hydroxy-1-methylcyclohexane and/or the geometric isomers of each. The inability to distinguish among these possibilities rested on the observation that under the best g.l.p.c.[20] conditions used, the retention times determined for the two experimental components (a and b) and those determined for authentic samples of the isomeric alcohols were too close to allow for reliable identification of the position and geometric isomers involved.

Oxidation of *R*-(+)-4-Methylcyclohexene (IIa) to *R*-(+)-3-Methylhexanedioic Acid (VII).—Into a stirred solution IIa (0.680 g., 0.071 mole, $[\alpha]^{23}\mathrm{D}$ +17.5°) in 15 ml. of absolute methanol, maintained near −78° by means of an external Dry Ice-acetone bath, was passed a stream of ozone-enriched oxygen[21] at a rate of nearly 180 cc./min. The ozonation was continued until the color of elemental iodine appeared (*ca.* 2 hr.) in the 300 ml. of 2% aqueous potassium iodide solution through which the stream of gases exciting the reaction mixture was passed. Methanol solvent was then carefully evaporated from the reaction mixture under reduced pressure (1 mm.), leaving a syrupy residue to which 10 ml. of 90% aqueous formic acid and 6 ml. of 30% aqueous hydrogen peroxide were added. The entire mixture was then carefully warmed to about 75° in a water bath, at which time a vigorous effervescence started and continued during about 30 min. The hydrolysate was then concentrated *in vacuo* until formation of a white precipitate was observed. After crystallization was complete, the material was collected on a suction filter, air dried, and recrystallized from benzene, giving VII: 0.31 g. (27% yield); m.p. 87–89°, lit.[9] m.p. 85–89°; $[\alpha]^{26}\mathrm{D}$ +1.3 ± 0.3° (*c* 3.84, chloroform), lit.[9] $[\alpha]^{26}\mathrm{D}$ +9.6° (chloroform).

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(21) Ozone generated with a Welsbach Corp., Philadelphia, Pa., zonator, Style T-23.

Ylide Methylation of Aromatic Nitro Compounds[1]

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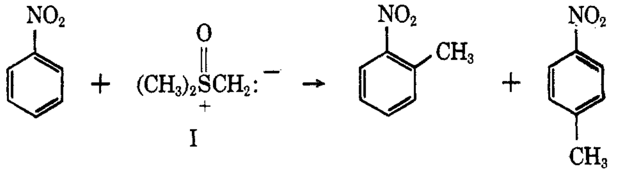
The reaction of dimethyloxosulfonium methylide (I) with nitrobenzene produced *o*- and *p*-nitrotoluenes in about 35% yield with an *ortho/para* ratio of about 10–15. Additional methylation reactions with 1-nitronaphthalene, *o*-, *m*-, and *p*-chloronitrobenzenes, *o*-, *m*-, and *p*-nitrotoluene, and *m*- and *p*-nitroanisoles are described. Some mechanistic possibilities for the origin of the products are considered.

The substitution of an alkyl group for one of the hydrogens in nitrobenzene may be accomplished, *a priori*, by an electrophilic, free-radical, or nucleophilic process, which requires displacement of hydrogen as H+, H·, or H−, respectively. The electrophilic Friedel–Crafts alkylation reaction requires severe experimental conditions or fails with nitrobenzene,[3] while free-radical alkylation[4] of nitro aromatic compounds is accompanied by the formation of by-products including tars. Nucleophilic aromatic alkylation, which requires displacement of hydride ion, is complicated by the fact that carbanions attack the nitro function.[5–8] In addition, carbanion attack on the ring may lead to highly colored substances[9] or condensation products[10] in which the nitro function has been reduced.

In this paper we wish to report the facile methylation of nitrobenzene and substituted nitrobenzenes by a process which appears to occur by aromatic nucleophilic substitution. Metzger, König, and Seelert[11] have published a brief report on the facile methylation of nitrobenzene by the method described in this paper. Their work appeared shortly before completion of this study.

When nitrobenzene and dimethyloxosulfonium methylide (I)[12] were allowed to react at room temperature, a mixture of *o*- and *p*-nitrotoluene (35% yield) was isolated. Identification of the products was accomplished by comparison of retention times in gas–liquid partition chromatography and the infrared spectra with those of authentic samples. The isomer distribution in the product, determined by g.l.p.c., gave an *ortho/para* ratio of about 10–15 and thus revealed a strong tendency for *ortho* isomer formation. After a study of the stability of dimethyloxosulfonium methylide (see Table I), the reaction of nitrobenzene and dimethyloxosulfonium methylide was investigated at various times, temperatures, and concentrations (see Table II).



Since the methylide I possesses carbanionic features and the reaction of carbanions with nitrobenzene can

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[3] G. A. Olah, Ed., "Friedel-Crafts and Related Reactions," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1964, pp. 68, 721. The former reference cites the alkylation of *o*-nitrotoluene, while the latter lists the chloromethylation of nitrobenzene.

[4] L. F. Fieser, R. C. Clapp, and W. H. Dandt, *J. Am. Chem. Soc.*, **64**, 2052 (1942); B. R. Cowley, R. O. C. Norman, and W. A. Waters, *J. Chem. Soc.*, 1799 (1959).

[5] H. Hepworth, *ibid.*, **117**, 1010 (1920).

[6] H. Gilman and R. McCracken, *J. Am. Chem. Soc.*, **51**, 828 (1929).

[7] A. K. Hoffmann, A. M. Feldman, and E. Gelblum, *ibid.*, **86**, 646 (1964).

[8] G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964).

[9] R. Foster and R. K. Mackie, *Tetrahedron*, **18**, 1131 (1962).

[10] R. B. Davis, L. C. Pizzini, and J. D. Benigni, *J. Am. Chem. Soc.*, **25**, 1884 (1960). See also subsequent papers.

[11] H. Metzger, H. König, and K. Seelert, *Tetrahedron Letters*, 867 (1964).

[12] This substance was first reported by E. J. Corey and M. Chaykovshy [*J. Am. Chem. Soc.*, **84**, 867 (1962)], who studied the reaction of this reagent with carbonyl compounds. See also subsequent papers.

TABLE I

STABILITY OF DIMETHYLOXOSULFONIUM METHYLIDE[a]

Time variation,[b] days			
Initial	2	4	7
0.110	0.104 (94)	0.094 (86)	0.080 (73)
0.957	0.567 (59)		
Temp. variation,[c] °C.			
25	40	70	100
0.091	0.087 (96)	. . .	0.081 (89)
0.993	0.957 (96)	0.722 (73)	0.249 (25)

[a] All concentrations are expressed in molarity and were determined by addition of aliquots of the methylide solution to standard acid followed by back titration with standard base. Numbers in parentheses indicate the percentage of methylide remaining. [b] These solutions were kept at room temperature for the indicated period of time. [c] Each solution was magnetically stirred under nitrogen at the temperature indicated for 15 min.

methylide produced nitrotoluenes in 13 and 8% yields, respectively. In each case the major product was again *o*-nitrotoluene. In the latter reaction, triphenylphosphine (11%) and triphenylphosphine oxide (12%) were also found. Control experiments ruled out the oxidation of triphenylphosphine by dimethyl sulfoxide or nitrobenzene as a source of triphenylphosphine oxide.

The reaction of 1-nitronaphthalene with dimethyloxosulfonium methylide produced 1-nitro-2-methylnaphthalene (12%) along with some resinous material. When 9-nitroanthracene or *m*-dinitrobenzene was treated with the methylide I, only resinous or tarlike materials were observed. However, the methylation reaction has been successfully extended to chloronitrobenzenes, nitrotoluenes, and nitroanisoles, with the results summarized in Table III. The composition of the product mixtures was determined by g.l.p.c. and in two cases by isolation from column chromatography. Products were separated by preparative g.l.p.c. and/or column chromatography, and the compounds were identified by physical constants, infrared spectra, and/or n.m.r. spectra. In those cases where reference infrared spectra were not available, the infrared spectrum of the substance was consistent with the assigned structure.

TABLE II

REACTION OF NITROBENZENE WITH DIMETHYLOXOSULFONIUM METHYLIDE

$C_6H_5NO_2$, g. (mmoles)			Distillate, g.	Mole % distribution in distillate			% yield[a] $CH_3C_6H_5NO_2$
				$C_6H_5NO_2$	o-$CH_3C_6H_5NO_2$	p-$CH_3C_6H_5NO_2$	
			Temperature Variation[b]				
		Temp., °C.					
6.3 (51)		25–30	3.65	56.8	40.3	2.88	35.5
6.2 (50)		45	3.48	56.5	41.0	2.46	33.2
6.4 (52)		65	3.49	60.3	35.0	4.70	30.3
			Time Variation[c]				
		Time, hr.					
6.6 (53)		0.50	3.71	86.5	13.5	. . .	14.8
6.3 (51)		1.0	3.65	56.8	40.3	2.88	35.5
6.7 (55)		2.25	3.58	49.5	47.5	3.25	34.1
6.6 (53)		4.0	3.52	66.9	31.9	1.2	26.1
			Concentration Variation[d]				
	Ylide, *M*	Mole ratio Ylide:$C_6H_5NO_2$					
5.0 (41)	1.5	4:1	2.12	47.0	53.0	. . .	26.2
6.7 (55)	1.0	2:1	3.58	49.5	47.5	3.24	34.1
9.4 (76)	0.8	1:1	5.31	58.5	32.2	9.2	32.7
12.2 (100)	0.5	1:1	6.84	63.1	33.2	3.6	30.0
5.8 (47)	0.1	1:1	2.98	81.0	12.6	6.4	16.2

[a] The per cent yield is for total nitrotoluenes based on unrecovered starting material. [b] Dimethyloxosulfonium methylide (0.1 mole) was prepared in 100 ml. of dimethyl sulfoxide and the reaction was performed at the specified temperature for 1 hr. [c] The methylide (0.1 mole) was generated in 100 ml. of dimethyl sulfoxide and the reaction temperature was maintained at 25° for the indicated times. [d] These reactions were carried out at 25° for 2.25 hr.

result in one-electron transfer,[8] the e.s.r. spectrum of the reaction mixture was investigated. A solution 1 *M* in both reactants produced an e.s.r. signal within 10 sec. after mixing. The e.s.r. spectrum recorded at higher dilution (10^{-3}–10^{-4} *M*) was assigned to the nitrobenzene radical anion by comparison with a spectrum of an authentic sample. The extent to which the one-electron transfer reaction occurs and the products of this reaction are under further study.

Since the nature of the reactants and products in the methylation reaction suggested the possibility of a nucleophilic aromatic substitution, the investigation of the scope of the reaction involved variation of the source of methylide and variation of the electron-withdrawing substituent in the aromatic substrate. When a mixture of diphenyl sulfone, methyl benzoate, benzonitrile, pyridine, or quinoline and dimethyloxosulfonium methylide was subjected to the most demanding conditions used for the nitrobenzene reaction, no methylation products were found, and the aromatic starting materials were recovered in 50–97% yield. On the other hand, the reaction of nitrobenzene with trimethylammonium methylide or triphenylphosphonium

Two interesting observations evolve from the study of these substituted nitrobenzenes (Table III): (1) methylation is directed toward the position *ortho* to the nitro function in preference to *para*, and (2) with *meta*-substituted nitrobenzenes methylation proceeds primarily to the more hindered *ortho* position (C-2) rather than the other *ortho* position (C-6). These features provide a unique character to the reaction which may offer some synthetic utility in the preparation of highly substituted nitro aromatic compounds.

In exploring the mechanistic possibilities for the reaction of dimethyloxosulfonium methylide with nitrobenzene, the aromatic substrate offers two points of at-

TABLE III

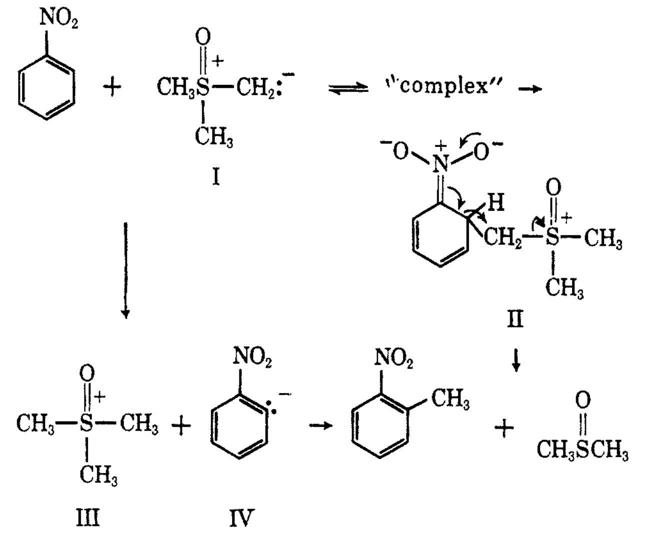
REACTION OF AROMATIC NITRO COMPOUNDS WITH DIMETHYLOXOSULFONIUM METHYLIDE

Aromatic substrate	Recovered starting material, %	Methylation products (% yield)	Isolation procedure	M.p., °C., and means of identification	By-products
1-Nitronaphthalene (1)	...	2-Methyl-1-nitronaphthalene (12)	Crystn.	78–80 (80–81[a]), b	55%[c] yellow-green amorphous solid, m.p. 140–146° dec.[d]
o-$ClC_6H_4NO_2$ (2)	21	3-Cl-$2NO_2C_6H_3CH_3$ (24)[e]	Column chromatog. on alumina	22–23 (21–22[f]), b,g	o-$ClC_6H_4NH_2$[h] and two other unidentified compounds (minor products)[i]
m-$ClC_6H_4NO_2$ (3)	16	2-Cl-6-$NO_2C_6H_3CH_3$ (14)[j]	Prep. g.l.p.c.	33–35 (37[k]), b,g	
		4-Cl-2-$NO_2C_6H_3CH_3$ + 2-Cl-4-$NO_2C_6H_3CH_3$ (3.6)[j]	Prep. g.l.p.c.	g	
p-$ClC_6H_4NO_2$ (4)	4	3-Cl-6-$NO_2C_6H_3CH_3$ (25)	Column chromatog. on alumina	25 (24.9[l]), b,g	
		5-Cl-1,3-$(CH_3)_2$-2-$NO_2C_6H_2$ (13)	Column chromatog. on alumina	41–44 (44–45[m]), b,g	
o-$NO_2C_6H_4CH_3$ (5)	31	1,3-$(CH_3)_2$-2-$NO_2C_6H_3$ (16)[n]	Prep. g.l.p.c.	b,g	
		1,3-$(CH_3)_2$-4-$NO_2C_6H_3$ (2)[n]	Prep. g.l.p.c.	b,g	
m-$NO_2C_6H_4CH_3$ (6)	25	1,2-$(CH_3)_2$-3-$NO_2C_6H_3$ (15)	Prep. g.l.p.c. and column chromatog. on alumina	g	
		1,4-$(CH_3)_2$-2-$NO_2C_6H_3$ (6)	Prep. g.l.p.c. and column chromatog. on alumina	g	
		1,2-$(CH_3)_2$-4-$NO_2C_6H_3$ (2)	Prep. g.l.p.c.	b,g	
p-$NO_2C_6H_4CH_3$ (7)	...	...	...	...	Unidentified amorphous solids
m-$NO_2C_6H_4OCH_3$ (8)	4	2-CH_3O-6-$NO_2C_6H_3CH_3$ (24)	Column chromatog. on alumina	52–53 (52[o]), b,g	Two other solids (minor components), not simple methylation products
p-$NO_2C_6H_4OCH_3$ (9)	48	5-CH_3O-2-$NO_2C_6H_3CH_3$ (17)	Column chromatog. on alumina	50 (50[o]), b,g	Minor solid, not simple methylation product

[a] H. E. Fierz-David and E. Mannhart, *Helv. Chim. Acta*, 20, 1024 (1937). [b] The n.m.r. spectrum was determined in carbon tetrachloride solution with tetramethylsilane as an internal standard. The spectrum was consistent with the structural assignments and is reproduced in the Ph.D. Dissertation of J. V. M. [c] This percentage is the ratio of weight of this unknown and weight of 1-nitronaphthalene. [d] Not identified. [e] 34% based on unrecovered starting material. [f] L. A. Elson, C. S. Gibson, and J. D. A. Johnson, *J. Chem. Soc.*, 2740 (1929). [g] Infrared spectrum was identical with that of authentic sample or consistent with assigned structure. [h] This amine was extracted from the product mixture with 10% HCl and identified by comparison of its infrared spectrum with that of an authentic sample. [i] The infrared spectrum of the mixture indicates one component is most likely 3-chloro-4-nitrotoluene. [j] 21% total methylation products based on unrecovered starting material. [k] A. Green and T. Lawson, *J. Chem. Soc.*, 59, 1017 (1891). [l] M. J. P. Wibaut, *Rec. trav. chim.*, 32, 301 (1913). [m] H. E. Dadswell and J. Kenner, *J. Chem. Soc.*, 1106 (1927). [n] The total nitroxylene yield based on unrecovered o-nitrotoluene was 26%. [o] P. Ruggli and W. Lemhardt, *Helv. Chim. Acta*, 7, 701 (1924).

tack, namely, the nitro function and the aromatic ring. One mode of reaction which has been observed at the nitro group involved a one-electron transfer leading to the nitrobenzene radical anion. With *o*-chloronitrobenzene this one-electron transfer was probably the start of a reduction process which ultimately produced *o*-chloroaniline.

A second mode of interaction with the nitro group may involve reversible formation of a complex which can serve as a precursor to the one-electron transfer or as an intermediate directing intramolecular attack on the *ortho* position of the aromatic ring. This attack of the aromatic ring appears to be nucleophilic in character and may also occur by direct attack of the methylide I on the ring. In either case, one can arrive at structure II which may collapse as shown to regenerate the aromatic ring. The hydride shift to the methylene with loss of neutral dimethyl sulfoxide may provide the unique feature which permits a facile nucleophilic aromatic methylation. This scheme may be applied to other ylides and would be consistent with the isolation of triphenylphosphine from the reaction of nitrobenzene and triphenylphosphonium methylide.



The suggestion of a complex involving the nitro group finds some support in the extent of *ortho* methylation in the compounds studied. In addition, one may cite the predominance of attack at the more sterically hindered *ortho* position in *meta*-substituted nitrobenzenes. However, the origin of the *p*-methylated products would require direct attack of the ylide on the aromatic ring to produce an intermediate analogous to structure II which would then proceed to products.

An alternate possibility for the methylation mechanism would involve initial abstraction of an *ortho* or *para* proton in nitrobenzene by I with the generation of trimethyloxosulfonium cation (III) and nitrophenyl anion (IV). Subsequent reaction of these two species by an S_N2 process would produce nitrotoluenes and dimethyl sulfoxide. This mechanism seems less likely since proton abstraction from an aromatic ring is difficult.[13] In the case of *m*-chloronitrobenzene, proton abstraction from the 2-position should produce an anion which could eliminate a chloride ion forming a benzyne intermediate. Such an intermediate would lead to nonchlorinated products. Although we have not observed such products, we cannot exclude the possible formation of a benzyne intermediate because of a poor material balance. However, a benzyne intermediate does not appear as an attractive precursor to the chloronitrotoluenes formed in this reaction.

Experimental Section[14]

Trimethyloxosulfonium iodide, m.p. 210°[15] (lit. m.p. 200°,[17] 220°[16]), was prepared in 54% yield by the procedure of Kuhn and Trischman[17] using only 0.3 mole instead of 1 mole excess of methyl iodide.

Methyltriphenylphosphonium iodide, m.p. 180–181° (lit.[18] m.p. 179–180°), was prepared in 90% yield from triphenylphosphine (0.14 mole) and methyl iodide (0.19 mole) in dry benzene.

The Reaction of Nitrobenzene with Dimethyloxosulfonium Methylide.—Dimethyloxosulfonium methylide was prepared according to the procedure of Corey and Chaykovsky[12] in dimethyl sulfoxide[19] under nitrogen by reaction of equimolar amounts of trimethyloxosulfonium iodide and a mineral oil suspension of sodium hydride or methylsulfinyl carbanion.[20] The effect of concentration, time, and temperature on the stability of dimethyloxosulfonium methylide in dimethyl sulfoxide is listed in Table I.

Nitrobenzene was added dropwise to a stirred solution of dimethyloxosulfonium methylide under nitrogen (the solution turned black immediately) and the reaction mixture was subjected to the conditions specified in Table II. The reaction was quenched with water (100 ml.) and extracted with either Skelly F or ether. Skelly F extracts were dried over anhydrous potassium carbonate while the ether extracts were washed with water and dried over anhydrous sodium sulfate. After the solvent was removed, the residue was distilled under reduced pressure and the distillate was analyzed by g.l.p.c.[21] The mole percentage of the components was based on relative peak heights which was justified by examination of authentic standard mixtures of the observed products. In five experiments the residues from the initial extract of the reaction mixture were analyzed by g.l.p.c. and the mole per cent distribution of products was not significantly different than the g.l.p.c. analysis of distilled material. Product identification was achieved by comparison of retention times and peak enhancement with authentic samples. In addition nitrobenzene and *o*-nitrotoluene were isolated by g.l.p.c. and had infrared spectra identical with those of authentic samples. Table II contains the data for the effect of time, temperature, and concentration of this reaction.

In a subsequent experiment performed in a solution cell placed in an e.s.r. spectrometer, the reaction of nitrobenzene and dimethyloxosulfonium methylide caused an e.s.r. signal to

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[13] The base-catalyzed hydrogen–deuterium exchange in trinitrobenzene is not observed except under vigorous conditions and the small exchange with *m*-nitrotoluene is attributed to impurities: M. S. Kharasch, W. S. Brown, and J. McNab, *J. Org. Chem.*, **2**, 36 (1937).

[14] All melting points and boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Infracord spectrophotometer, the n.m.r. spectra were recorded by Mr. D. Schifferl with a Varian Associates 60-Mc. high-resolution n.m.r. spectrometer, Model V-4300B, and the e.s.r. measurements were made by Professor Robert G. Hayes. We gratefully acknowledge the help of Professor Hayes in the interpretation of these measurements.

[15] The melting point was determined on a Kofler hot-stage melting point apparatus. When a sample was inserted at room temperature and heated, it melted with decomposition at 190°; however, when the sample was placed on the hot stage at 185°, it melted with decomposition at 210°. Smith and Winstein[16] stated that the melting point of this salt depended on the rate of heating.

[16] S. F. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).

[17] R. Kuhn and H. Trischmann, *Ann.*, **611**, 117 (1958).

[18] C. H. Collins and G. S. Hammond, *J. Org. Chem.*, **25**, 1434 (1960).

[19] The authors wish to thank the Chemical Products Division of the Crown Zellerbach Co. for making generous samples of this material available for this work.

[20] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962). Essentially complete conversion of trimethyloxosulfonium iodide by action of methylsulfinyl carbanion to dimethyloxosulfonium methylide was indicated by its reaction with benzophenone which gave the expected 1,1-diphenyloxirane (90% yield).[12] The hydroxy sulfoxide resulting from the reaction of methylsulfinyl carbanion and benzophenone was not observed in the above reaction.

[21] All analytical g.l.p.c. was performed with a Wilkens Aerograph instrument, Model No. A-90, using a 10-ft. column packed with silicone GE-SF-96 on firebrick at 160–170° wtih 18–25 p.s.i. of helium.

appear within 10 sec. after mixing the reactants and grew to a maximum intensity in about 15 min. A reaction mixture 0.5 *M* in methylide and nitrobenzene was diluted with dimethyl sulfoxide to 10^{-3}–10^{-4} *M* shortly after mixing the reactants and the e.s.r. spectrum was recorded. The radical species was identified as the nitrobenzene radical anion by comparison of the above spectrum with that of an authentic sample prepared by the electrolytic reduction of nitrobenzene in dimethyl sulfoxide.

The Reaction of Nitrobenzene with Triphenylphosphonium Methylide.—A solution of nitrobenzene (3.0 g., 0.025 mole) in dimethyl sulfoxide (25 ml.) was added dropwise to a solution of triphenylphosphonium methylide at 25° which was prepared by the procedure of Corey[22] from methylsulfinyl carbanion (0.50 mole) in dimethyl sulfoxide (50 ml.) and methyltriphenylphosphonium iodide (20.2 g., 0.50 mole) in dimethyl sulfoxide (25 ml.). The reaction mixture turned black and the temperature rose to 32°. After the reaction mixture was cooled and maintained at room temperature for 45 min., then at 60–65° for 2 hr., water was added and the mixture was extracted with ether. The ether extract was washed with water and dried over anhydrous sodium sulfate and the solvent was removed. After the mineral oil phase was separated, 6.0 g. of residue remained, 5.5 g. of which was chromatographed on 100 g. of Florisil. Elution with Skelly F-ether (80:20) gave 0.79 g. of triphenylphosphine, m.p. 80–81° (lit.[23] m.p. 79°), the mixture melting point with authentic material was undepressed. Subsequent chromatography fractions gave a total of 1.03 g. of material which was shown by g.l.p.c. to contain nitrobenzene (83 mole %). The nitrotoluene yield based on unrecovered nitrobenzene was 8%.

From the mineral oil phase (2.0 g.) there crystallized an additional 0.25 g. of triphenylphosphine, m.p. 80°, for a total yield of 1.04 g. (11%).

The initial aqueous dimethyl sulfoxide layer was acidified with 10% hydrochloric acid and extracted with ether. After the extract was washed with water and dried and the solvent was removed, the dark viscous residue was extracted with hot Skelly F from which crystallized 1.66 g. (12%) of triphenylphosphine oxide, m.p. 145–148° (lit.[24] m.p. 153.5°). Its infrared spectrum was identical with that of an authentic sample.

Control Experiments with Triphenylphosphine.—After a solution of triphenylphosphine (6.6 g., 0.025 mole) in dimethyl sulfoxide (100 ml.) was stirred at room temperature for 3 hr. and at 60–65° for 1 hr., the mixture was cooled and diluted with water, and the precipitate upon recrystallization from Skelly F gave 6.2 g. (94%) of recovered triphenylphosphine, identified as above.

In a second experiment a mixture of triphenylphosphine (6.5 g., 0.025 mole), nitrobenzene (3.0 g., 0.025 mole), and dimethyl sulfoxide was stirred at room temperature under nitrogen for 15 min. and heated at 60° for 2 hr. The reaction mixture was diluted with water and the precipitate gave, after recrystallization from Skelly F, 6.2 g. (95%) of triphenylphosphine, identified as above. From the diluted reaction mixture 2.8 g. (91%) of nitrobenzene was isolated by extraction.

The Reaction of Nitrobenzene with Trimethylammonium Methylide.—Methyllithium (50 ml., 1.69 *N*, 0.085 mole) was added dropwise over a period of 45 min. to a stirred mixture of tetramethylammonium chloride (9.37 g., 0.085 mole) and anhydrous ether (80 ml.) under nitrogen at 10–12°. After the reaction mixture was stirred at room temperature for 1.5 hr., nitrobenzene (5.75 g., 0.047 mole) in ether (25 ml.) was added slowly, keeping the reaction temperature at 12–20°. The reaction mixture was stirred at room temperature for 2 hr., diluted with water, and extracted with ether. After the ether extract was washed with water and dried and the solvent was removed, the dark residue (5.0 g.) was distilled and gave 2.58 g. of liquid, b.p. 42–50° (0.45 mm.) which, by g.l.p.c.,[21] was composed of nitrobenzene (81 mole %), *o*-nitrotoluene (12.5 mole %), and *p*-nitrotoluene (6.5 mole %). The yield of nitrotoluenes was 13% based on unrecovered nitrobenzene.

Attempted Reactions of Dimethyloxosulfonium Methylide with Aromatic Substrates Other than Nitro Compounds.—The reaction mixture of various aromatic substrates and dimethyloxosulfonium methylide was subjected to conditions of temperature and time similar to or more vigorous than the best conditions for the nitrobenzene reaction. After the reaction was diluted with water, the products were isolated and purified by standard procedures. The following summarizes the results [compound, (moles methylide:moles substrate), per cent recovered starting material]: diphenyl sulfone (2:1), 97; methyl benzoate (1:1), 85 (7% benzoic acid also); benzonitrile (1:1), 87; pyridine (2:1), 50–60; quinoline (2:1), 65.

Reactions of Dimethyloxosulfonium Methylide with Aromatic Nitro Compounds. General Procedure.—The aromatic nitro compound, neat or in dimethyl sulfoxide, was added dropwise to a stirred solution of dimethyloxosulfonium methylide (preparation reviewed in the nitrobenzene experiment) in dimethyl sulfoxide under nitrogen. After an induction period, the reaction temperature slowly rose to 35–60°, except in the case of the three chloronitrobenzenes and *p*-nitroanisole where the temperature was kept below 30°. The reaction mixtures were allowed to cool to room temperature or cooled with an ice bath, and 2 hr. from the time reactants were mixed the reaction mixture was diluted with water. Any solid which formed at this stage was isolated and the filtrate was extracted with ether. After the ether extract was washed with water and dried and the solvent was removed, the residue, when liquid, was distilled and the composition of the distillate was determined by g.l.p.c.[21] Separation and isolation of the products was by preparative g.l.p.c. and/or column chromatography and identificatione involved melting point, infrared spectra, and/or n.m.r. spectra. The data are summarized in Table III.

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