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 (DCCl₃) 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.

(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

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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.

(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.

directly compared our oxidant with previous preparations, except in the case of the nitrogen compounds mentioned above, it remains for interested investigators to determine its suitability for various specific purposes.

Experimental Section

A.—A solution of 20 g of potassium permanganate in 250 ml of water contained in a 600-ml beaker was heated to the boiling point, removed from the source of heat, and treated portionwise over 5–7 min with 6.25 g of activated carbon.[7] The frothing was allowed to subside between additions. After complete addition of the carbon the mixture was boiled for 2–4 min until the purple color was completely discharged, allowed to stand at room temperature for 10–15 min and filtered on a Büchner funnel. The precipitate was washed four times with 50-ml portions of water and spread out to dry in the air. The air-dried material amounted to 22.2 g. After drying in an oven at 105–110° for 8–24 hr, the weight dropped to 18.7 g. After either air- or oven-drying, the oxidant was obtained as a fine powder which could be used directly without grinding.

B.—A solution of 20 g of potassium permanganate in 250 ml of water was stirred at room temperature with 10 g of activated carbon for 16 hr. Filtration and drying as in A gave 26.5 g of the air-dried or 22.2 g of the oven-dried oxidant.

Registry No.—Manganese dioxide, 1313-13-9; carbon 7440-44-0.

(7) Since it was on the shelf at the time this work was initiated, we have generally used activated carbon supplied by the J. T. Baker Co., Phillipsburg, N. J. Unfortunately this material, which proved to be the most active of all the carbon samples tested, was subsequently removed from the market. Some commercial samples of activated carbon were completely unreactive toward permanganate under the conditions studied. Of the various carbons tested to date, Nuchar C-190N appeared to give the best results, nearly comparable to those obtained with the J. T. Baker material. In general the "fluffy" carbons are effective whereas the dense ones are not. Effective, although yielding an oxidant less active than that obtained from J. T. Baker or Nuchar C-190N (possibly an advantage in the oxidation of some nitrogen compounds), were the following: Darco G-60 and Mallinckrodt USP. Ineffective were Fisher C-263 and Norit-neutral.
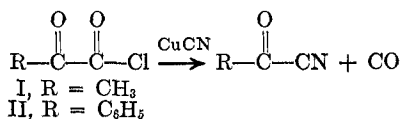

On the Thermal and Free-Radical Reactions of Pyruvyl Chloride and Benzoylformyl Chloride

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During the attempted synthesis of pyruvyl cyanide and benzoyl formyl cyanide from the reaction of the corresponding acyl chlorides (I and II) with cuprous cya-

$$\text{R}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{Cl} \xrightarrow{\text{CuCN}} \text{R}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{CN} + \text{CO}$$

I, R = CH₃
II, R = C₆H₅

nide, a reaction purported to be successful with other acid halides,[2a-c] it was found that only acetyl cyanide or benzoyl cyanide could be obtained. Since both benzoyl

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(1) Postdoctoral Fellow, University of Alberta, 1968–1969.

(2) (a) T. S. Oakwood and C. A. Weisgerber, "Organic Syntheses," Coll. Vol. III, Wiley, New York, N. Y., 1955, p 112; (b) H. Sutter, *Justus Liebigs Ann. Chem.*, **499**, 47 (1932); (c) L. Claisen, *Ber.*, **31**, 1023 (1898).

chloride and acetyl chloride will form acyl cyanides under these conditions,[2] the fragmentation of the corresponding keto acyl chlorides to form their acid chlorides was investigated.

Carbon tetrachloride solutions (0.2 M) of I were shown to undergo a free-radical chain fragmentation to yield acetyl chloride. The fragmentation could be initiated thermally (140°), or, under conditions where the keto acid chloride was stable, I could be converted to its acid chloride by photolysis (40°), by trace initiation with benzoyl peroxide (5%, 98°), or with AIBN (3%, 40°).

On the basis of its initiation by light and by benzoyl peroxide or AIBN the fragmentation reaction can be postulated as a chain sequence[3] (Scheme I).

SCHEME I

In· + CH₃COCOCl ⟶ CH₃COCO· + InCl

CH₃COCO· ⟶ CH₃CO· + CO

CH₃CO· + CH₃COCOCl ⟶ CH₃COCl + CH₃COCO·
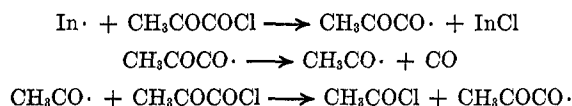
In cyclohexane the reaction took a somewhat different course; not only was acetyl chloride produced but also a series of radical displacement reactions on I yielded as products cyclohexanecarboxylic acid chloride, cyclohexyl methyl ketone, and cyclohexyl chloride (see Table I). In addition to the products listed

TABLE I

PRODUCTS FROM THE INITIATED REACTION OF PYRUVYL CHLORIDE (0.2 M) IN CYCLOHEXANE

Initiator	Temp, °C	CH₃-COCl	C₆H₁₁-COCH₃	C₆H₁₁-COCl	C₆H₁₁Cl
		Products, %			
Benzoyl peroxide (5%)	98	50.3	10.0	39.5	3.0
Light	40	54.3	10.2	35.5	5.0
AIBN (8%)	40	75	3	17	Trace

in Table I, a significant quantity of gaseous material was produced during the reaction. These products could be fractionated by standard vacuum line procedures. Analysis of the gaseous products obtained from the photoinduced reaction of a solution of pyruvyl chloride (1.00 mmol) in cyclohexane (see Table I) showed hydrogen chloride (0.10 mmol), methane (0.41 mmol), and carbon monoxide (1.00 mmol). A combination of the yields of both the gaseous and nongaseous products constituted, within experimental limits, a quantitative material balance for the initial pyruvyl chloride.

On the basis of the products, the excellent material balance obtained, and the trace initiation observed, and by analogy to the reactions in cyclohexane of this system with those of oxalyl chloride[4] and biacetyl,[5] the following chain propagating steps are proposed to rationalize the observed reactions (see Scheme II). The inclusion in the mechanism of the propagation steps contained in Scheme I with those of Scheme II constitutes a plausible explanation for the initiated reactions of pyruvyl chloride in cyclohexane.

The competitive attack of the cyclohexyl radical on the carbonyl adjacent to the electron-donating methyl

(3) The possible inclusion of a chain transfer sequence with solvent has been suggested by the referee to account for the smooth conversion of I to acetyl chloride.

(4) M. S. Kharasch and H. C. Brown, *J. Amer. Chem. Soc.*, **64**, 329 (1942).

(5) W. G. Bentrude and K. R. Darnall, *ibid.*, **90**, 3588 (1968).