evaporated under reduced pressure. The resulting solid was recrystallized from 95% ethanol to afford white crystalline product.

Phenyl α-Toluenesulfonate.—α-Toluenesulfonyl chloride (19.06 g, 0.10 mol) gave 16.8 g (68%) of phenyl α-toluenesulfonate, mp 84.5–85.5°.

Anal. Calcd for $C_{13}H_{12}O_3S$: C, 62.90; H, 4.85; S, 12.05. Found: C, 62.98; H, 4.98; S, 12.16.

p-**Tolyl α-Toluenesulfonate.**—α-Toluenesulfonyl chloride (15.0 g, 0.079 mol) afforded 16.2 g (78%) of *p*-tolyl α-toluenesulfonate, mp 87–88°.

p-**Bromophenyl α-Toluenesulfonate.**—α-Toluenesulfonyl chloride (15.0 g, 0.079 mol) gave 19.3 g (75%) of *p*-bromophenyl α-toluenesulfonate, mp 84–85°.

Phenyl *p*-**Methyl-α-toluenesulfonate.**—*p*-Methyl-α-toluenesulfonyl chloride (10.0 g, 0.049 mol) gave 10.5 g (83%) of phenyl *p*-methyl-α-toluenesulfonate, mp 98–99°.

Phenyl *p*-**Chloro-α-toluenesulfonate.**—*p*-Chloro-α-toluenesulfonyl chloride (20.2 g, 0.09 mol) afforded 16.0 g (67%) of phenyl *p*-chloro-α-toluenesulfonate, mp 81–82.5°.

General Procedure for the Preparation of α-Sulfonylsulfonates.—To 150 ml of THF under nitrogen at 5–10° was added 0.030 mol of sublimed KO-*t*-Bu. This mixture was allowed to stir for 15 min after which 0.028 mol of the sulfonate ester in 50 ml of THF was added dropwise. After stirring for 8 hr at room temperature, 0.030 mol of glacial acetic acid was added and the mixture filtered. The solid was washed with four 50-ml portions of THF; the combined filtrates were evaporated *in vacuo*. The resulting solid was taken up in chloroform and the chloroform solution washed with three 50-ml portions of water and with 50 ml of a saturated sodium chloride solution and dried over Na_2SO_4 and the chloroform evaporated *in vacuo* leaving a white solid, which was recrystallized from absolute ethanol.

Phenyl α-(Benzylsulfonyl)-α-toluenesulfonate (3).—Phenyl α-toluenesulfonate (7.45 g, 0.030 mol) afforded 4.45 g (69%) of **3** (Table I): nmr (acetone d_6) δ 4.85 (s, 2), 6.40 (s, 1), 7.48 (m, 15); mol wt, calcd, 408; found, 405.

p-**Tolyl α-(Benzylsulfonyl)-α-toluenesulfonate (4).**—*p*-Tolyl α-toluenesulfonate (10.0 g, 0.039 mol) gave 4.85 g (60%) of **4** (Table I): nmr (acetone-d_6) δ 2.32 (s, 3), 4.77 (s, 2), 6.30 (s, 1), 7.35 (m, 14); mol wt, calcd, 416; found, 422.

p-**Bromophenyl α-(Benzylsulfonyl)-α-toluenesulfonate (5).**—*p*-Bromophenyl α-toluenesulfonate (10.0 g, 0.0306 mol) gave 4.32 g (59%) of **5** (Table I): nmr (acetone-d_6), δ 4.75 (s, 2), 6.38 (s, 1), 7.45 (m, 14); mol wt, calcd, 487; found, 477.

Phenyl α-(*p*-Chlorobenzylsulfonyl)-*p*-chloro-α-toluenesulfonate (6).—Phenyl *p*-chloro-α-toluenesulfonate (7.94 g, 0.028 mol) yielded 4.09 g (62%) of **6** (Table I): nmr ($CDCl_3$) δ 4.75 (q, 2), 5.30 (s, 1), 7.50 (m, 13); mol wt, calcd, 471; found, 475.

Phenyl α-(*p*-Methylbenzylsulfonyl)-*p*-methyl-α-methyl-α-toluenesulfonate (7).—Phenyl *p*-methyl-α-toluenesulfonate (6.0 g, 0.23 mol) gave 2.10 g (52%) of **7** (Table I): nmr (acetone-d_6) δ 2.40 (d, 6), 4.75 (s, 2), 6.30 (s, 1), 7.33 (m, 13); mol wt, calcd, 430; found, 428. A small amount of phenyl *p*-methyl-α-toluenesulfonate, 1.00 g (17%), was also recovered.

Attempted Reaction of Potassium *tert*-Butoxide with Neopentyl α-Toluenesulfonate.—Neopentyl α-toluenesulfonate (5.09 g, 0.021 mol) and KO-*t*-Bu (2.80 g, 0.025 mol) were stirred in 100 ml of dry THF under nitrogen at 5° for 14 hr. After careful acidification of the reaction mixture with glacial acetic acid (1.50 g, 0.025 mol), the solution was filtered, the solid was washed with three 50-ml portions of THF and the combined filtrates were evaporated *in vacuo*. The resulting white solid was recrystallized from 95% EtOH to afford 3.86 g (76%) recovery of starting ester.

Registry No.—**3,** 17074-71-4; **4,** 25894-34-2; **5,** 25894-35-3; **6,** 25894-36-4; **7,** 25957-56-6; phenyl α-toluenesulfonate, 10271-81-5; *p*-tolyl α-toluenesulfonate, 25894-38-6; *p*-bromophenyl α-toluenesulfonate, 25894-39-7; phenyl *p*-methyl-α-toluenesulfonate, 25894-40-0; phenyl *p*-chloro-α-toluenesulfonate, 25894-41-1.

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Formation of an α-Chlorovinylamine and Its Interconversion to a Ketenimmonium Salt

HAROLD WEINGARTEN

Central Research Department, Monsanto Company
St. Louis, Missouri 63166

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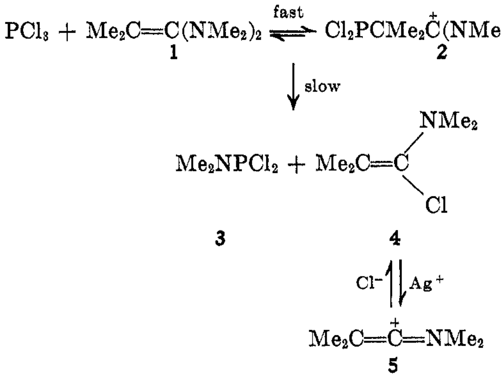
While studying the reactions of enamines with inorganic halides,[1] we observed a reaction that should be of interest to organic chemists. Phosphorus trichloride reacts with 2-methylpropenylidenebisdimethylamine (**1**) to form first a one-to-one complex which we believe to have structure **2** (see Scheme I). The proton nmr of **2** displays a broadened singlet at τ 6.50 consistent with amidinium *N*-methyl protons and a broadened doublet at τ 7.98 (J = 8.6 Hz) consistent with *C*-methyl protons coupled to phosphorus. Compound **2** was not isolated and is known only by its nmr. This spectrum disappears in 24–72 hr depending on temperature and concentration, and new resonances, a doublet[2] at τ 7.15 (J = 12.5 Hz) and sharp singlets at τ 7.63 and 8.22 in the ratio 1:1:1, are generated. This secondary reaction mixture was separated by preparative vpc into components **3** corresponding to the doublet above and **4** corresponding to the two sharp singlets. Compound **3** was shown to be dichloro(dimethylamino)phosphine by vpc and proton nmr comparison with an authentic sample prepared by equilibrating phosphorus trichloride with tris(dimethylamino)phosphine[3]. Compound **4**, a colorless, distillable, thermally unstable liquid was prepared more conveniently by reaction of **1** with dichlorophenylphosphine. Although the reaction was slower, the products, chloro(dimethylamino)phenylphosphine and **4**, have sufficiently different volatilities to allow separation *via* simple fractional distillation.

SCHEME I



Subtracting the elements of the phosphorus containing products from those of the starting materials permits only a limited number of alternatives for the structure of **4**. Furthermore, hydrolysis of **4** yields *N*,*N*-dimethylisobutyramide which seemed to exclude most reasonable possibilities except the structure shown

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[1] H. Weingarten and J. S. Wager, *Chem. Commun.*, 854 (1970).

[2] Demonstrated by decoupling experiments on a Varian Model HA-100 spectrometer.

[3] J. R. Van Wazer and L. Maier, *J. Amer. Chem. Soc.*, **86**, 811 (1964).

in Scheme I, but the observed nmr spectrum of two sharp singlets seemed inconsistent with this structure, which apparently requires three lines. However, if **4** were shown to be ionizing rapidly and reversibly to structure **5** the nmr spectrum could be rationalized.

Low temperature nmr in chloroform showed substantial broadening of the peak at τ 8.22 consistent with the ionization hypothesis. It was subsequently observed that when the nmr of **4** was examined in nonpolar solvents the peak attributed to the *C*-methyl protons was split into the expected pair of quartets, even at normal probe temperatures, confirming structure **4**.[4]

Finally, it was of interest to know if **5**, previously proposed as a reaction intermediate,[5] could be observed directly. To this end a 5% solution of **4** in acetonitrile-d_3 was treated with increasing amounts of $AgPF_6$. Silver chloride was precipitated and the nmr peaks of **4** were broadened and displaced downfield, the peak attributed to the *N*-methyl protons being the most influenced. In the presence of excess silver ion, two new sharp singlets appear at τ 6.48 and 8.02 in agreement with structure **5**. Compound **5**, which has a half-life of *ca.* 10 min under the experimental conditions, can be reconverted to **4** by addition of anhydrous tetrabutylammonium chloride.

It is not known if **3** and **4** arise *via* rearrangement of **2** or direct reaction of starting materials, although the latter appears more attractive.

Experimental Section

General.—Proton nmr spectra were obtained from a Varian Model T60 or A-56/60 spectrometer, the latter equipped with a variable temperature probe. Elemental analyses were performed in the Physical Sciences Center, Central Research Department, Monsanto Co. All reactions were carried out in an atmosphere of dry nitrogen.

Preparation of 1-Chloro-*N*,*N*,2-trimethylpropenylamine (4).—To a solution of 2.7 g (0.015 mol) of dichlorophenylphosphine in 10 ml of chloroform was slowly added a solution of 2.0 g (0.014 mol) of **1** in 5 ml of chloroform. The resulting solution was allowed to stand at room temperature for 14 days, while monitoring the progress of the reaction by proton nmr. At the end of this period the solvent was removed and the more volatile portion of the residue was distilled into a Dry Ice trap, yielding 1.4 g (75%) of **4**: bp 40° (25 mm); nmr ($DCCl_3$) τ 7.63 (s, 1), 8.22 (s, 1).

Anal. Calcd for $C_6H_{12}NCl$: C, 53.9; H, 9.1; N, 10.5; mol wt, 133. Found: C, 53.7; H, 9.3; N, 10.2; mol wt, 133 (mass spectrum).

When a solution of **4** in acetonitrile-d_3 was treated with a small amount of water, the nmr spectrum immediately changed to that of *N*,*N*-dimethylisobutyramide.[6]

Proton Nmr Study of 1-Chloro-*N*,*N*,2-trimethylpropenylamine (4).—An nmr spectrum of **4** (5% in chloroform) changed in the following way as the temperature was decreased. The width at half height changed, in going from +36° to −75°; for the tetramethylsilane resonance from 0.38 Hz to 0.44 Hz; for the resonance at τ 8.22 (CH_3-C) from 0.46 Hz to 2.60 Hz; and for the resonance at τ 7.63 (CH_3-N) from 0.42 Hz to 1.00 Hz.

In toluene-d_8 or benzene, the *C*-methyl resonance becomes two quartets[7] centered at τ 8.29 and 8.31 (*J ca.* 0.4 Hz) at normal probe temperature.

Registry No.—**4**, 26189-59-3; **5**, 26189-60-6.

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[4] Several α-chloroenamines have been reported: see A. J. Speziale and R. C. Freeman, *ibid.*, **82**, 903 (1960); E. Ott, G. Dittus, and H. Weisenburger, *Chem. Ber.*, **76**, 84 (1943).

[5] C. F. Hobbs and H. Weingarten, *J. Org. Chem.*, **33**, 2385 (1968).

[6] The nmr spectrum of *N*,*N*-dimethylisobutyramide in acetonitrile-d_3 is sensitive to acid concentration.

[7] The spectra are sensitive to tetramethylsilane concentration and the values reported are for 10% tetramethylsilane solutions.

A Simple Preparation of "Active" Manganese Dioxide from "Activated" Carbon

LOUIS A. CARPINO

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002

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In view of the usefulness[1] of "active" manganese dioxide as an oxidant in organic chemistry, it is unfortunate that current methods of preparing or "activating" this material are experimentally so tedious. By accident we noted that ordinary decolorizing carbon discharges the purple color of aqueous permanganate solutions with the precipitation of a brown-black powder, presumably manganese dioxide, on the excess carbon.[2] Whether because of the nature of the material precipitated in this way or the presence of excess carbon, the powder can be filtered rapidly and washed with ease in a few minutes on an ordinary Büchner funnel.[3] We have used this mixture routinely for several years in the oxidation of a variety of hydrazine derivatives (hydrazones, hydrazo compounds, 1,1-disubstituted hydrazines) and find it to be as effective for such purposes as the MnO_2 oxidants previously described.[6] Drying the oxidant mixture in an oven at 105–110° for 8–24 hr increases its activity to the point where its effectiveness in the oxidation of allylic and benzylic alcohols appears comparable with that of the material described by Attenburrow and coworkers. Some results are listed in Table I. Since we have not

TABLE I

OXIDATION OF CINNAMYL ALCOHOL[a]

Oxidant	% cinnamaldehyde after 30 min
MnO_2–C, BP, air-dried[b]	30–35
MnO_2–C, BP, oven-dried[b]	46–51
MnO_2–C, RT, air-dried[c]	48–54
MnO_2–C, RT, oven-dried[c]	82–91

[a] Test oxidations were carried out by stirring, at room temperature, a solution containing 0.5 g of cinnamyl alcohol in 5.5 g of benzene and 19 g of ligroin (bp 30–60°) with 5.0 g of the oxidant. Extent of conversion to the aldehyde was determined by infrared analysis according to the method of R. J. Gritter and T. J. Wallace, *J. Org. Chem.*, **24**, 1051 (1959). [b] Precipitated at the boiling point of the solution (method A). [c] Precipitated at room temperature (method B). The increased activity of the oxidant mixture obtained by precipitation at room temperature is at the expense of slightly reduced ease of filtration.

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[1] For pertinent reviews see (a) O. Meth-Cohn and H. Suschitzky, *Chem. Ind. (London)*, 443 (1969); (b) S. P. Korshunov and L. I. Vereshchagin, *Russ. Chem. Rev.*, **35**, 942 (1966); (c) R. M. Evans, *Quart. Rev. (London)*, **13**, 61 (1959).

[2] We have no evidence as to the exact composition of the material precipitated but assume it to be a mixture of MnO_2 and unoxidized carbon. Elemental analysis of an air-dried sample of the oxidant obtained on the scale given in method A showed the presence of about 20% carbon.

[3] In the most common procedure[4] for the preparation of active manganese dioxide, a thick paste is obtained which is most easily collected and washed by repeated centrifugation. Activation by azeotropic removal of water through distillation of a suspension in benzene has recently been recommended.[5]

[4] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jensen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

[5] I. M. Goldman, *J. Org. Chem.*, **34**, 1979 (1969).

[6] Details regarding the oxidation of benzalhydrazone to phenyldiazomethane (50–70%), 1,1-disubstituted hydrazines to hydrocarbon products, and hydrazo compounds to azo compounds will be described separately.