dried over molecular sieves. Rotary evaporation of solvent gave 10.3 g (96%) of a syrupy residue which was dissolved in 45 ml of dry benzene. To the resulting solution was added 11.2 g (88.5 mmol) of oxalyl chloride. Gas evolution continued for 45 min and stirring was maintained for an additional hour. Solvent was removed at reduced pressure and the residue was heated at 145° for 45 min. The reaction was followed by quenching samples in methanol and determining the cis:trans ratio of methyl esters by glpc. At the end of the isomerization the mixture was 95% trans and 5% cis. The acid chloride was allowed to cool before water was added. The trans acid was isolated as described above; yield 6.3 g (61%).

Samples of *trans*-4 from several isomerizations, 9.6 g (68 mmol), were allowed to react with 22.0 g (68 mmol) of quinine, and the resulting salt was partially resolved by recrystallization from 40:60 ethyl acetate–diethyl ether. After four recrystallizations, treatment of a less soluble fraction with dilute hydrochloric acid followed by extraction with diethyl ether yielded 1.54 g of optically active carboxylic acid, $[\alpha]^{25}D$ +72.5° (*c* 4.95, CH_3OH). From a more soluble fraction of the quinine salt, (−)-*trans*-**4**, $[\alpha]^{25}D$ −90.7° (*c* 4.84, CH_3OH), was obtained: nmr δ ($CDCl_3$) 0.7–2.3 (4, m, H at C_1, C_2, and C_3), 1.67 and 1.74 (6, two d, methyls at $C_{2'}$, $J \simeq$ 1.5 Hz), and 4.63 ppm (1, d of septets, H at $C_{1'}$, $J_{2,1'}$ = 9 Hz).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.80; H, 8.75.

(+)-Methyl *trans*-2-(2′-Methylpropenyl)cyclopropanecarboxylate, (+)-*trans*-5. *N*-Methyl-*N*-nitrosourea, 3.0 g (29 mmol), was stirred with 9 ml of 50% aqueous KOH and 36 ml of diethyl ether in an acetone–ice bath for 7 min, before the resulting yellow ether layer was decanted into a flask containing 1.54 g (11.0 mmol) of (+)-*trans*-**4**, $[\alpha]^{25}D$ + 72.5°. The reaction mixture was allowed to stand in the hood until the ether had evaporated, fresh ether was added, and the resulting organic fraction washed successively with saturated sodium bicarbonate and brine solutions. The organic layer was dried, and the ether evaporated, yielding 1.46 g (87%) of a colorless oil. Samples for spectra and analysis were purified by glpc (Carbowax 20M): $[\alpha]^{25}D$ +103° (*c* 2.33, $CHCl_3$); nmr δ 0.6–2.2 (4, m, cyclopropyl H), 1.63 and 1.70 (6, two d, methyls at $C_{2'}$, $J \simeq$ 1.5 Hz), 3.57 (3, s, carbomethoxy), and 4.52 ppm (1, d of septets, H at $C_{1'}$, $J_{2,1'}$ = 9 Hz); ir (CCl_4) 2950, 2900, 1725, 1660, 1450, 1180, and 1040 cm^{-1}.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.13; H, 9.28.

(+)-*trans*-1,2-Diacetoxymethylcyclopropane, (+)-*trans*-6. Ozone was passed through a solution of 107 mg (6.7 mmol) of (+)-*trans*-**5** in 15 ml of dry methylene chloride at −78° until a pale blue color persisted. Excess ozone was removed at −78° with a stream of dry nitrogen, and solvent was removed at reduced pressure. The residue was dissolved in 30 ml of dry ether to which was added 150 mg of $LiAlH_4$, and the mixture was allowed to stir overnight. Excess hydride was decomposed by addition of a saturated solution of NH_4Cl, and addition continued until the inorganic salts precipitated. The clear ether layer was decanted, and the precipitate was washed repeatedly with ether. The combined ether fractions were dried over anhydrous $MgSO_4$ and solvent was removed at reduced pressure, leaving 73 mg (100%) of a colorless oil:[5] nmr ($CDCl_3$) δ 0.1–1.4 (4, m, H at C_1, C_2, and C_3) 3.0–4.0 (4, m, hydroxymethyls at C_1 and C_2), and 4.25 ppm (2, br s, OH).

To a solution of 73 mg (0.70 mmol) of the trans diol and 500 mg (6.5 mmol) of pyridine in 10 ml of dry benzene was added 256 mg (3.26 mmol) of acetyl chloride. Heat was evolved and a white precipitate formed. After 30 min the reaction was diluted with 30 ml of ether and extracted with successive 10-ml portions of water, 3 *N* HCl, water, and saturated $NaHCO_3$. The ether layer was dried, and solvent removed at reduced pressure, yielding 101 mg (79%) of (+)-*trans*-**6**.[5] Analytical samples were purified by glpc (Carbowax 20M): $[\alpha]^{25}D$ +9.60° (*c* 1.57, EtOH); nmr ($CDCl_3$) δ 0.47–0.75 (2, m, H at C_3), 0.97–1.35 (2, m, H at C_1 and C_2), 2.13 (6, s, acetate methyls), and 4.08 ppm (4, d, acetoxymethyl at C_1 and C_3, J = 7 Hz).

(+)-2-[*trans*-2′-(2″-Methylpropenyl)cyclopropyl]propan-2-ol, (+)-*trans*-1. In a 100-ml three-necked flask with condenser, addition funnel, and N_2 inlet was placed 1.08 g (7.0 mmol) of (+)-*trans*-**5**, $[\alpha]^{25}D$ +103°, in 25 ml of anhydrous ether, and 10 ml of 1.5 *M* MeLi (15 mmol) was added dropwise. After stirring for an hour, 2 ml of saturated NH_4Cl was carefully added, and the clear ether layer was decanted and washed with brine. The ether solution was filtered through sodium sulfate and dried over molecular sieves. The solvent was evaporated at reduced pressure, leaving 0.97 g (90%) of a colorless, fragrant oil. Samples for analysis were collected by glpc: $[\alpha]^{25}D$ +18.1° (*c* 2.28, $CHCl_3$); nmr ($CDCl_3$) δ 0.6–2.2 (4, m, cyclopropyl H), 1.18 (6, s, H at C_1 and C_3), 1.63 and 1.70 (6, pair of d, CH_3's at $C_{2''}$, $J \simeq$ 1 Hz), and 4.58 ppm (1, d of septets, H at $C_{1''}$, $J_{2',1''}$ = 8 Hz); ir (CCl_4) 3500, 2900, 1660, 1440, 1370, 1160, and 910 cm^{-1}. Our spectra are similar to those reported by Robinson for racemic trans-1.[3]

Registry No.—(+)-*trans*-**1**, 52152-29-1; **2**, 926-56-7; *cis*-**3**, 53166-49-7; *trans*-**3**, 53166-50-0; *trans*-**4**, 53166-51-1; (+)-*trans*-**4**, 53187-84-1; (−)-*trans*-**4**, 53187-85-2; (+)-*trans*-**5**, 53187-86-3; (+)-*trans*-**6**, 53166-30-6; (+)-*trans*-**6** free diol, 53187-82-9; ethyl diazoacetate, 623-73-4.

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Homolysis of Methyl Phenylazo Sulfones

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Kice and Gabrielsen studied the thermolysis of methyl phenylazo sulfone (Ia) and concluded that the decomposition is homolytic on the basis of the product studies.[1] However, thermolysis of azo sulfones tends to contain some acid-catalyzed ionic decomposition because of the production of sulfinic or sulfonic acids.

When Ia was decomposed in nitrobenzene, the nitrobiphenyls formed were rich in its meta isomer, as shown in Table I. The isomer distribution suggests that both homolysis and heterolysis are taking place. In the decompositions of phenylazo *p*-tolyl sulfone (II), acid-catalyzed heterolysis was effectively prevented by the addition of a base.[2a] Therefore, I was decomposed in the presence of pyridine. When 2 mol of pyridine per mol of I was present, the isomer distribution found indicated that the decomposition is

Table I
Products of Decomposition of Azo Sulfones in Nitrobenzene

Azo sulfone	Pyridine, mol/mol I	Temp, °C	Nitrobiphenyls: Yield, %	Orientation, % Ortho	Meta	Para	Nitrogen, %
I_a	0	80.5	*a*	33	41	26	38
I_a	2/1 I_a	80.2	77.1	67.0	10.0	23.0	86
I_a	3/1 I_a	80.1	75.3	68.3	9.4	22.3	95
II[b]	2/1 II	60.0	54.4	64.5	7.7	27.8	*a*

[a] Not determined. [b] In ref 2.

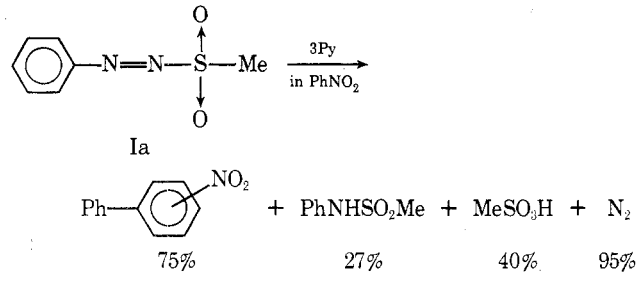
Table II
Coupling Constants of Nitroxide Radicals

	Nitroxide radical										
	V		VI		VII			VIII			
	A_N	g	A_N	g	A_N	A_H	g	A_N	$A_{o,pH}$	A_{mH}	g
Found											
Ether	15.1	2.0060	12.9	2.0059	13.6	2.8	2.0061				
C_6H_6	15.3	2.0060	12.9	2.0060				12.4	1.9	0.9	2.0060
Lit.[6]											
C_6H_6	15.2							12.3	2.0	0.9	

homolytic.[2] The presence of a greater amount of the base did not affect the isomer distribution greatly.

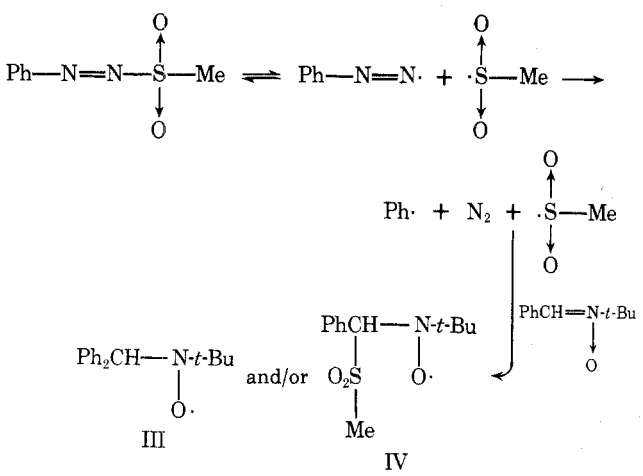
The rates of homolysis of Ia were determined in nitrobenzene in the presence of 3 mol of pyridine per mol of Ia, and were of first order in Ia; the first-order rate constants were 2.53 (80.1°), 4.25 (84.8°), 6.43 (89.5°), and 18.4×10^{-5} sec^{-1} (95.0°). The activation parameters obtained (ΔH^* = 33.5 kcal/mol, ΔS^* = 19.3 eu) are similar to those reported for azo sulfone II.[2]

The products of decomposition of Ia are summarized below.



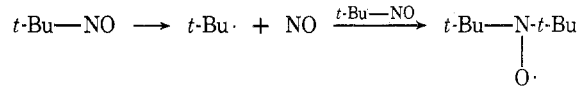
Formation of methanesulfonanilide is of interest. Since the yield of nitrogen gas is almost quantitative, the anilide moiety must come from nitrobenzene. When methyl *p*-tolylazo sulfone (Ib) was decomposed under similar conditions, methanesulfonanilide was found in a 24% yield. This finding ascertains that the anilide moiety comes from nitrobenzene. When a reaction mixture was concentrated under reduced pressure, a yellowish-green liquid was distilled, which was identified as nitrosobenzene. This suggests that nitrobenzene is reduced during the decomposition of I.

Spin Trapping. When Ia was decomposed in the presence of α-phenyl-*N*-*tert*-butylnitrone (PBN) in benzene, esr signals observed were a triplet of doublets with A_N = 14.5, A_H = 2.3 G, and g = 2.0061. These signals must be ascribable to either the adduct III or IV. As for the coupling

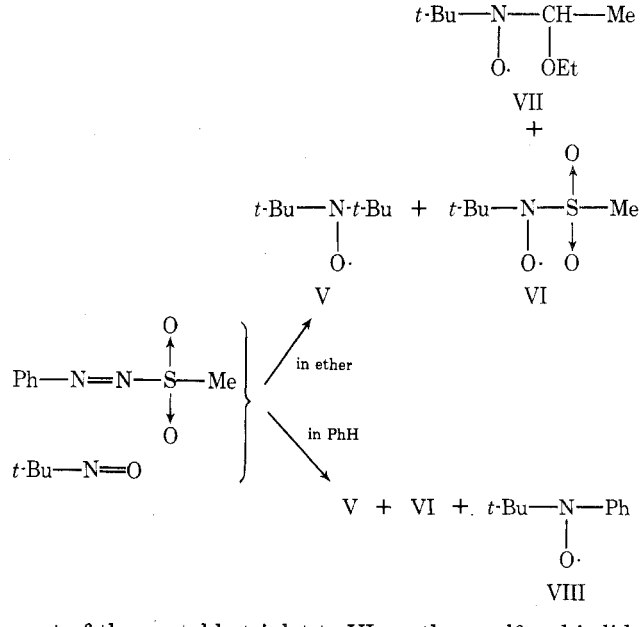


constants of III, Janzen and Blackburn[4] reported that A_N = 13.8 G and A_H = 2.1 G, while Bluhm and Weinstein[5] reported that under deoxygenated conditions A_N = 14.7 G and A_H = 2.18 G. In our reaction conditions nitrogen gas is continuously evolved and the system is virtually deoxygenated; our coupling constants are similar to those reported by Bluhm and Weinstein. Thus PBN effectively traps phenyl radical, but not methanesulfonyl radical.

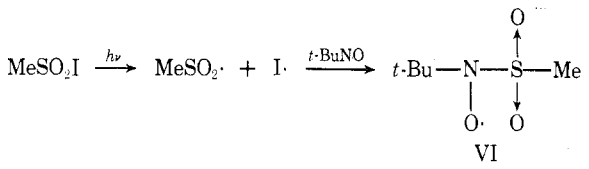
In an attempt to trap the methanesulfonyl radical, Ia was decomposed in the presence of 2-nitroso-2-methylpropane in diethyl ether. The ether was used as the solvent because phenyl radical will abstract the α hydrogens and the trapping of only methanesulfonyl radical is expected. The esr spectrum observed showed a stable triplet, a very unstable triplet, and a triplet–doublet. The stable triplet was ascribed to di-*tert*-butyl nitroxide radical (V), which could be formed by the addition of *tert*-butyl radical to 2-nitroso-2-methylpropane.



When benzene was used as the solvent, the triplet–doublet was not observed. Therefore, it must be due to radical VII, the adduct of the ether radical to the spin trap. The coupling constants and assignments of these nitroxide radicals are summarized in Table II. In order to check the assign-

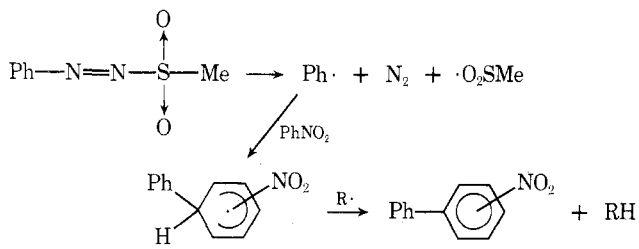


ment of the unstable triplet to VI, methanesulfonyl iodide was photolyzed in the presence of 2-nitroso-2-methylpropane; an unstable triplet ($\tau_{1/2}$ = about 50 sec) with A_N = 12.9 G and g = 2.0060 was observed. Thus the identity of the radical VI was established.

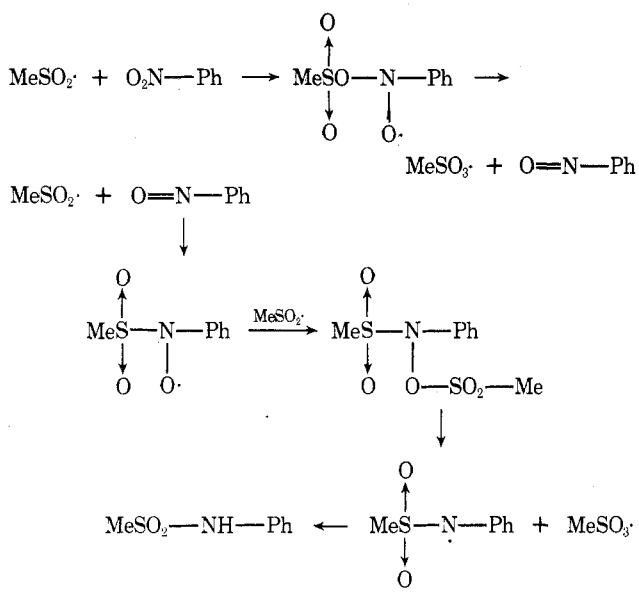


VI

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