able, nevertheless, the possibility of an equilibrium between 3-phenylazirine and β-styrylnitrene prior to rearrangement to phenylacetonitrile is recognized.[6] Formation of the nitrile requires migration of hydrogen either from carbon to nitrogen, followed by tautomerization, or from α- to β-carbon. Initial formation of a ketenimine follows the established pattern of 1,2 migration of hydrogen from carbon to nitrogen for primary and secondary alkyl nitrenes.[7]

Styrene azidohydrin, obtained from phenacyl azide by reduction with sodium borohydride,[8] was transformed into styrene azidochloride. At −25° potassium *t*-butoxide in ether removes both hydrogen chloride and hydrogen azide from styrene azidochloride. The major portion of the product was an oil from which known α-chlorostyrene (17%) could be separated by distillation, bp 28–32° (0.6 mm), $n^{25}\text{D}$ 1.5606. By chromatographic purification of the pot residue over alumina, β-styryl azide (44%) was isolated, infrared absorption (cm^{-1}) at 2100 (s) (N_3), 1645 (s) (C=C), nmr (ppm) 7.14 (five phenyl protons), 6.32 and 6.11 (a pair of doublets representing two vinyl protons (probably *trans*), $J = 14.0$ cps). The azide could not be distilled and decomposed at about 70°. This low temperature for elimination of nitrogen probably reflects assistance through participation by the adjacent olefinic bond.

Neat β-styryl azide was pyrolyzed in the injection port of an Aerograph Autoprep Model 700 gas chromatograph. Two products accounted for 90% of the total peak area on the chromatogram, and the remaining 10% represented impurities known to be present and traces of unidentified material. The major product (74%) was collected after elution from a 20-ft 20% SE-30 silicone gum on Chromosorb W column and identified by comparing its infrared absorption, refractive index, and glpc retention time with authentic phenylacetonitrile.

A *n*-heptane solution of β-styryl azide in a quartz vessel was photolyzed overnight in a Rayonet photochemical reactor with light at 2537 A supplied by 16 35-w low-pressure mercury lamps. An unidentified solid (74%), apparently polymeric, was separated. The concentrated filtrate gave a dark oil containing phenylacetonitrile whose presence was indicated by nmr (ppm) centered at 7.21 and 3.50, corresponding to absorption at 7.19 and 3.48 for authentic material, and by glpc retention time. From the chromatogram a maximum of 8% yield was indicated.

Under similar conditions, photolysis of *trans*-β-styryl isocyanate[9] produced an unidentified, apparently polymeric, solid, judged by infrared absorption to be identical with a product, described above, from β-styryl azide. Analysis of the filtrate by glpc indicated the presence of two components whose chromatographic peaks corresponded with peaks similarly obtained not only from β-styryl azide but also from phenylacetonitrile after comparable photolytic treatment. The component with the longer retention time represented a maximum of 20% yield of phenylacetonitrile from β-styryl isocyanate, as determined from the chromatogram and further identified by comparison of its infrared spectrum with that of a known sample.

Acknowledgment. Financial assistance was received from NASA Grant NGR 14-012-004.

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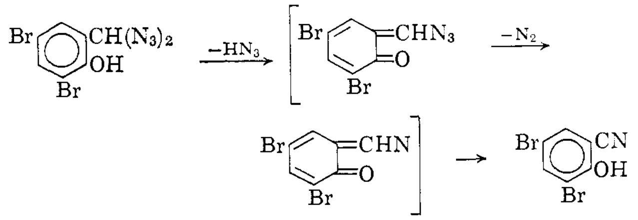
[6] Cadogan and Todd discuss the possible equilibrium between a bicyclic azirine and phenylnitrene.[2]

[7] Five terminal vinyl azides have been reported either in fact or implication: A. N. Nesmeyanov and M. I. Rybinskaya (*Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 816 (1962); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 761 (1962); *Chem. Abstr.*, **58**, 3408 (1963)) reported $C_6H_5COCH{=}CHN_3 + HCl \longrightarrow C_6H_5COCH_2CN$ + other products. J. H. Boyer and F. C. Canter (*Chem. Rev.*, **54**, 34 (1954)) explain the pyrolysis of 3,5-dibromo-2-hydroxybenzaldiazide (H. Lindemann and H. Thiele, *Ber.*, **61**, 1529 (1928)) in terms of an intermediate terminal vinyl azide.



F. W. Fowler, A. Hassner, and L. A. Levy (*J. Am. Chem. Soc.*, **89**, 2077 (1967)) have reported the preparation of $(CH_3)_3CCH{=}CHN_3$. J. S. Meek and J. S. Fowler (*ibid.*, **89**, 1967 (1967)) reported the isomerization of β-azidovinyl *p*-tolyl sulfone to 4(5)-*p*-toluenesulfonyltriazole. R. H. Wiley and J. Moffat (*J. Org. Chem.*, **22**, 995 (1957)) reported the preparation and polymerization of vinyl azide.

[8] J. H. Boyer and S. E. Ellzey, Jr., *ibid.*, **23**, 127 (1958).

[9] L. W. Jones and J. P. Mason, *J. Am. Chem. Soc.*, **49**, 2528 (1927).

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Sulfur Trioxide in the Oxidation of Alcohols by Dimethyl Sulfoxide

Sir:

Following the discovery of Kornblum and coworkers[1] that halides or tosylates may be oxidized with dimethyl sulfoxide (DMSO) to carbonyl compounds, the intermediacy of dimethylsulfoxonium ions was hypothesized[2] and, quite recently, has been substantiated by Torssell.[2d] On this basis, Barton, *et al.*,[3] described a procedure involving the formation of the intermediate dimethylsulfoxonium ions by the action of DMSO on alkyl chloroformates and a novel catalysis of their decomposition with triethylamine.[2d]

Agents such as dicyclohexylcarbodiimide (DCC),[4] acetic anhydride,[5] and phosphorus pentoxide[6] in combination with DMSO have also been reported to effect oxidation of alcohols.[7] The function of dicyclohexylcarbodiimide has been elegantly elucidated and a di-

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[1] N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. O. Larson, O. Levand, and W. M. Weaver, *J. Am. Chem. Soc.*, **79**, 6562 (1957); N. Kornblum, W. J. Jones, and G. J. Anderson, *ibid.*, **81**, 4113 (1959).

[2] (a) S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958); (b) I. M. Hunsberger and J. M. Tien, *Chem. Ind.* (London), 88 (1959); (c) N. R. Nace and J. J. Monagle, *J. Org. Chem.*, **24**, 1792 (1959); (d) K. Torssell, *Tetrahedron Letters*, 4445 (1966); *Acta Chem. Scand.*, **21**, 1 (1967).

[3] D. H. R. Barton, B. J. Garner, and R. H. Wightman, *J. Chem. Soc.*, 1855 (1964).

[4] K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963); *ibid.*, **87**, 5661 (1965); **87**, 5670 (1965).

[5] J. D. Albright and L. Goldman, *ibid.*, **87**, 4214 (1965); **89**, 2416 (1967).

[6] K. Onodera, S. Hirano, and N. Kashimura, *ibid.*, **87**, 4651 (1965).

[7] See recent reviews by (a) N. Kharasch and B. S. Thyagarajan, *Quart. Rept. Sulfur Chem.*, **1**, 16 (1966); (b) W. W. Epstein and F. W. Sweat, *Chem. Rev.*, **67**, 247 (1967).

methylsulfoxonium intermediate has been confirmed.[8] Of these agents, the combination of DMSO and DCC[4] appears to be the most satisfactory because of its broad applicability and mildness.

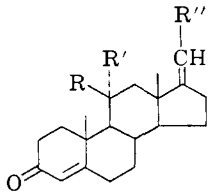
We now wish to report yet another novel reagent which consists of sulfur trioxide, conveniently in the form of its pyridine complex, and DMSO, in the presence of triethylamine. This reagent appears to find general application in the oxidations of primary and secondary alcohols to aldehydes and ketones, respectively. An attractive feature of this reagent is its property of effecting oxidation of allylic alcohols to the corresponding α,β-unsaturated carbonyl compounds. The oxidations are very rapid at room temperature and reach completion usually within minutes.

A by-product, the methyl thiomethyl ether derivative of alcohol, which often arises significantly in the oxidation with acetic anhydride–DMSO, is negligible.[9] The isolation of desired product is simple and free from complications such as that of separating the dicyclohexylurea produced in the DCC–DMSO method. The yields of saturated aldehydes or ketones compare favorably with those obtained in the DCC–DMSO method.

In general, the oxidation is conveniently carried out by addition of a solution of pyridine–SO_3 complex[10] (12–13.2 mmoles) in DMSO (10 ml)[11] to a mixture of the alcohol (4 mmoles), DMSO (10 ml), and triethylamine (26–66 mmoles),[12] maintained at 25° during the addition and subsequent reaction period, the duration of which may be determined by thin layer or gas–liquid partition chromatography. After acidification of the reaction mixture to pH 4.5–5, the product is precipitated by addition of water and isolated by conventional methods.

Following this procedure, many steroidal and nonsteroidal alcohols have been successfully oxidized, a few examples of which are described here.[13] Testosterone was oxidized almost instantaneously to androst-4-ene-3,17-dione in nearly quantitative yield. The 17α-hydroxyl group in epitestosterone required about 35 min for completion of oxidation. In the case of 11-hydroxy steroids, the difference in reactivities of the corresponding axial and equatorial conformers was quite pronounced. While 11α-hydroxyprogesterone was oxidized to 11-ketoprogesterone (isolated in 70% yield), the corresponding 11β epimer was virtually inert. This observation was further confirmed by selective and rapid (~30 min) oxidation of the 20α-hydroxyl function in 11β,17α,20α,21-tetrahydroxy-4-pregnen-3-one 21-acetate ("triol acetate") to the corresponding 20-ketone (hydrocortisone acetate) which was isolated in 88–90% of the theoretical yield. The 20-hydroxyl group of opposite configuration in 20β-hydroxy-4-pregnen-3-one was likewise oxidized to progesterone. Oxidation of "triol acetate" with acetic anhydride–DMSO led to a mixture of at least four discernible (tlc) products, of which three were isolated and identified. The two major products were the 20α-methyl thiomethyl ether derivative of the starting material and hydrocortisone acetate. One of the minor products was 20α-methyl thiomethyl-17α,21-dihydroxy-4-pregnen-3,11-dione 21-acetate. Oxidation of "triol acetate" with DCC or diisopropylcarbodiimide and DMSO, in the presence of pyridinium trifluoroacetate, took nearly 16 hr to reach completion. The major product was hydrocortisone acetate. The presence of the corresponding ureas in the final products required elaborate and wasteful purifications. The primary allylic hydroxyl in 11β,21-dihydroxy-4,17-pregnadien-3-one (**1a**) was oxidized to the corresponding α,β-unsaturated aldehyde 11β-hydroxy-4,17-pregnadien-3-on-21-al (**1b**) which was isolated in 70% of theoretical yield.

Oxidation of **1a** with acetic anhydride–DMSO led to a mixture of at least six products which were isolated and identified as the corresponding 21-methylthiomethyl (**1c**), 11-keto-21-methylthiomethyl (**1d**), 21-acetate (**1e**), 11-keto-21-acetate (**1f**), 11-keto-21-al (**1g**), and 21-al (**1h**) derivatives. Oxidation of **1a** with DCC–DMSO showed no appreciable formation of the desired aldehyde **1b**. As additional examples of oxidations of steroidal alcohols, cholestanol was oxidized to cholestanone (83% yield) and 17α-hydroxypregnenolone and 16-dehydropregnenolone were oxidized to the corresponding 3-keto-Δ^5 compounds which, after acid-catalyzed isomerization, were isolated as 3-keto-Δ^4 compounds in 68 and 72% yield, respectively. Of the nonsteroidal alcohols, *p*-nitrobenzyl alcohol and *l*-menthol were oxidized to the corresponding aldehyde and ketone, respectively. Full details of our further studies with SO_3–DMSO reagent will be reported shortly.



1a, R = OH; R' = H; R'' = CH_2OH
b, R = OH; R' = H; R'' = CHO
c, R = OH; R' = H; R'' = $CH_2OCH_2SCH_3$
d, RR' = O; R'' = $CH_2OCH_2SCH_3$
e, R = OH; R' = H; R'' = $CH_2OCOOCH_3$
f, RR' = O; R'' = $CH_2OCOOCH_3$
g, RR' = O; R'' = CHO
h, R = OH; R' = H; R'' = CHO

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[8] A. H. Fenselau and J. G. Moffatt, *J. Am. Chem. Soc.*, **88**, 1762 (1966); F. W. Sweat and W. W. Epstein, *J. Org. Chem.*, **32**, 835 (1967).

[9] Similar formation of the methylthiomethyl ether derivative, as a side product, in the oxidation with phosphorus pentoxide–DMSO has been reported by K. Onodera, S. Hirano, N. Kashimura, F. Masuda, T. Yajima, and N. Miyazaki, *ibid.*, **31**, 1291 (1966).

[10] Pyridine–SO_3 complex is available from Allied Chemicals, General Chemical Division, Morristown, N. J., or may be prepared following directions in L. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955, p 337.

[11] DMSO (Crown-Zellerbach, Camas, Wash.) was dried over Linde Molecular Sieves Type A4.

[12] If the reaction is carried out in such an order that the hydrogen sulfate of the alcohol is first formed, no oxidation ensues. A mechanism is tentatively assumed in which (a) dimethyl sulfoxide and sulfur trioxide react to form O-dimethylsulfoxonium sulfate, (b) displacement occurs on sulfur to produce an O-alkyl dimethylsulfoxonium intermediate which (c) suffers base-catalyzed elimination.

[13] Acceptable elemental analyses and infrared and pmr spectra have been obtained on all new compounds reported herein. The known compounds were characterized by comparison of their physical constants and infrared and pmr spectra with those of authentic samples from the Upjohn collection.

Acknowledgment. We wish to thank Mr. F. A. Mackellar, Dr. A. Rozanski, and Mr. J. Loher of The Upjohn Company for analytical and spectral data.

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The Complexes of Bromine and Iodine with Bis(diphenylglyoximato)nickel(II) and Bis(diphenylglyoximato)palladium(II)

Sir:

Several years ago Simek[1] reported magnetic studies of Ni(dpg)$_2$Br and Ni(dpg)$_2$I [dpg = $(C_6H_5)_2C_2N_2O_2H^-$, the anion of diphenylglyoxime] from which he concluded that these are not simple nickel(III) complexes. We have prepared the two palladium members of this series, and we wish to summarize evidence that the four compounds are inclusion-like molecular complexes stabilized by charge-transfer interaction.

Mixing warm *o*-dichlorobenzene solutions of bis(diphenylglyoximato)nickel(II), Ni(dpg)$_2$, or bis(diphenylglyoximato)palladium(II), Pd(dpg)$_2$, and the elemental halogen gave upon standing analytically pure samples of Ni(dpg)$_2$Br, Ni(dpg)$_2$I, and Pd(dpg)$_2$I. Pd(dpg)$_2$Br was formed as a mechanical mixture with Pd(dpg)$_2$, from which individual crystals could be separated and then identified by appearance, X-ray diffraction patterns, and epr spectra. The four M(dpg)$_2$X compounds occur as black needles and are easily distinguished from the two parent compounds, dark red Ni(dpg)$_2$ and yellow Pd(dpg)$_2$.

The needle-like crystals of the four M(dpg)$_2$X compounds are isomorphous. Dimensions of the tetragonal unit cells, measured from sodium chloride calibrated (a = 5.628 A) single-crystal precession photographs made with Mo Kα radiation, are given in Table I. Density measurements show that there are four M(dpg)$_2$X formula units per primitive unit cell. Systematic extinctions give P4/ncc (D_{4h}^8) as the common space group.[2]

Table I. Crystal Data for M(dpg)$_2$X Complexes

	Ni(dpg)$_2$Br	Ni(dpg)$_2$I	Pd(dpg)$_2$Br	Pd(dpg)$_2$I
Unit cell				
a, ± 0.06, A	19.51	19.92	19.78	20.17
c, ± 0.02, A	6.72	6.56	6.57	6.52
Density				
Calcd, g/cm^3	1.60	1.69	1.72	1.78
Found, g/cm^3	1.64	1.72	1.70	1.78
Epr data				
$g_\perp$ ± 0.0002	2.0221	2.0222	2.0177	2.0166
$g_\parallel$ ± 0.0004	2.0118	2.0121	2.0097	2.0088
Δg ± 0.0006	0.0103	0.0101	0.0080	0.0078

The unit cell dimensions together with a consideration of the distribution of the metal and halogen atoms among the equipoints of rank four[3] of space group P4/ncc strongly suggest that the structures are derived from those of Ni(dpg)$_2$ and Pd(dpg)$_2$[4] and consist of M(dpg)$_2$ molecules (with square-planar coordination) arranged like interlocking blocks in stacks parallel to the c direction with a metal–metal distance of $c/2$ in each stack. Both the equipoint analysis and the three-dimensional Patterson function (calculated with the intensity data collected from Ni(dpg)$_2$I) indicate that the halogens lie in channels which are surrounded by phenyl groups and are parallel to the M(dpg)$_2$ stacks. These halogen chains are thought to be the source of the strong, broad visible absorption which is more intense for light polarized parallel to the c direction. The 001 projection of this structural model can be refined with the $hk0$ data for Ni(dpg)$_2$I to a residual parameter $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.11$. The complete three-dimensional solution of the structure has not yet been achieved.

Elemental iodine is evolved slowly when Ni(dpg)$_2$I is left standing at room temperature and more rapidly when it is warmed in an oven. The loss of iodine is eventually quantitative. The iodine-free solid residue is initially rust colored and has an X-ray powder pattern and a visible absorption spectrum (mull) which are different from those of either solid Ni(dpg)$_2$I or solid Ni(dpg)$_2$. We believe this initial residue to be a metastable empty "host" form of Ni(dpg)$_2$. Either recrystallization from chloroform or baking at 140° for 24 hr converts it to a more reddish solid which has been shown to be "normal" Ni(dpg)$_2$ by comparison of X-ray powder patterns and visible absorption spectra.

Single crystals of Ni(dpg)$_2$I were examined with a polarizing microscope from time to time while being baked at 50°. The loss of iodine was marked by a substantial reduction in visible absorption which progressed along the needle-like crystals. Single crystal precession X-ray photographs taken before and after this mild heating show that the unit cell constants remain about the same even though a good deal of mechanical damage occurs during the loss of iodine.

The density of Ni(dpg)$_2$I falls to 1.42 ± 0.02 g/cm^3 (flotation method) when the iodine is removed by mild heating.[5] After standing for 24 hr at 145° the density is found to be 1.47 ± 0.01 g/cm^3, the same value obtained for normal Ni(dpg)$_2$.

The visible absorption spectrum of a mulled powdered sample of Ni(dpg)$_2$ shows two bands with λ_{max} 427 and 514 mμ, respectively. The empty host form has a similar spectrum except with λ_{max} 447 and 567 mμ. The shift of the two visible bands to longer wavelength in the metastable host form of Ni(dpg)$_2$ probably results from the shorter Ni–Ni distance (approximately 3.27 A compared to 3.52 A in normal Ni(dpg)$_2$[4]) and is consistent with Drickamer's report[6] of a shift to longer

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(1) M. Simek, *Collection Czech. Chem. Commun.*, 27, 337 (1962).

(2) "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1952, p 225.

(3) M. J. Buerger, "Crystal Structure Analysis," John Wiley and Sons, Inc., New York, N. Y., 1960, pp 242–258.

(4) Although the crystal structures of the nickel and palladium complexes of diphenylglyoxime are not known in detail, they are reported to be essentially the same as the structure of bis(dimethylglyoximato)nickel(II); see C. V. Banks and D. W. Barnum, *J. Am. Chem. Soc.*, **80**, 4767 (1958); and D. E. Williams, G. Wohlauer, and R. E. Rundle, *ibid.*, 81, 755 (1959).

(5) One calculates a density of 1.37 g/cm^3 for the metastable form of Ni(dpg)$_2$, assuming unit cell constants identical with those of Ni(dpg)$_2$I.

(6) J. C. Zahner and H. G. Drickamer, *J. Chem. Phys.*, **33**, 1625 (1960).