in the presence of iodine was slow. The mixture was refluxed for 8 hr., then cooled and poured onto a mixture of ether and powdered Dry Ice. Customary separation gave an acidic and a neutral fraction. The former gave a trace of a residue, while the latter, on distillation, gave a liquid b.p. 64° (1.0 mm.) to 140° (0.15 mm.), giving a precipitate with aqueous silver nitrate, apparently unreacted starting material.

Reaction of IIIe *with methylmagnesium iodide.* To the Grignard solution, prepared from 0.50 mole of each magnesium and methyl iodide in a total of 300 ml. of ether, there was added dropwise 175 ml. a cold ether solution of the above chloro compound (from a 0.50-mole run). The reaction was very exothermic and addition took 1.5 hr. After all the chloride was added, the mixture was refluxed 45 min. during which time it became intensely green-colored and a green oil precipitated. After allowing to stand at room temperature for 0.5 hr., the mixture was decomposed with a saturated ammonium chloride solution and extracted with ether. After removal of the solvent the residue was distilled to obtain 25 g. of a dark orange liquid, b.p. 44° (11 mm.) to 45° (10 mm.). This was washed with a sodium sulfite solution and redistilled to obtain 23 g. (33%) of a nearly colorless liquid, b.p. 68–69° (34 mm.), n_D^{23} 1.4357, which decolorized bromine in carbon tetrachloride and exhibited an infrared spectrum which contained no hydroxyl or carbonyl absorption.

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.08, 77.28; H, 11.35, 11.36.

Reaction of IIIe *with phenylmagnesium bromide.* To a Grignard solution prepared from 1.0 mole of reagents in 400 ml. of ether there was added with stirring over a period of 1.5 hr. a solution of 0.54 mole of the chloro compound in 100 ml. of benzene. The reaction was exothermic and a solid precipitated at the end of addition. The resulting mixture was refluxed for 16 hr., then was cooled and decomposed with an excess of a saturated ammonium chloride solution and extracted with petroleum pentane (b.p. 30–60°). Distillation gave 106 g. (96%) of a yellowish liquid, b.p. 35° (0.2 mm.) to 105° (0.03 mm.). This was fractionated twice to obtain 82.8 g. (76%) of a colorless liquid, b.p. 87–99° (0.1 mm.). A middle fraction, b.p. 95–96° (0.1 mm.), n_D^{24} 1.5219, was analyzed.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 84.23; 84.55; H, 8.44, 8.62.

Acknowledgment. The author is indebted to Mr. Raymond F. Cornuet for the able technical assistance.

SPRINGDALE, PA.

[CONTRIBUTION FROM THE DEVELOPMENT DEPARTMENT, UNION CARBIDE CHEMICALS CO., DIVISION OF UNION CARBIDE CORP.]

The Chemistry of α,β-Unsaturated Ethers. IV. Addition of Methanol to 1-Methoxy-1,3-butadiene[1]

D. G. KUBLER[2]

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Methanol adds 1,4 to 1-methoxy-1,3-butadiene in the presence of acid catalysts. The product, 1,1-dimethoxy-2-butene, also adds 1,4 to 1-methoxy-1,3-butadiene with sulfuric acid as a catalyst at 20° to 60° to yield 1,1,5-trimethoxy-2,6-octadiene. Below 20° with sulfuric acid as the catalyst or at 40° with hydrochloric acid as the catalyst no 1,1,5-trimethoxy-2,6-octadiene is formed. 1,1,5-Trimethoxy-2,6-octadiene has been converted to 1,1,5-trimethoxyoctane, 5-methoxyoctanal, 5-methoxyoctanol, 2,4,6-octatrienal, and 1-octanol.

There is a paucity of information concerning the addition of various reagents to 1-alkoxy-1,3-butadienes. Flaig[3] has reported that the bromination of 1-ethoxy-1,3-butadiene is a 1,4-addition as is the Diels-Alder reaction.[3,4] The addition of ethanol to 1-ethoxy-1,3-butadiene has been reported[5] to yield 1,1-diethoxy-2-butene, again a 1,4-addition.

The addition of an alcohol to an α,β-unsaturated ether in the presence of an acid catalyst proceeds rapidly and in nearly quantitative yield.[6] Because of this and because the addition of an alcohol to a 1-alkoxy-1,3-butadiene could yield four different products, we have investigated the addition of methanol to 1-methoxy-1,3-butadiene. The possible products are 1,1-dimethoxy-2-butene (by 1,4-addition), 1,1-dimethoxy-3-butene (by 1,2-addition), 1,3-dimethoxy-1-butene (by 3,4-addition), and 1,1,3-trimethoxybutane (by complete addition).

Two of these products were obtained with hydrochloric acid as a catalyst: 1,1-dimethoxy-2-butene (32% yield) and 1,1,3-trimethoxybutane[7] (7% yield). In contrast with these results, when sulfuric acid was used as the catalyst, no 1,1,3-trimethoxybutane was formed but 1,1-dimethoxy-2-butene was isolated in 30% yield. This product, however, also added 1,4 to the 1-methoxy-1,3-butadiene forming 1,1,5-trimethoxy-2,6-octadiene in 23% yield. Inasmuch as no other products were

(1) Paper III, R. I. Hoaglin, D. G. Kubler, and A. E. Montagna, *J. Am. Chem. Soc.*, **80**, 5460 (1958).

(2) Furman University, Greenville, S. C.

(3) W. Flaig, *Ann.*, **568**, 1 (1950).

(4) C. G. Farmilo and R. V. V. Nicholls, *Can. J. Research* **28B**, 689 (1950).

(5) Consortium fur Electrochemische Ind. Gmbh., British Patent **757,907** (September 26, 1956).

(6) H. S. Hill, *J. Am. Chem. Soc.*, **50**, 2725 (1928).

(7) This product probably can form by the addition of methanol to 1,1-dimethoxy-2-butene. R. H. Hall and E. S. Stern [*J. Chem. Soc.*, 3388 (1954)] have shown that ethanol adds to 3,3-diethoxy-1-propene in 93% yield with hydrogen chloride catalyst.

TABLE I

METHANOLATION OF 1-METHOXY-1,3-BUTADIENE[a]

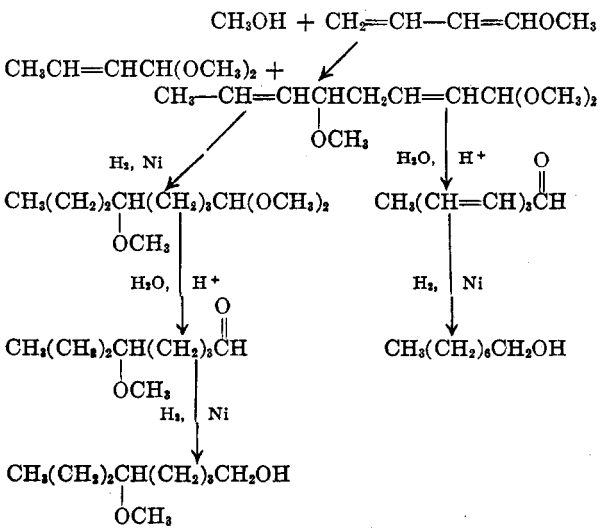
CH_3OH, Moles	MBD,[b] Moles	Reaction Temp.	Residence Time, Min.	DMB,[c] % Yield	TMO,[d] % Yield
		A. MOLE RATIO			
1. 4	2	40	10	29.8	30.0
2. 20	4	40	10	30.0	23.5
3. 20	2	40	20	38.3	16.5
		B. TEMPERATURE			
4. 20	2	0	360	32.7	0.0
5. 20	4	20	10	9.9	0.0
6. 20	4	40	10	30.0	23.5
7. 20	4	60	10	32.3	26.5
		C. RESIDENCE TIME			
8. 20	4	40	10	30.0	23.5
9. 20	4	40	20	20.0	27.2
10. 20	4	40	30	13.8	25.5
		D. TYPE OF CATALYST			
11. 20	4(H_2SO_4)	40	10	30.0	23.5
12. 15	3(HCl)	40	60	32.0	0.0[e]
13. 6	2(H_3PO_4)	60[f]	960[g]	20.7	0.0

[a] The reactions were all performed essentially as described in the Experimental section. The amount of sulfuric acid catalyst was 0.1% by weight for all of the runs, except experiments 4 and 13 (0.2% by weight). [b] 1-Methoxy-1,3-butadiene. [c] 1,1-Dimethoxy-2-butene. [d] 1,1,5-Trimethoxy-2,6-octadiene. [e] A 7% yield of 1,1,3-trimethoxybutane was also isolated. [f] A similar run using 0.2% by weight, phosphoric acid for 2.5 hr. at 40° gave no reaction. [g] The total time at 60°. In addition, the mixture was allowed to stand for 30 hr. at room temperature.

isolated, and substantially all of the unchanged, 1-methoxy-1,3-butadiene was recovered we conclude that the addition of methanol and of 1,1-dimethoxy-2-butene is almost exclusively 1,4.

The 1,1-dimethoxy-2-butene was identified on the basis of its physical properties and its infrared spectrum as compared to an authentic sample, as well as by hydrogenating the material to 1,1-dimethoxybutane. The 1,1,5-trimethoxy-2,6-octadiene and its derivatives were identified on the basis of elemental analyses, functional group analyses and by means of their infrared and mass spectra.[8]

The conversions we have made of 1,1,5-trimethoxy-2,6-octadiene are:



To demonstrate that 1,1,5-trimethoxy-2,6-octadiene can form from the intermediate addition product, 1,1-dimethoxy-2-butene was reacted with 1-methoxy-1,3-butadiene in the presence of sulfuric acid. The yield of 1,1,5-trimethoxy-2,6-octadiene was 56%, and the product was identical (infrared spectra) to the product obtained from the methanolation reaction. A brief study of the reaction variables was made and the results are summarized in Table I.

It is seen that there is some control of the ratio of the amounts of 1,1-dimethoxy-2-butene and 1,1,5-trimethoxy-2,6-octadiene which are formed. The yields are each about 20% to 30% for the temperature range of 40° to 60° for most of the variations. If the reaction is conducted at 0°, the yield of 1,1-dimethoxy-2-butene is maintained to the exclusion of the formation of 1,1,5-trimethoxy-2,6-octadiene, but a considerably longer reaction time is necessary. Similarly, by using hydrochloric acid as a catalyst the yield of 1,1-dimethoxy-2-butene can be maintained with no 1,1,5-trimethoxy-2,6-octadiene being formed, while a small yield of 1,1,3-trimethoxybutane can be isolated. Phosphoric acid is a poor catalyst for either stage of the reaction.

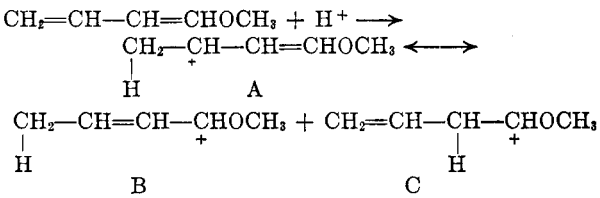
Under the best conditions used for the reaction of methanol and 1-methoxy-1,3-butadiene, the reaction of ethanol and 1-ethoxy-1,3-butadiene was very sluggish and provided low yields of 1,1-diethoxy-

(8) The spectral study by V. A. Yarborough, B. L. Tuffly, and W. J. Lambdin of this laboratory is to be reported elsewhere.

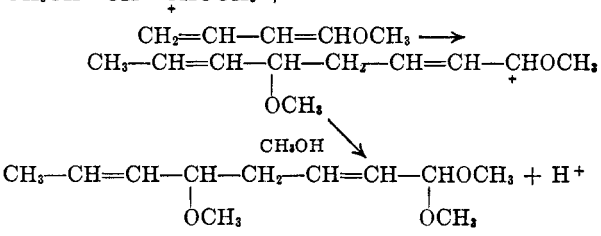
2-butene (15.7%). The higher boiling product was assumed to be 1,1,5-triethoxy-2,6-octadiene(17.6%; b.p. 78–83°/0.5 mm., n^{20}D 1.4440).

This acetal addition is rather interesting in that it is catalyzed by sulfuric acid. The normal acetyl-vinyl ether addition reaction is best catalyzed by boron trifluoride etherate and will not proceed with sulfuric acid as the catalyst.[9] The enhanced reactivity in this case is probably due to labilization of the acetal by the allylic double bond. The resultant carbonium ion would have considerable resonance stabilization.

We suggest also that this resonance stabilization may be responsible for the apparent exclusive 1,4-addition. Thus, of the two principal carbonium ions that would logically form from an attack of the acid on 1-methoxy-1,3-butadiene, the ion represented by A-B should have the greatest resonance stabilization (with form B being the more important to the ion A–B, due to participation of the allylic double bond and the unshared electrons of oxygen). We expect then, that carbonium ion A–B would form at a rate significantly greater than ion C.



This carbonium ion may attack a molecule of methanol to form the 1,1-dimethoxy-2-butene. It may also attack a molecule of 1-methoxy-1,3-butadiene providing a new carbonium ion followed by a reaction with methanol to form the 1,1,5-trimethoxy-2,6-octadiene.



EXPERIMENTAL[10]

Methanolation of 1-methoxy-1,3-butadiene.[11] To 640 g. (20.0 moles) of methanol and 0.98 g. of sulfuric acid (0.1% based on the total charge weight) at 40° there was added 336 g. (4.0 moles) of 1-methoxy-1,3-butadiene over a period of 9 min. The solution was maintained at 40° by slight cooling; 1 min. after all the diene had been added, the acid was neutralized with 2.4 g. of 50% sodium hydroxide.

The reaction mixture was distilled to give 690 g. of forerun consisting of methanol and 1-methoxy-1,3-butadiene. The 1,1-dimethoxy-2-butene distilled at 60–61° (100 mm.) and amounted to 140 g. (30%). The infrared spectrum of this material was identical to that of an authentic sample of 1,1-dimethoxy-2-butene prepared from crotonaldehyde. The final fraction was 1,1,5-trimethoxy-2,6-octadiene (94 g., 23.5%) and distilled at 75–82° (1–1.5 mm.).

For the purpose of identification, a large sample from several runs was fractionally distilled to yield a series of fractions having a constant refractive index; b.p. 83° (2 mm.); n^{20}D 1.4480; sp. gr.$^{20}_{20}$ 0.936.

Anal. Calcd. or $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 66.00; H, 10.50.

Infrared examination indicated no terminal unsaturation or carbonyl group, but there were strong ether bands and an intense band at 10.35 μ, indicative of RCH=CHR.

The most significant peaks of the mass spectrum were of $\frac{m}{e}$ ratios of 55, 75, 85, and 125. The $\frac{m}{e}$ ratio of 75 is characteristic of all dimethyl acetals $(CH(OCH_3)_2)^+$, and the $\frac{m}{e}$ ratio of 125 could be the fragment remaining from cleavage of the dimethyl acetal grouping. No specific peak could be rationalized for the molecular weight but the combination of the $\frac{m}{e}$ ratios of 125 and 75 would suggest a molecular weight of 200. The largest $\frac{m}{e}$ ratio of the spectrum was 85 which would be characteristic of $[CH_3CH{=}CHCHOCH_3]^+$.

1,1,5-Trimethoxyoctane. 1,1,5-Trimethoxy-2,6-octadiene (125 g.) was hydrogenated over 5 g. of Raney nickel in a stirred autoclave. The product was distilled to afford 98 g. (77%) of 1,1,5-trimethoxyoctane which boiled at 79–80° (1.5 mm.); n^{20}D 1.4248.

Anal. Calcd. for $C_{11}H_{24}O_3$: C, 64.66; H, 11.84. Found: C, 64.71; H, 11.84.

5-Methoxyoctanal. To the kettle of a distillation column there were added 204 g. (1 mole) of 1,1,5-trimethoxyoctane, 230 ml. of water, and 4.6 ml. of concd. phosphoric acid. The mixture was distilled slowly over a period of 3 hr. to remove 57 g. of methanol. The distillation residue was cooled and the water layer removed. The water layer was extracted once with diethyl ether and the extract combined with the organic layer. Distillation afforded 108 g. (68%) of 5-methoxyoctanal which boiled at 70–73° (4 mm.); n^{20}_{D} 1.4315.

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.31; H, 11.46; equiv. wt., 158.2. Found: C, 67.80; H, 11.30; equiv. wt., 159.5 (oximation).

5-Methoxy-1-octanol. A charge of 105 g. (0.66 mole) of 5-methoxyoctanal was hydrogenated over Raney nickel. Distillation of the product provided 76 g. (71%) of 5-methoxy-1-octanol; b.p. 82–84° (1.2 mm.); n^{20}D 1.4389.

Anal. Calcd. for $C_9H_{20}O_2$: C, 67.45; H, 12.58; equiv. wt., 160.2. Found: C, 66.96; H, 12.26; equiv. wt., 162.3 (phthalation).

2,4,6-Octatrienal and 1-octanol. A mixture of 198 g. (0.98 mole) of 1,1,5-trimethoxy-2,6-octadiene, 150 ml. of water, 100 ml. of methanol, and 2.2 ml. of concd. sulfuric acid was heated at the reflux temperature on a fractionating column for 3.5 hr. A total of 190 ml. of methanol then was removed slowly by distillation until the temperature could no longer be maintained below 70°. The distillation residue was cooled and the water layer removed. The organic layer was washed with aqueous sodium bicarbonate and distilled. The product (66 g.), which was impure 2,4,6-octatrienal, was distilled at 80–83° (2.5 mm.) and was a deep yellow semisolid.[12]

(9) R. I. Hoaglin and D. H. Hirsh, *J. Am. Chem. Soc.*, **71**, 3468 (1949) and private communication.

(10) The author gratefully acknowledges assistance from Mr. W. H. Rankin for much of the laboratory work, and from Mr. J. Bodenschatz for the elemental analyses.

(11) 1-Alkoxy-1,3-alkadienes are conveniently prepared by a method previously described; A. E. Montagna and D. H. Hirsh, U. S. Patent 2,905,722 (September 22, 1959). This method involves a liquid-phase dealcoholation with phosphoric acid as a catalyst.

(12) M. Badoche, *Compt. rend.*, **214**, 845 (1942) lists b.p. 75–77° (3 mm.).

To facilitate identification, the product was hydrogenated in methanol solvent over Raney nickel. Approximately one third of the mixture was lost by accidental spillage. After the methanol was removed, there was no intermediate fraction to the 1-octanol fraction (ruling out a possibility for 2-ethyloctanol which would have formed by the initial 1,2-addition of dimethoxy-2-butene to methoxybutadiene). There was 25 g. of 1-octanol which distilled at 87.5–89° (10 mm.); n^{20}D 1.4308; α-naphthylurethane, m.p. 64–65°.[13,14] After the octanol was removed, there was a trace of a mid-fraction followed by 10 g. of the previously identified 5-methoxy-1-octanol; b.p. 103–106° (10 mm.); n^{20}D 1.4380.

Anal. Calcd. for $C_9H_{20}O_2$: Equiv. wt. 160.2. Found: Equiv. wt. 159.8 (phthalation).

Reaction of 1,1-dimethoxy-2-butene and 1-methoxy-1,3-butadiene. To 10 ml. of diethyl ether and 0.24 ml. of concd. sulfuric acid there was added, with stirring and cooling (at 40°), a mixture of 348 g. (3 moles) of 1,1-dimethoxy-2-butene and 84 g. (1 mole) of 1-methoxy-1,3-butadiene over a period of 6 min. After an additional 4 min., the acid was neutralized with sodium hydroxide and the mixture distilled to recover 112 g. (56%) of 1,1,5-trimethoxy-2,6-octadiene which distilled at 72–83° (1–1.5 mm.). The infrared spectrum of this material was identical to that recorded for the 1,1,5-trimethoxy-2,6-octadiene isolated from the reaction of methanol and 1-methoxy-1,3-butadiene.

SOUTH CHARLESTON, W. VA.

(13) Heilbron, *Dictionary of Organic Compounds*, Oxford University Press, New York, 1953, lists for 1-octanol; b.p. 90.2° (11.8 mm.) $n^{20.5}$D 1.43035.

(14) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., John Wiley and Sons, Inc., New York, 1956, p. 281, lists for 1-octanol α-naphthylurethane, m.p. 66°.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Phosphine as a Reducing Agent

SHELDON A. BUCKLER, LOIS DOLL, FRANK K. LIND, AND MARTIN EPSTEIN

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Phosphine readily reduces aromatic nitro and sulfonyl chloride groups in basic media. The reduction of the nitro compounds has been carried out under a standard set of conditions and the corresponding azoxy derivatives obtained in 80–95% yields. The products produced from sulfonyl chlorides vary markedly with the conditions employed. These products include mercaptans, disulfides and trithiophosphate esters. Some related reactions of secondary phosphines and arylsulfonyl chlorides are also reported.

One of the significant chemical properties of phosphine is the ease with which it reacts with inorganic oxidizing agents such as halogens, metal ions and oxygen.[1,2] However, little attention has been given to the reduction of organic compounds by phosphine. The only directly relevant literature which has been found describes the reduction by phosphine of *N*-chloro-*p*-toluenesulfonamide to *p*-toluenesulfonamide,[3] and α-naphthol to naphthalene.[4] In addition, Weyl has speculated that nascent phosphine is the active reducing agent in the conversion of nitrobenzene to aniline by red phosphorus and water.[5]

In considering areas in organic chemistry where phosphine might act as a reducing agent, our attention was drawn to oxygenated functionalities of nitrogen and sulfur by certain reports of the reducing action of other trivalent phosphorus species.[6] Exploratory experiments showed that under proper conditions some functional groups of this type were indeed reduced readily. This paper describes our findings in reducing aromatic nitro compounds and arylsulfonyl chlorides with phosphine, and some related reactions of secondary phosphines.

RESULTS AND DISCUSSION

Reduction of aromatic nitro compounds. Phosphine and nitrobenzene did not react at room temperature in a neutral solution or in solutions containing small amounts of ferric or cupric ions. However, in the presence of potassium hydroxide a reaction occurred readily and azoxybenzene was formed in high yield. Examination of other nitro compounds showed that the reaction was general; good yields of azoxy compounds were obtained in all cases. Further reduction products were not detected. The results are presented in Table I.

The general method of carrying out this reaction consisted of passing phosphine into a nearly saturated solution of the nitro compound in aqueous ethanol containing four molar equivalents of potassium hydroxide. The azoxy derivatives usually

(1) J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, Green and Co., New York, 1928, Vol. VIII, p. 810.

(2) N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Oxford University Press, London, 1950, p. 729.

(3) J. R. Bendall, F. G. Mann, and D. Purdie, *J. Chem. Soc.*, 157 (1942).

(4) H. Wichelhaus, *Ber.*, **38**, 1725 (1905).

(5) T. Weyl, *Ber.*, **39**, 4340 (1906); **40**, 970, 3608 (1907).

(6) A. H. Kohlase, *J. Am. Chem. Soc.*, **54**, 2441 (1932). W. H. Hunter and B. E. Sorenson, *J. Am. Chem. Soc.*, **54**, 3368 (1932). E. E. Gilbert and C. J. McGough, U.S. Patent **2,690,450** (1954). F. W. Hoffmann, T. R. Moore, and B. Kagan, *J. Am. Chem. Soc.*, **78**, 6413 (1956). A. C. Poshkus and J. E. Herweh, *J. Am. Chem. Soc.*, **79**, 4245 (1957). F. Ramirez and A. Aguiar, Abstracts of Papers presented at the 134th Meeting of the American Chemical Society, Chicago, Ill., September 1958, p. 42. N. E. Howard, Jr., and W. F. Olszewski, *J. Am. Chem. Soc.*, **81**, 1483 (1959).