Activated manganese dioxide was purchased from Beacon Chemicals Industries, Inc. The source of the amines were: *tert*-butylamine from Rohm and Haas, hexahydro-1*H*-azepine from E. I. DuPont de Nemours and Co., and 3-azabicyclo[3.2.2]nonane from Eastman Chemical Products, Inc. All compounds obtained from commercial sources were used as received.

Procedure for the Preparation of the Phenylphosphonous Diamides.[10]—The reaction of phenylphosphonous dichloride with *tert*-butylamine is described as an example of the preparation of the phenylphosphonous diamides.

A solution of 18.0 g. (0.1 mole) of phenylphosphonous dichloride in 75 ml. of benzene was added dropwise with stirring to a solution of 30.0 g. (0.4 mole) of *tert*-butylamine in 175 ml. of benzene. The temperature reached a maximum of 50° during the addition of the phenylphosphonous dichloride. At the completion of the addition, stirring at 50° was continued for 1.5 hr. The reaction mixture was filtered, and the amine hydrochloride precipitate was washed thoroughly with benzene and ethyl ether. The combined filtrate and washings were stripped of solvents by rotary evaporation at reduced pressure. The yellow, viscous residue was fractionated, b.p. 98–100°/0.4 mm., and the product weighed 14.9 g. (64% yield).

Procedure for the Oxidation of the Phenylphosphonous Diamides.—The phenylphosphonous diamides were converted to the corresponding phenylphosphonic diamides by reaction with activated manganese dioxide. The preparation of N,N'-di-*tert*-butyl-P-phenylphosphonic diamide (II) is described as an example of this method.

To a stirred solution of 5.0 g. (0.02 mole) of N,N'-di-*tert*-butyl-P-phenylphosphonous diamide (I) in 50 ml. of dry benzene was added 10.0 g. (0.12 mole) of activated manganese dioxide. The mixture was stirred at reflux for 2 hr., cooled, and filtered. The solids were washed with small portions of dry benzene. The solvent from the combined filtrate and washings was removed by rotary evaporation at reduced pressure, and the residue was air-dried. The product weighed 3.8 g. (93% yield). It crystallized from ethyl acetate as white needles, m.p. 188–189°.[11]

Procedure for the Formation of Phenylphosphonothioic Diamides by the Direct Addition of Sulfur to Phenylphosphonous Diamides.—A mixture of 1.2 g. (3.0 mmoles) of di(3-azabicyclo-[3.2.2]non-3-yl)phenylphosphine, 0.1 g. (3.0 mg.-atom) of sulfur and 50 ml. of dry benzene was stirred at reflux for 2 hr., filtered, and the solvent removed from the filtrate by rotary evaporation at reduced pressure. The product weighed 1.3 g. (quantitative yield), and crystallized from aqueous acetone in fine needles.

Procedure for the Quaternization of Phenylphosphonous Diamides.—A mixture of 2.5 g. (0.01 mole) of N,N'-di-*tert*-butyl-P-phenylphosphonous diamide, 1.4 g. (0.01 mole) of methyl iodide, and 50 ml. of benzene was stirred at 45–50° for 1 hr. The reaction product was filtered, and the solids washed thoroughly with ethyl ether, and air-dried. The white, crystalline product weighed 3.5 g. (88% yield) and melted at 168–170°. It crystallized from aqueous ethanol as white, glistening prisms, m.p. 176–177°.

Bis(*tert*-butylamino)benzylphenylphosphonium chloride (V), *p*-phenylenedimethylene)bis[bis-(*tert*-butylamino)phenylphosphonium chloride] (VI), bis(3-azabicyclo[3.2.2]non-3-yl)benzylphenylphosphonium chloride (XII), and bis(3-azabicyclo[3.2.2]-non-3-yl)methylphenylphosphonium iodide (XI) were prepared by the procedure described except that monochlorobenzene was used as solvent for the chloromethyl compounds.

Adduct of Carbon Disulfide and (3-Azabicyclo[3.2.2]non-3-yl)-diphenylphosphine.—A mixture of 3.1 g. (0.01 mole) of (3-azabicyclo[3.2.2]non-3-yl)diphenylphosphine,[1,2] 0.75 g. (0.01 mole) of carbon disulfide, and 35 ml. of dry benzene was stirred at 35–40° for 30 min. and then allowed to stand overnight at room temperature. The white powder which separated was filtered and washed with petroleum ether (39–50°). The product melted at 168–169°. The mother liquors yielded an additional crop, making a total of 3.1 g. (81% yield).

Its infrared spectrum in Nujol mull showed absorption bands (cm.$^{-1}$) at 695, 715, 746, 825, 945, 1010, 1120, 1260, 1345, 1440, 1460, and 2900.

Anal. Calcd. for $C_{21}H_{24}NPS_2$: C, 65.33; H, 6.29; N, 3.64; P, 8.06; S, 16.68. Found: C, 65.00; H, 6.52; N, 3.47; P, 8.35; S, 16.66.

Bis(hexahydro-1*H*-azepin-1-yl)phenylphosphine Oxide (XIV).—A solution of 19.5 g. (0.1 mole) of phenylphosphonic dichloride in 75 ml. of benzene was added with stirring to a solution of 40.0 g. (0.4 mole) of hexahydro-1*H*-azepine in 175 ml. of benzene. After the addition of phenylphosphonic dichloride, the reaction product was stirred at reflux for 1 hr. The product was filtered while hot, and the solids were washed thoroughly with boiling ethyl ether. The solvents were removed from the combined filtrates and washings at reduced pressure, and the residue fractionated, b.p. 188–190°/0.25 mm. The yellow oil weighed 6.0 g. (19% yield).

Bis(3-azabicyclo[3.2.2]non-3-yl)benzylphenylphosphonium Tetrachloroaurate (III) (XIII).—To a solution of 1.0 g. (2.0 mole) of $AuCl_3 \cdot HCl \cdot 4H_2O$ in 10 ml. of water was added with stirring a solution of 1.0 g. (2.0 mmoles) of bis(3-azabicyclo[3.2.2]non-3-yl) benzylphenylphosphonium chloride. A yellow precipitate formed immediately. The product was filtered and the solids washed with water. It crystallized from acetone in yellow granules, m.p. 166–167°, and weighed 1.4 g. (88% yield).

(3-Azabicyclo[3.2.2]non-3-yl)methyldiphenylphosphonium Chloride.—A mixture of 0.50 g. (1.6 mmoles) of 3-azabicyclo-[3.2.2]non-3-yl)diphenylphosphine, 0.25 g. (1.6 mmoles) of methyl iodide, and 25 ml. of dry benzene was stirred at reflux for 1 hr. The reaction product was cooled and filtered. The solids were washed thoroughly with ethyl ether and air-dried. It crystallized from benzene and ethyl ether as white granules, m.p. 206° dec. and weighed 0.4 g. (55% yield).

Anal. Calcd. for $C_{21}H_{27}I\,NP$: C, 55.88; H, 6.03; N, 3.10; P, 6.86; I, 28.12. Found: C, 56.00; H, 6.03; N, 3.22; P, 6.67; I, 28.26.

Acknowledgment.—The author expresses his appreciation to Dr. Leonard T. Capell of the Chemical Abstracts Service for suggestions on nomenclature.

---

[10] There is no spectral evidence that compound $(tert\text{-}C_4H_9NH)_2PC_6H_5$ exists in the tautomeric form $tert\text{-}C_4H_9N = \underset{H}{P}(C_6H_5)(tert\text{-}C_4H_9NH)$ since the PH (2440–2350 cm.$^{-1}$) and N = P (1300 cm.$^{-1}$) linkages are absent. The existence of a tautomeric form was suggested as a possibility by one of the referees.

[11] V. Gutmann, D. E. Hagen, and K. Utvary, *Monatsh. Chem.*, **91**, 836 (1960), reported the same melting point for the diamide prepared by the reaction of phenylphosphonic dichloride with *tert*-butylamine.

The Reaction of Phenyl Sulfoxide with Phenyllithium

KENNETH K. ANDERSEN AND SANDRA A. YEAGER[1]

Department of Chemistry, University of New Hampshire,
Durham, New Hampshire

Received October 18, 1962

The reaction of sulfoxides with organomagnesium or organolithium compounds leads to various products depending on the nature of the sulfoxide, the organometallic compound, and the reaction conditions. Present evidence indicates sulfoxides containing the methylsulfinyl group react with organomagnesium halides to give sulfides derived from the parent sulfoxide[2,3]:

$$RMgX + CH_3SOR' \longrightarrow RCH_2SR'$$

Phenyl sulfoxide and arylmagnesium halides react to give diphenylaryl sulfonium salts[4] or phenyl sulfide[5] depending on the conditions. Some dialkyl sulfoxides have been reported to give the alkyl sulfide derived from the sulfoxide plus alcohols and olefins derived

---

[1] National Science Foundation Fellow, Summer, 1962.

[2] H. Potter, Abstracts of Papers, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, p. 3-0.

[3] R. Oda and K. Yamamoto, *J. Org. Chem.*, **26**, 4679 (1961).

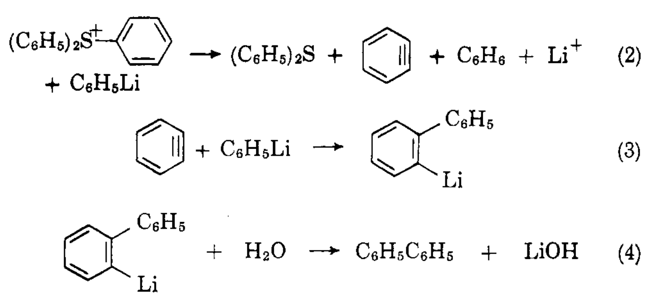
[4] B. S. Wildi, S. W. Taylor, and H. A. Potratz, *J. Am. Chem. Soc.*, **73**, 1965 (1951).

[5] H. Hepworth and H. W. Clapham, *J. Chem. Soc.*, 1188 (1921).

from the organomagnesium halide.[6] The reaction of phenyl sulfoxide with phenyllithium has been reported to give a very small amount of triphenylsulfonium bromide. This paper concerns this last reaction. The major products of the reaction are described and a mechanism for their formation is proposed.

Addition of phenyl sulfoxide to four to five molar equivalents of phenyllithium in ethyl ether gives phenyl sulfide (87% yield) and biphenyl (65% yield). These results can be explained by equations 1 through 4.

$$C_6H_5Li + C_6H_5SOC_6H_5 \longrightarrow (C_6H_5)_3S^+ OLi^- \quad (1)$$



Wildi, Taylor, and Potratz[4] formed triphenylsulfonium bromide from phenyl sulfoxide and phenylmagnesium bromide in a reaction analogous to equation 1. These workers also treated phenyl sulfoxide with phenyllithium and obtained a 0.2% yield of the sulfonium salt. This evidence makes equation 1 a reasonable reaction.

Franzen and Mertz[7] demonstrated that triphenylsulfonium bromide exchanges phenyl groups with phenyllithium very rapidly. Franzen, Joschek, and Mertz[8] also presented evidence that triphenylsulfonium bromide and tri(2-methoxyphenyl)sulfonium chloride react with phenyllithium to give the corresponding arynes, as in equation 2, but in poor yields. They state that the principal reaction is the formation of an unstable intermediate involving tetravalent sulfur and the exchange reaction. We do not believe the experimental facts warrant this conclusion. Additional comments on this statement are given below.

Although the mechanism involving benzyne as an intermediate is plausible, a nucleophilic substitution reaction on the triphenylsulfonium ion with the phenyllithium acting as the nucleophile and the phenyl sulfide as the leaving group would also explain the experimental results. When the reaction mixture was carbonated before hydrolysis, however, some 2-biphenylcarboxylic acid (13%) was isolated. No other acidic product except benzoic acid from the excess phenyllithium was obtained. The 2-biphenylcarboxylic acid could not arise from metalation of biphenyl by phenyllithium, since biphenyl metalates slowly under the reaction conditions and gives a different mixture of acidic products.

When the reaction was run in the presence of a 1.2 molar equivalent of lithium thiophenoxide, a nucleophile which reacts more rapidly than phenyllithium with benzyne,[9] the yield of phenyl sulfide increased to 120% based on the amount of phenyl sulfoxide used while the yield of biphenyl was 56%. This increase is expected if the lithium thiophenoxide is competing with the phenyllithium for the benzyne. When the phenyllithium was added to phenyl sulfoxide and benzenethiol, the reverse of the normal procedure, a 120% yield of phenyl sulfide and a 48% yield of biphenyl were obtained. If all of the biphenyl came from a tetracovalent sulfur intermediate, an unlikely assumption since phenyllithium adds to benzyne about as rapidly as thiophenolate ion, the maximum amount of products which could be formed from this intermediate is about 50%. This means that the benzyne mechanism would account for approximately 30% of the products. This argument assumes the most favorable case for the tetracovalent intermediate. Since the phenyllithium should compete favorably with the rather insoluble lithium thiophenoxide for the benzyne, it may be that a tetravalent sulfur intermediate does not contribute significantly to the reaction if at all.

The increased yield of phenyl sulfide does not arise from a nucleophilic substitution reaction on the triphenylsulfonium ion, since no reaction takes place when lithium thiophenoxide prepared from phenyllithium and thiophenol in ether is stirred with triphenylsulfonium chloride.

The reaction of triphenylsulfonium bromide with phenyllithium proceeds as indicated by equations 2 to 4 to give phenyl sulfide (38%) and biphenyl (34%). Our work agrees with Franzen's although our experimental techniques were somewhat different. When the reaction was repeated in the presence of lithium thiophenoxide, the yield of phenyl sulfide was 25% while the yield of biphenyl was 7%. An argument for the maximum amount of a tetravalent sulfur intermediate can be given as above.

Recently Sheppard[10] reported that phenylsulfur trifluoride reacts with phenyllithium to give phenyl sulfide and biphenyl. Perhaps two of the fluorine atoms are replaced from the sulfur to give a triphenylsulfonium ion which leads to the observed products.

It is the opinion of the authors that more work is needed in this area before the differences in interpretation of the reactions discussed above can be reconciled.

Experimental

Reaction of Phenyl Sulfoxide with Phenyllithium.—Phenyl sulfoxide (5.0 g., 0.025 mole) in anhydrous ethyl ether (150 ml.) was added dropwise over a 15-min. period with stirring to an ethereal solution of phenyllithium made from bromobenzene (20 g., 0.13 mole) and lithium (1.8 g., 0.26 g.-atom). The mixture was hydrolyzed with dilute hydrochloric acid after stirring for several hours. Phenyl sulfide (3.5 g., 0.019 mole, 75% yield) and biphenyl (1.6 g., 0.010 mole, 40% yield) were isolated from the organic layer by distillation. The purity and yields of the products were checked using quantitative vapor phase chromatography. The phenyl sulfide was identified by comparison of its infrared spectrum with that of an authentic sample, oxidation to the sulfone, mixed m.p. of the sulfone with an authentic sample, and infrared spectra comparison with that from an authentic sample of the sulfone. The biphenyl was identified by infrared spectra comparison with that of an authentic sample and by a mixed m.p. The best yields obtained in any single reaction were 87% of phenyl sulfide and 65% of biphenyl.

Carbonation of Phenyl Sulfoxide-Phenyllithium Reaction Mixture.—Phenyl sulfoxide (5.0 g., 0.025 mole) was added to phenyllithium prepared from bromobenzene (20 g., 0.13 mole)

---

[6] V. Grignard and L. Zorn, *Compt. rend.*, **150**, 1177 (1910).

[7] V. Franzen and C. Mertz, *Ann.*, **643**, 24 (1961).

[8] V. Franzen, H.-I. Joschek, and C. Mertz, *ibid.*, **654**, 82 (1962).

[9] R. Huisgen in "Organometallic Chemistry," H. Zeiss, ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp. 36-87.

[10] W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3058 (1962).

and lithium (1.8 g., 0.26 g.-atom) as described above. The reaction mixture was poured onto Dry Ice. The mixture was hydrolyzed with dilute hydrochloric acid. The ether layer was extracted with 10% sodium carbonate solution. Acidification of the carbonate gave some acidic material. Recrystallization from chloroform and chromatography of this acidic material on alumina gave, besides benzoic acid, some 2-biphenylcarboxylic acid (0.63 g., 0.0032 mole, 13% yield), m.p. 111–113°, which was identified by an infrared spectra comparison and by a mixed melting point with an authentic sample.

Reaction of Phenyl Sulfoxide with a Phenyllithium–Lithium Thiophenoxide Mixture.—Thiophenol (3.2 g., 0.029 mole) in ethyl ether (5 ml.) was added dropwise over a 10-min. period with stirring to an ether solution of phenyllithium made from bromobenzene (20 g., 0.13 mole) and lithium (1.8 g., 0.26 g.-atom). After 10 additional minutes, phenyl sulfoxide (5.0 g., 0.025 mole) in ether was added dropwise over a 20-min. period. The reaction mixture was poured into water, acidified with dilute hydrochloric acid, and the organic layer removed and extracted with dilute sodium hydroxide to remove any thiophenol. Distillation of the organic layer gave a biphenyl–phenyl sulfide mixture (7.86 g.). Vapor phase chromatography indicated 73% of the distillate to be phenyl sulfide (5.7 g., 0.031 mole, 120% yield) and 27% to be biphenyl (2.1 g., 0.0014 mole, 56% yield).

Addition of an ethereal phenyllithium solution prepared from bromobenzene (39 g., 0.250 mole) and lithium (3.5 g., 0.50 g.-atom) to phenyl sulfoxide (5.0 g., 0.025 mole) and thiophenol (13.8 g., 0.125 mole) in ether over a 45-min. period with stirring gave upon working up the reaction phenyl sulfide (5.6 g., 0.030 mole, 120% yield) and biphenyl (1.8 g., 0.12 mole, 48% yield).

Reaction of Triphenylsulfonium Bromide with Phenyllithium.—Triphenylsulfonium bromide (2.8 g., 0.0082 mole) was added in one portion to an ethereal solution of phenyllithium prepared from bromobenzene (5.2 g., 0.033 mole) and lithium (0.46 g., 0.066 g. atom). After stirring for 4 hr. the reaction mixture was hydrolyzed. The ether layer was worked up as in the preceding reaction to give a biphenyl–phenyl sulfide mixture (1.01 g.). The yield of each component was determined by vapor phase chromatography: biphenyl (0.43 g., 0.0028 mole, 34% yield); phenyl sulfide (0.58 g., 0.0031 mole, 38% yield). Extraction of the aqueous layer with chloroform did not give any unchanged sulfonium salt.

Reaction of Triphenylsulfonium Bromide with a Phenyllithium–Lithium Thiophenoxide Mixture.—Thiophenol (1.0 g., 0.0091 mole) in ethyl ether (5 ml.) was added dropwise to an ethereal phenyllithium solution prepared from bromobenzene (2.8 g., 0.018 mole) and lithium (0.28 g., 0.040 g.-atom). Triphenylsulfonium bromide (1.5 g., 0.0044 mole) was added in one portion to the reaction mixture. After stirring for 15 min., the reaction mixture was hydrolyzed and the ether layer worked up as in the preceding reaction to give phenyl sulfide (0.20 g., 0.0011 mole, 25% yield) and biphenyl (0.05 g., 0.0003 mole, 7% yield). Extraction of the aqueous layer gave 0.09 g. of a white solid which was probably unreacted sulfonium salt.

Reaction of Triphenylsulfonium Chloride with Lithium Thiophenoxide.—Thiophenol (5.5 g., 0.050 mole) in ether was added dropwise to an ethereal phenyllithium solution prepared from bromobenzene (7.9 g., 0.050 mole) and lithium (0.76 g., 0.11 g.-atom). Triphenylsulfonium chloride (1.7 g., 0.0057 mole) was added all at once and the mixture stirred for 2.5 hr. The mixture was hydrolyzed with 10% hydrobromic acid (100 ml.). The aqueous layer was extracted with chloroform to give triphenylsulfonium bromide (1.54 g., 91% recovery).

Monomers and Polymers, A Synthesis of Vinyl Cyclopropane and Dicyclopropyl[1]

C. G. Overberger and George Walter Halek[2]

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn 1, New York

Received October 11, 1962

During a recent search for a convenient route to vinylcyclopropane suitable for stereospecific polymerization, the Simmons–Smith[3] route to cyclopropane *via* addition of :CH_2 to a double bond was applied to butadiene. Since the behavior of this system with a conjugated diolefin has not been reported, we are describing the results here. Mass spectral fragmentation patterns of vinyl cyclopropane and dicyclopropyl are also presented.

Butadiene reacted with methylene iodide and a zinc–copper couple in *p*-dioxane at 60° in a closed reaction tube. Analysis of the reaction products by gas chromatography showed the presence of three compounds in addition to the starting butadiene and *p*-dioxane solvent. Concentration of these products by distillation followed by removal of *p*-dioxane on a polar gas chromatography column yielded a mixture of the three unknown compounds and some butadiene.

Removal of the butadiene and complete separation of the three compounds was accomplished on a nonpolar gas chromatography column. Mass spectrometry showed one of the components to be methyl iodide, arising from the hydrolysis of the iodomethylzinc component formed from the methylene iodide and zinc employed in the reaction. The other two pure components had a molecular weight of 68 and 82 and their fragmentation patterns (shown in Table I) indicated formulas of C_5H_8 and C_6H_{10}. An infrared spectrum on a mixture of the two compounds collected in 50% carbon tetrachloride at this point matched the published infrared spectra of vinylcyclopropane[4] and dicyclopropyl[5] in every detail, with no extraneous peaks

Table I

Mass Spectrometer Fragmentation of Vinyl Cyclopropane (A) and Dicyclopropyl (B)[a]

	Relative intensity			Relative intensity	
m/e	A	B	m/e	A	B
13	1.1	0.7	54		100.0
14	4.4	3.0	55	3.3	26.0
15	5.5	8.2	56	2.2	3.7
16	1.1	0.7	57	3.3	1.5
25	1.1		58		0.7
26	11.1	14.8	60	1.1	
27	40.9	58.8	61	2.2	0.7
29	17.7	13.3	62	3.3	1.5
30		1.5	63	5.0	4.5
31	2.2	0.7	64	1.1	1.5
36		0.7	65	10.0	11.9
37	7.6	5.9	66	7.6	5.6
38	18.3	14.8	67	100.0	96.3
39	75.5	92.0	68	91.3	
40	42.0	22.6	70		1.5
41	46.5	89.3	74		1.7
42	24.3	15.9	75		0.7
43	6.6	4.5	77		8.0
44	2.2	0.7	78		2.6
49	2.2	1.5	79		12.2
50	7.6	13.6	80		1.9
51	10.0	18.9	81		32.2
52	4.4	11.5	82		34.8
53	65.5	37.0			

[a] Electron energy 70, volts; trap current, 0.1 μ amp.; helium carrier gas.

---

(1) This is the 24th in a series of papers concerned with new monomers and polymers; for the previous paper in this series see C. G. Overberger and J. J. Ferraro, *J. Org. Chem.*, **27**, 3539 (1962).

(2) Present address: Celanese Corporation of America, Summit Research Laboratories, Summit, N. J.

(3) H. E. Simmons and R. D. Smith, (a) *J. Am. Chem. Soc.*, **81**, 4256 (1959); (b) **80**, 5323 (1958).