *trans*-2-bromocyclohexanol was also detected.

*Oxidation of isobutanol, cyclohexanol, trans-2-bromocyclohexanol, VIb and VIc according to Albright and Goldman.*<sup>15</sup> One mmole of the alcohol or the salts VIb and VIc was allowed to stand for 18 h with dimethylsulfoxide (3 ml) and acetic anhydride (2 ml). The mixture was poured in ice water (15 ml) and extracted with ether (2 × 5 ml), then dried and carefully evaporated. The DNP test was negative or only very weakly positive. The products were analyzed by gas chromatography. Isobutanol and cyclohexanol afforded only minor amounts of isobutyraldehyde and cyclohexanone, respectively; the main products were iso-butyl acetate and cyclohexyl acetate together with the starting material (acetic acid, acetic anhydride, and dimethylsulfoxide were present in larger amounts). Addition of triethyl amine or pyridine (0.3 ml) to the reaction mixture catalyzed the formation of acetates; no alcohol was detected by gas chromatography. VIb gave a still lower yield of isobutyraldehyde; the main products were isobutanol, benzene, and traces of isobutyl acetate.

*Oxidation of isobutanol, trans-2-bromocyclohexanol, VIb and VIc by the DCC method.*<sup>16,17</sup> Isobutanol was oxidized to isobutyraldehyde in 41 % yield (calc. as crude DNP derivative, identical to an authentic sample) by the *DCC method* (TFA, Py, 20 h). *Trans*-2-bromocyclohexanol (0.35 g) afforded by the same method 0.35 g of a crude DNP derivative. VIb (1 mmole) gave only traces of a precipitate with DNP and from VIc (0.54 g) only ca. 50 mg of an impure DNP derivative was obtained. Analysis of the oxidation product of VIb (0.22 g, TFA 0.02 ml, Py 0.04 ml, DCC 0.26 g, DMSO 0.6 ml, ether 0.5 ml, 24 h) by gas chromatography revealed the presence of isobutanol and isobutyraldehyde in the proportions 2:1 whereas the oxidation of isobutanol (35 mg) was complete under the same conditions.

*Oxidation of p-bromophenacyl bromide.* The NMR spectrum of a small sample of the bromide, dissolved in DMSO, D<sub>6</sub>, was run immediately after dissolution and also after 2 h at 70°. The oxidation to glyoxal was complete; no labelled dimethyl sulfide XI was formed.

*NMR measurements.* The mechanistic studies were performed directly in the NMR tube by dissolving an appropriate amount of the compound in DMSO, D<sub>6</sub>. The instrument had thermostated heating equipment.

*Trans-1,2-bromochlorocyclohexane.* Bromotrinitromethane (4.6 g) was added slowly to a mixture of dimethylsulfoxide (10 ml), dimethoxyethane (10 ml), cyclohexane (1.7 g) and lithium chloride (1.2 g). After 1.5 h water (120 ml) and carbon tetrachloride (10 ml) were added. The organic layer was separated, heated on a steam bath at 80° for 5 min, then washed twice with sodium bicarbonate, dried over sodium sulfate, and evaporated. The product contained *trans*-2-bromocyclohexanol, which was removed by chromatography on a silica column with carbon tetrachloride as eluent. Distillation afforded *trans*-1,2-bromochlorocyclohexane in a yield of 38 %, b.p. 74–75°/8.

*Trans-1,2-bromonitratocyclohexane* was obtained by the same method using sodium nitrate (2.0 g) instead of lithium chloride. Yield 32 %, b.p. 108–109°/9.

*Acknowledgements.* This work has been supported by grants from *Statens Naturvetenskapliga Forskningsråd*. I would like to thank Mrs. Inger Lindgren and Dr. B. Östman, FOA, for running the NMR spectra, and Mrs. Monika Nilsson for running the gas chromatograms.

## REFERENCES

1. Torssell, K. *Arkiv Kemi* **23** (1965) 537.
2. Torssell, K. *Arkiv Kemi* **23** (1965) 543.
3. Tartakovskii, V. A., Sjlénov, I. E., Lagodzinskaja, G. V. and Novikov, S. S. *Dokl. Akad. Nauk. SSSR* **161** (1965) 136.
4. Meerwein, H., Battenberg, E., Gold, H., Pfeil, W. and Willfang, G. *J. prakt. Chem.* **2** **154** (1939) 83.
5. Meerwein, H., Zenner, K. F. and Gipp, R. *Ann.* **688** (1965) 67.
6. Smith, S. G. and Winstein, S. *Tetrahedron* **3** (1958) 317.
7. Natus, G. and Goethals, E. J. *Bull. Soc. Chim. Belges* **74** (1965) 450.
8. Kornblum, N., Jones, W. J. and Anderson, G. J. *J. Am. Chem. Soc.* **81** (1959) 4113.
9. Hunsberger, I. M. and Tien, J. M. *Chem. Ind. (London)* **1959** 88.
10. Jarreau, F.-X., Tschoubar, B. and Goutarel, R. *Bull. Soc. Chim. France* **1962** 887.
11. Barton, D. H. R., Garner, B. J. and Wightman, R. H. *J. Chem. Soc.* **1964** 1855.
12. Jones, D. N. and Saeed, M. A. *J. Chem. Soc.* **1963** 467.
13. Johnson, C. R. and Phillips, W. G. *Tetrahedron Letters* **1965** 2101.
14. Jones, J. B. and Wigfield, D. C. *Tetrahedron Letters* **1965** 4103.
15. Albright, J. D. and Goldman, L. *J. Am. Chem. Soc.* **87** (1965) 4214.
16. Pfitzner, K. E. and Moffat, J. G. *J. Am. Chem. Soc.* **87** (1965) 5661.
17. Pfitzner, K. E. and Moffat, J. G. *J. Am. Chem. Soc.* **87** (1965) 5670.
- 17a. Fenselau, A. H. and Moffat, J. G. *J. Am. Chem. Soc.* **88** (1966) 1762.
18. Kornblum, N., Powers, J. W., Anderson, G. J., Jones, W. J., Larsson, H. O., Levand, O. and Weaver, W. M. *J. Am. Chem. Soc.* **79** (1957) 6562.
19. Onodera, K., Hirano, S., Kashimura, N. and Yayima, T. *Tetrahedron Letters* **1965** 4327.
20. Krause, E. *Ber.* **57** (1924) 813.

Received July 11, 1966.