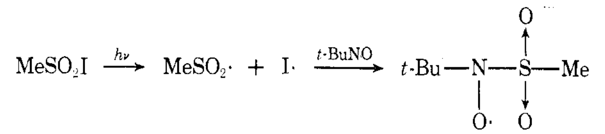
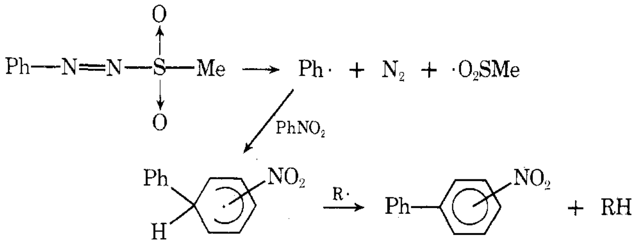
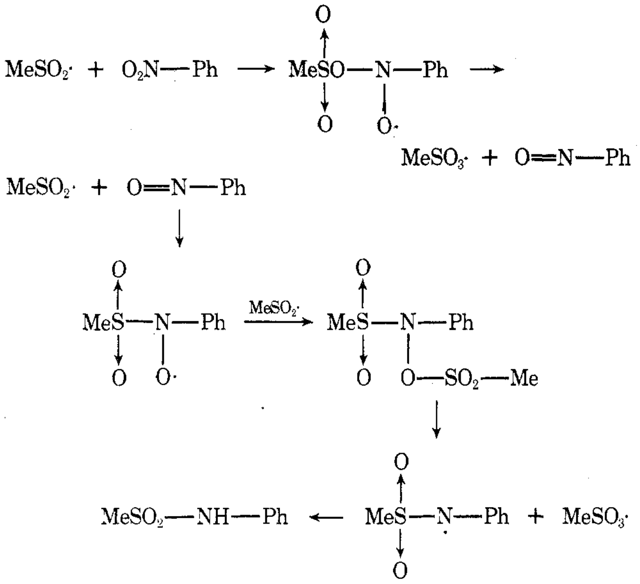


VI

All the data obtained show that Ia decomposes homolytically, yielding phenyl radical and methanesulfonyl radical.



Phenyl radical attacks nitrobenzene, yielding nitrobiphenyls. Methanesulfonyl radical also attacks nitrobenzene and reduces it. Details of the reaction mechanism are not clear, but the following reaction steps are possible.



It is known that sulfonyl radicals do not attack arene nuclei,[7] and it appears reasonable that methanesulfonyl radical reacts with the nitro group, forming a nitroxide radical.

Experimental Section

Materials. Nitrobenzene and pyridine were purified according to conventional procedures. Methyl phenylazo sulfone (Ia) was prepared from sodium methanesulfinate[8] (2.62 g, 2 mmol) according to the method of Kice and Gabrielsen:[1] yield, 2.29 g (65%); mp 69.5–70.3° (lit.[1] 73–74.5°).

Methyl *p*-tolylazo sulfone (Ib) was prepared from sodium methanesulfinate (2.8 g, 2 mmol) by the method of Dutt:[9] yield, 1.5 g (37%); mp 109.3–111.5° dec (lit.[9] 112–113°).

α-Phenyl-*N*-*tert*-butylnitrone,[10] 2-nitroso-2-methylpropane,[11] and methanesulfonyl iodide[13] were synthesized according to the methods described in the literature.

Rates of Decomposition of Ia. A reaction vessel containing nitrobenzene (40 ml) and pyridine (0.451 g, 6.0 mmol) was placed in a constant-temperature bath under a nitrogen atmosphere and then Ia (0.362 g, 2.0 mmol) was mixed. The amount of nitrogen gas evolved was determined with a gas buret. The reaction vessel was covered with aluminum foil in order to prevent photolysis.

Products of Decomposition of Ia. After the decomposition was complete, the pyridinium sulfonate which precipitated was removed, and the solution was washed with water. When the aqueous extracts were made alkaline with Na_2CO_3 and evaporated, sodium methanesulfonate was obtained. The pyridinium salt and sodium salts were dissolved in D_2O, and their amounts were determined by nmr spectroscopy.

The nitrobenzene solution was concentrated under reduced pressure. Nitrobiphenyls were determined by glc, and methanesulfonanilide was determined by nmr spectroscopy.

Spin Trapping. With PBN. When a mixture of Ia, PBN, and pyridine in benzene was placed in an esr spectrometer (a JES-ME-3X), weak signals were observed. When the sample tube was irradiated with a 500-W mercury lamp, the signals became very strong. When the esr spectra were determined under a nitrogen atmosphere, the same results were obtained.

With 2-Nitroso-2-methylpropane. When a mixture of Ia, the dimer of 2-nitroso-2-methylpropane,[11] pyridine, and benzene (or ether) was placed in an esr tube in a JES-ME-3X, weak signals were observed, which were ascribable to VI. The mixture was irradiated with a 500-W mercury lamp using a Toshiba Filter UV-D2 (in order to decrease the formation of V). 2-Nitroso-2-methylpropane absorbs at 680 nm,[12] and the UV-D2 has maximum transparency at 360 nm, absorbing at a longer wavelength region.

Registry No.—Ia, 23265-32-9; Ib, 53188-52-6; II, 26788-89-6; V, 2406-25-9; VI, 53188-53-7; VII, 52704-27-5; VIII, 3229-61-6.

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One-Step Preparation of Tetrakis(bromomethyl)ethylene from Pinacolyl Alcohol

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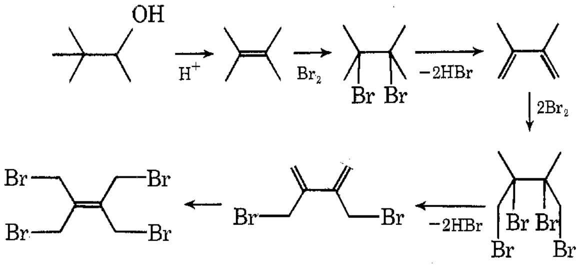
Tetrakis(bromomethyl)ethylene, $(BrCH_2)_2C{=}C(CH_2Br)_2$, has been used as a means of synthetic entry into the bicyclo[3.3.0]oct-1-ene[2a] and other[2b] alicyclic systems. During other work we have found that it can be prepared conveniently and inexpensively by treating the readily available pinacolyl alcohol with a large excess of neat bromine at 40–50°.

The bromination of pinacolyl alcohol has been investigated over many years; in 1907 Delacre reported the preparation of a compound, mp 132–133°, whose bromine analysis (no CH analysis was given) corresponded to the formula $C_6H_{11}Br_3$.[3] He further alluded to a dibromide, $C_6H_{12}Br_2$, prepared earlier by Friedel. In repeating this reaction we obtained instead products of widely varying melting point, which by recrystallization or sublimation gave samples identical in and homogeneous by tlc, but having melting points varying between 145 and 163°. The nmr spectrum showed only one sharp singlet at δ 2.0, ruling out a $C_6H_{11}Br_3$ formula. However, these data serve to identify the compound as 2,3-dibromo-2,3-dimethylbutane, which has the same nmr spectrum,[4] and whose melting point has been variously reported (*e.g.*, 159°,[5] 170–175°,[6] 177–177.5°,[7] 180–182°[8]). No other compounds were detected in significant amounts in our repetitions of Delacre's reaction.

Increasing the amount of bromine and prolonging the reaction gave a new compound, mp 156–157°, which had a singlet at δ 4.10 as the only nmr signal. These data are in agreement with those for tetrakis(bromomethyl)ethylene, which Stetter and Tresper[9] have recently prepared by treating 2,3-dimethyl-2-butene, 2,3-dimethyl-1-butene, 2,3-dimethyl-1,3-butadiene, 1,2,3,4-tetrabromo-2,3-dimethylbutane, or 2,3-dimethyl-2-butanol with liquid bromine containing a little hydrogen bromide. We consider that these brominations of pinacolyl alcohol first involve the acid-catalyzed (hydrogen bromide added or generated *in situ*) conversion of the alcohol into tetramethylethylene,[10] which may then be transformed as shown in Scheme I. This scheme accounts also for Stetter and Tresper's results.[9] We believe that Delacre's compound may have been a mixture of 2,3-dibromo-2,3-dimethylbutane with either or both the tetrabromides shown in the scheme.

Scheme I
Suggested Reaction of Pinacolyl Alcohol with Bromine



The above synthesis of tetrakis(bromomethyl)ethylene represents an exceptionally easy and inexpensive preparation of this compound.

Experimental Section

Reaction of Pinacolyl Alcohol with Bromine (Cf. Ref 3). Bromine (5 ml) was added gradually to pinacolyl alcohol (10 ml) in a 50-ml flask. Considerable heat was generated and much HBr was evolved. After the reaction was complete, the colorless mixture was cooled to room temperature, which caused partial solidification. The mixture was partitioned between light petroleum and water. The pale yellow organic layer was decolorized (Norit) and concentrated to a partly solid mass, which was triturated with methanol. The methanol-insoluble portion (mp ~130°) was recrystallized repeatedly from cyclohexane or sublimed below the melting point (water aspirator) to give 2,3-dibromo-2,3-dimethylbutane as colorless crystals with a camphor-like odor: mp (different samples) 145°, 157–158°, 162–163°; homogeneous in tlc with silica gel–light petroleum; nmr ($CDCl_3$) δ 2.0 (s); ref 4 quotes δ 2.0.

Tetrakis(bromomethyl)ethylene from Pinacolyl Alcohol (Cf. Ref 9). To pinacolyl alcohol (0.1 mol, 12.6 ml) and concentrated hydrobromic acid (1 ml) in a flask fitted with a reflux condenser and set up in a hood was added, dropwise at first, neat bromine (40 ml), so that reaction was as gentle as possible. The temperature was maintained at 40–50° during 8 hr, at 20° overnight, and again at 50° for 2 hr. The red solid product was broken up in the presence of a little light petroleum, and excess bromine neutralized by adding solid sodium bisulfite and cracked ice under ice cooling. Water was finally added, and the crude tetrakis(bromomethyl)ethylene filtered off as pale yellow crystals, mp 133–136° (17.1 g, 43%). This material is substantially pure, but may be efficiently recrystallized once or twice from ethyl acetate to give colorless crystals, mp 156–157°; nmr δ 4.12 (s) in $CDCl_3$ [ref 9 cites light yellow crystals, mp 158.5°, δ 4.25 (s) in liquid bromine].

Registry No.—Pinacolyl alcohol, 464-07-3; bromine, 7726-95-6; 2,3-dibromo-2,3-dimethylbutane, 594-81-0; tetrakis(bromomethyl)ethylene, 30432-16-7.

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