

sure and assuring that the mercury resonance radiation will penetrate deeper into the reaction cell and therefore minimize any possible wall effects. Reaction products were analyzed by mass spectrometry, gas chromatography, and standard manometric methods. The reactions were run under static conditions at room temperature.

The major products found were hydrogen, acetylene, and *n*-butane. Ethane, propane, propylene, and *n*-butene-1 were determined in smaller amounts. The yields of the major products in 10-min. runs increased with the ethylene pressure up to about 60 to 70 torr. With further increase in total pressure the yields decreased. Assuming that the maximum corresponds to the onset of the complete quenching, we can estimate that the quenching cross section of ethylene with the Hg 6(¹P₁) atoms is about 20 to 25 times the value with the Hg 6(³P₁) atoms (about 37 Å.²), *i.e.*, about 740 to 925 Å.².

A mixture of equal amounts of C₂H₄ and C₂D₄ at a total pressure of 70 torr produced hydrogen in the following per cent ratio: D₂:HD:H₂ equal to 31.0:2.7:66.3. The approximately 1:2 ratio of D₂ and H₂ is in keeping with similar isotope effects found with the Hg 6(³P₁) atom reactions.⁵ From the product and the hydrogen isotope analyses it can be concluded that intramolecular hydrogen molecule elimination takes place. Hydrogen atom elimination, if it occurs at all under these conditions, is a very minor process.

From the decrease of the product yield with increasing pressure one can conclude that in this case too we are dealing with an electronically excited ethylene molecule. The excited molecule then decomposes into hydrogen and acetylene molecules or is quenched by the other ground-state ethylene molecules, the latter process becoming more predominant as the pressure increases. In the case of the Hg 6(³P₁) atom reactions it has been found that the isotopic composition of hydrogen from *cis*- and *trans*-dideuterioethylenes was identical.⁶ In the case of the Hg 6(¹P₁) atom reactions we have found marked differences between *cis* and *trans* isomers as well as when compared to the results of the triplet atom reactions in Table I.

Table I. Isotopic Composition of Hydrogen from *cis*- and *trans*-Dideuterioethylene Reactions

	Hg 6(¹ P ₁)		Hg 6(³ P ₁) <i>cis</i> and <i>trans</i>
	<i>cis</i>	<i>trans</i>	
H ₂	33.1 ± 0.6	44.2 ± 2.0	23.1
HD	59.9 ± 0.5	48.9 ± 1.6	65.5
D ₂	7.0 ± 0.2	6.8 ± 0.5	11.4

We can conclude from the data that the excited state of ethylene from which the decomposition takes place must be different from the state involved in the Hg 6(³P₁) atom reactions. From recent spectroscopic evidence obtained by electron impact excitation it has been determined that ethylene has an excited triplet state (³B_{1u}) at about 4.6 e.v. above the ground state and an excited singlet state at about 6.5 e.v. above the ground state.⁷ The latter state has been ascribed to a transition analogous to the π* ← n transition in formaldehyde.⁸

(5) R. J. Cvetanović and A. B. Callear, *J. Chem. Phys.*, **23**, 1182 (1955).

(6) P. Ausloos and R. Gorden, *ibid.*, **36**, 5 (1962).

(7) A. Kupperman and L. M. Raff, *ibid.*, **37**, 2497 (1962).

(8) R. S. Berry, *ibid.*, **38**, 1934 (1963).

The excited mercury atoms in the triplet and singlet states correspond to 4.89 and 6.70 e.v., respectively, thus making it very natural to assume that they can produce the above-mentioned states of ethylene. The strong singlet-singlet transition resulting in the ¹B_{1u} state at about 7.7 e.v. is probably ruled out in the participation of the Hg 6(¹P₁) atom reaction, since it is generally recognized that the ¹B_{1u} and ³B_{1u} states of ethylene have probably the same configurations, *i.e.*, the methylene groups twisted about 90° with respect to each other. This in turn would make it necessary that the isotopic composition of hydrogen from the *cis*- and *trans*-substituted dideuterioethylenes be the same. This was not observed in this study. It is conceivable, of course, that a collision complex between the excited mercury atoms and ethylene molecules is formed in the primary process. In that case we cannot make use of the spectroscopic states of ethylene in our discussion. Still the main conclusions remain unchanged: an excited "species" is produced in the primary process and it is different from the one produced by the Hg 6(³P₁) atoms.

A more extensive paper about this reaction will be prepared in the near future from Mr. N. L. Ruland's Ph.D. thesis. This is the first of a contemplated series of papers about the Hg 6(¹P₁) atom reactions.

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Dimethyl Sulfoxide-Acid Anhydride Mixtures. New Reagents for Oxidation of Alcohols¹

Sir:

We wish to report a novel method of oxidation of alcohols to their corresponding carbonyl derivatives with dimethyl sulfoxide (DMSO) and certain acid anhydrides. This method appears to be a general one and is particularly useful for the oxidation of sterically hindered hydroxyl groups. In addition this procedure has certain advantages over other oxidative methods, especially with compounds such as indole alkaloids which are sensitive to nonselective oxidizing reagents.²

In general the oxidation is carried out by allowing a mixture of 1 mmole of primary or secondary alcohol, 3 ml. of DMSO, and 2 ml. (*ca.* 20-mmole excess) of acetic anhydride to stand at room temperature for 18-24 hr. Thus yohimbine (1) undergoes oxidation to give yohimbine^{3,4} (2) consistently in 80-85% yields⁵:

(1) A previous study of oxidation of alcohols: J. D. Albright and L. Goldman, *J. Org. Chem.*, **30**, 1107 (1965).

(2) For a discussion of oxidation of secondary alcohols in the indole alkaloid field see ref. 1.

(3) Literature compounds were identified by agreement of their physical constants with published values.

(4) M.-M. Janot, R. Goutarel, E. W. Warnhoff, and A. Le Hir, *Bull. soc. chim. France*, 637 (1961).

(5) An especially mild Oppenauer oxidation of yohimbine gave yohimbine in 51% yield (ref. 4); yohimbine was oxidized by means of N,N'-dicyclohexylcarbodiimide, DMSO, and phosphoric acid to give yohimbine in about 80% yield (ref. 1).

and **2** is also obtained from β -yohimbine (**3**). The 17-hydroxyl group of ajmaline is selectively oxidized to give ajmalidine.^{3,6} Testosterone affords Δ^4 -androstene-3,17-dione^{3,7} in 34% yield, and 11 α -hydroxyprogesterone (equatorial hydroxyl group) affords 13% of 11-ketoprogesterone.^{3,8} The axial 11 β -hydroxyl of hydrocortisone 21-acetate is oxidized smoothly, but slowly, to give cortisone 21-acetate^{3,9} in 53% yield.¹⁰

Benzoic anhydride, phosphorus pentoxide, and polyphosphoric acid can be substituted for acetic anhydride (yohimbine, phosphorus pentoxide, and DMSO at 65° for 18 hr. give 45% of yohimbine; polyphosphoric acid gives 50%) but trifluoroacetic anhydride is unsatisfactory. With tetramethylene sulfoxide yohimbine gives yohimbine in 80% yield.

Information bearing on the mechanism of this oxidation is forthcoming from studies on the following alcohols. The product (quantitative yield calculated as β -keto ester) obtained by the action of DMSO and acetic anhydride on α -yohimbine (equatorial hydroxyl) is found (thin layer chromatography and integration of p.m.r. signals) to consist of a mixture of approximately equal amounts of two components, from which 42% of methyl 17-hydroxyallo-yohimb-16-ene-16-carboxylate^{1,3} and 10% of α -yohimbine methylthiomethyl ether¹¹ (**4**) (melting indefinitely from ~100 to 120°) are obtained. Methyl reserpate (equatorial hydroxyl) affords 33% of methyl ketoreserpate^{3,12} and 11% of methyl reserpate methylthiomethyl ether¹¹ (m.p. 248–252° dec.). When subjected to the action of the oxidizing reagent, *p*-nitrobenzyl alcohol gives a mixture of *p*-nitrobenzaldehyde (75%) and *p*-nitrobenzyl acetate (25%).

Some tentative conclusions about the mechanism of this oxidation can be drawn. Carboxylic acid anhydrides are known to react with sulfoxides to give α -acyloxy sulfides,¹³ and this rearrangement has been visualized as proceeding through acyloxysulfonium salts like **5**. Nucleophilic attack of an alcohol on the positively charged sulfur atom of **5** with back-side displacement of acetate ion leads to alkoxy-sulfonium salt **6**.¹⁴ Base-promoted elimination of an α -proton from **6**¹⁵ then gives carbonyl derivative **9** and dimethyl sulfide. The methylthiomethyl ether **7** is probably formed in a competitive reaction through intermediate **8**¹⁶ which arises by elimination of acetic

(6) M. Gorman, N. Neuss, C. Djerassi, J. P. Kutney, and P. J. Scheuer, *Tetrahedron*, **1**, 328 (1957).

(7) E. S. Wallis and E. Fernholz, *J. Am. Chem. Soc.*, **57**, 1511 (1935).

(8) D. H. Peterson, H. C. Murray, S. H. Eppstein, L. M. Reineke, A. Weintraub, P. D. Meister, and H. M. Leigh, *ibid.*, **74**, 5933 (1952).

(9) T. Reichstein, *Helv. Chim. Acta*, **20**, 978 (1937).

(10) Contrast with the results of K. E. Pfitzner and J. G. Moffatt [*J. Am. Chem. Soc.*, **85**, 3027 (1963)], who found that the 11 β -hydroxyl of corticosterone 21-acetate is completely inert to the oxidizing action of a mixture of *N,N'*-dicyclohexylcarbodiimide, DMSO, and pyridinium trifluoroacetate.

(11) Satisfactory elemental analyses were obtained for all new compounds; infrared, ultraviolet, and p.m.r. spectra were consistent with structural assignments.

(12) M. M. Robison, W. G. Pierson, R. A. Lucas, I. Hsu, and R. L. Dziemian, *J. Org. Chem.*, **28**, 768 (1963).

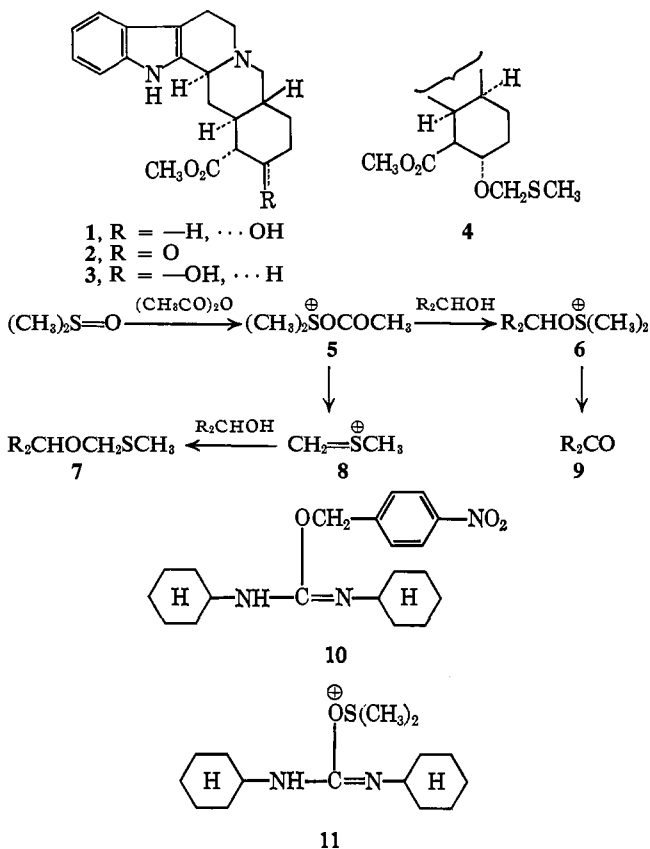
(13) R. Pummerer, *Ber.*, **43**, 1401 (1910); L. Horner and P. Kaiser, *Ann.*, **626**, 19 (1959).

(14) An alkoxy-sulfonium salt **6** has been proposed as an intermediate in the base-promoted oxidation of halides and tosylates with DMSO: N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Am. Chem. Soc.*, **81**, 4113 (1959).

(15) C. R. Johnson and W. G. Phillips, *Tetrahedron Letters*, No. **25**, 2101 (1965), have described reactions of alkoxy-sulfonium salts with alkoxides.

(16) Johnson and Phillips (ref. 15) have presented evidence for this type of intermediate.

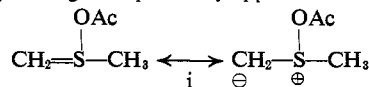
acid from acyloxysulfonium salt **5**, either in a concerted process or through an ylid.¹⁷ The fact that axial alcohols give more ketone **9** and less methylthiomethyl ether **7** than do equatorial alcohols is thought to result from the faster rate of oxidation of sterically hindered hydroxyl groups.¹⁸ The trapping of **8** by reaction with an alcohol suggests that the Pummerer reaction proceeds through a sulfonium intermediate of type **8**.



Evidence that oxidation of alcohols by reagents prepared from mixtures of DMSO and suitable electrophiles proceeds *via* oxysulfonium salts **6**, and that this is a general phenomenon, is provided by experiments with ¹⁸O-labeled alcohols. Oxidation of ethanol-¹⁸O (1.9% ¹⁸O) and benzhydrol-¹⁸O (4.8% ¹⁸O) with *N,N'*-dicyclohexylcarbodiimide, DMSO, and orthophosphoric acid gave unlabeled *N,N'*-dicyclohexylurea; with benzhydrol-¹⁸O 42% of the label was found in the benzophenone isolated.¹⁹ In addition pseudourea **10**,^{11,20} m.p. 55–57°, was unaffected by the oxidizing reagent. These results indicate that DCC and DMSO interact to give sulfonium salt **11** which, when attacked by an alcohol, gives intermediate alkoxy-sulfonium salt **6**.

In a further extension of this general concept, testosterone is found to be oxidized to Δ^4 -androstene-3,17-

(17) It is conceivable that ylid **i** is the reactive intermediate in formation of ether **7**, although this possibility appears unlikely.



(18) An analogy is the chromic acid oxidation of steroidal alcohols: E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 289.

(19) Per cent ¹⁸O was determined by mass spectral analysis. Partial loss of label in the benzophenone probably resulted from exchange with solvent during aqueous acidic workup.

(20) Prepared by the method of E. Schmidt and F. Moosmüller, *Ann.*, **597**, 235 (1955); E. Schmidt and W. Carl, *ibid.*, **639**, 24 (1961).

dione by a mixture of ethoxyacetylene, DMSO, pyridine, and orthophosphoric acid.

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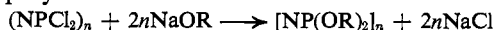
Synthesis of High Polymeric Alkoxy- and Aryloxyphosphonitriles

Sir:

High molecular weight phosphonitrilic halide polymers (polydichlorophosphazenes) have received wide attention in recent years because they are elastomeric and do not decompose thermally below 300°; they are, however, extremely susceptible to hydrolytic degradation. This sensitivity to moisture is due principally to hydrolysis of the phosphorus-halogen bonds. Many attempts have been made to prepare linear, high molecular weight organophosphonitrile polymers in the belief that total replacement of the halogen atoms by organic groups would reduce or eliminate the hydrolytic instability. Thus, polymeric bis(trifluoromethyl)phosphonitrile, $[\text{NP}(\text{CF}_3)_2]_n$, and diphenylphosphonitrile, $[\text{NP}(\text{C}_6\text{H}_5)_2]_n$, were synthesized by Tesi, Haber, and Douglas,¹ by Tesi and Douglas,² and by Herring³ from bis(trifluoromethyl)phosphinic azide,¹ bis(trifluoromethyl)phosphinous amide,² and from diphenylchlorophosphine,³ respectively. These polymers were hydrolytically stable, and the trifluoromethyl derivative was thermally stable up to 380°. However, these materials were not fully characterized, and no information was reported concerning the molecular weights or the detailed molecular structure. Attempts have also been made to prepare polymeric alkoxyphosphonitriles by the direct replacement of halogen in phosphonitrilic chloride rubber by alkoxy groups.^{5,6} These attempts did not yield linear polymers. Goldschmidt and Dishon⁵ obtained cross-linked, partially substituted products using alcohol-pyridine or sodium alkoxide reagents, and Lenton, Lewis, and Pearce⁶ recently reported similar results when swelled phosphonitrilic chloride rubber was treated with ethanol-pyridine or trifluoroethanol-pyridine reagents. The trifluoroethoxy polymer was not stable above 200°.

We now wish to report the synthesis of the first examples of soluble, uncross-linked, fully substituted, high molecular weight organophosphonitrile polymers. The method used involved the polymerization of phosphonitrilic chloride trimer (hexachlorocyclotriphos-

phazene), $(\text{NPCl}_2)_3$, to a mixture of *soluble*, high polymers, $(\text{NPCl}_2)_n$, in which n ranged from 3 to over 15,000. The higher molecular weight, soluble polymer appears to be an open-chain precursor of the cross-linked material which is commonly described as "phosphonitrilic chloride rubber." The soluble polymer can be obtained by termination of the polymerization at a stage before cross-linking occurs. This mixture of soluble chlorophosphonitrile polymers was then allowed to react with sodium alkoxide or phenoxide to give a mixture of fully substituted organophosphonitrile polymers

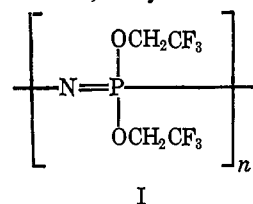


from which the higher homologs could be isolated by fractional precipitation. The following example illustrates one of the experimental procedures employed.

Phosphonitrilic chloride trimer (200 g.) was polymerized under vacuum for 4 hr. at 250°. The mixture of phosphonitrilic chloride polymers (1.725 moles of NPCl_2) was then dissolved in dry benzene (1000 ml.) and was treated with a solution of sodium trifluoroethoxide (3.45 moles) in diethyl ether (1500 ml.) for 28 hr. at 57°. The mixture was then neutralized to litmus with concentrated hydrochloric acid, and the precipitate was filtered off, washed with methanol and with water, and dried. This product was a mixture of fully substituted oligomers and polymers. The high polymers were obtained by fractional precipitation of an acetone solution of the products into benzene to give poly[bis(trifluoroethoxy)phosphonitrile] (55 g.).

Anal. Calcd. for $\text{C}_4\text{H}_4\text{F}_6\text{NO}_2\text{P}$: C, 19.77; H, 1.66; F, 46.9; N, 5.76; P, 12.74. Found: C, 20.28; H, 1.95; F, 47.21; N, 5.73; P, 12.99; Cl, 0.

The number-average molecular weight was found by osmotic pressure to be 90,000; the weight-average molecular weight was found by light scattering in ethyl trifluoroacetate to be 1,700,000 ($\pm 500,000$); and the intrinsic viscosity of the polymer in acetone at 30° was 1.92 dl./g. An infrared spectrum showed a P=N stretching peak as part of a multiple band in the 1270 cm^{-1} region, and ³¹P n.m.r. spectra showed a single peak at +7.5 p.p.m., both of these values being consistent with a linear, fully substituted structure (I).



The polymer was soluble in acetone, tetrahydrofuran, ethyl acetate, ethylene glycol dimethyl ether, and methyl ethyl ketone, but insoluble in many other organic liquids. It was completely stable to water. The polymer was crystalline over a wide temperature range, with a glass transition temperature (determined by differential thermal analysis) of -66° and a crystalline melting temperature (determined by optical birefringence) in the 240° region. The chain repeating distance of 4.81 Å., measured by X-ray diffraction, is close to the value of 4.92 Å. reported for $(\text{NPCl}_2)_n$.⁸

(7) The rate of polymerization varies enormously with the presence of trace impurities. Polymerization times up to 48 hr. were sometimes required in order to achieve satisfactory conversions to soluble polymer.

(8) E. Giglio, F. Pompa, and A. Ripamonti, *J. Polymer Sci.*, **59**, 293 (1962).

(1) G. Tesi, C. P. Haber, and C. M. Douglas, *Proc. Chem. Soc.*, 219 (1960).

(2) G. Tesi and C. M. Douglas, *J. Am. Chem. Soc.*, **84**, 549 (1962).

(3) D. L. Herring, *Chem. Ind.* (London), 717 (1960).

(4) C. P. Haber, *Inorganic Polymers*, International Symposium, Nottingham, July 18-21, 1961, Special Publication No. 15, The Chemical Society, London, p. 119.

(5) F. Goldschmidt and B. Dishon, *J. Polymer Sci.*, **3**, 481 (1948).

(6) M. V. Lenton, B. Lewis, and C. A. Pearce, *Chem. Ind.* (London), 1387 (1964).