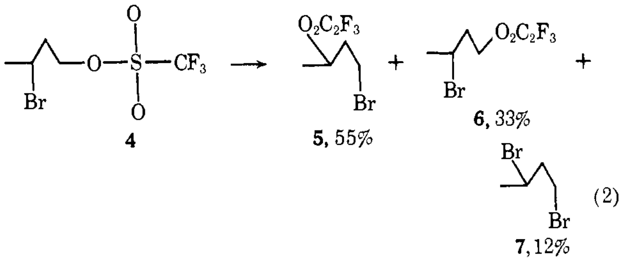
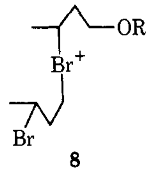
during a deamination of 3-bromo-2,2-bis(bromomethyl)-1-d_2-propylamine perchlorate. A four-membered ring halonium ion intermediate has been postulated in the bromination of a substituted bicyclo[2.2.1]heptane[4a] and in the bromination of bicyclo[2.1.0]pentene.[4b]

Our results for the trifluoroacetolysis of 0.1 *M* bromotriflate at 60° in the presence of 0.125 *M* sodium trifluoroacetate are summarized in eq 2. Also given are relative mole per cent yields, estimated by analysis of time-averaged nmr spectra at 100 MHz of the trifluoroacetic acid solution from solvolysis of 0.1 *M* triflate. Analysis of distilled material (58% yield) gave similar results (eq 2). In addition to the formation of 55% 1,3-halogen shifted product, the presence in the product of substantial amounts of 1,3-dibromobutane (7) was of interest as an unanticipated result. The "disproportionation product" 1,3-butanediol bistrifluoroacetate was shown to be absent. The relative yield of 7 was shown to be independent of the per cent reaction and of the initial concentration of 4. These observations rule out formation of 7 *via* the dialkylhalonium ion 8. Presumably, therefore, 7 is derived from the reaction of 4 with bromide ions in the solution.



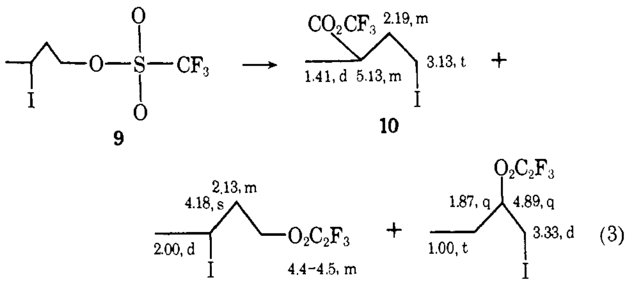
4 5, 55% 6, 33% 7, 12% (2)



8

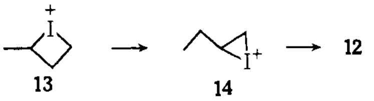
Bromide ions may result from elimination in 4 to give highly reactive allylic bromide or, less likely, *via* the 1,3 cleavage of 4 or cycloreversion of the intermediate halonium ion (suggested by the results of ref 3). The absence of the anticipated products of β cleavage[3] or cycloreversion[3] of the halonium ion intermediate, ethylene bromide, and acetaldehyde, serve to support the first alternative for the formation of 7. Acetaldehyde was stable under the reaction conditions and detectable by nmr at a concentration equivalent to a 2% yield. In support of the postulated origin of dibromide 7, triflate 4 reacted rapidly with tetraethylammonium bromide in trifluoroacetic acid–sodium trifluoroacetate to give 7. Furthermore, the dibromide 7 was stable under the conditions of solvolysis of triflate 4. For the reaction of 4, $t_{1/2}$ was approximately 4 hr. Identification of 6 and 7 was accomplished by glc and nmr analysis, using authentic samples.

The reaction of 3-iodo-1-butyl triflate showed qualitative evidence of modest rate enhancement ($t_{1/2}$ approximately 20 min, 60°). Nmr analysis (100 MHz) of the reaction mixture before or after extraction into CCl_4 surprisingly indicated the presence of a tentatively identified rearranged component 12, in addition to the expected product of iodine shift, 10. The relative mole per cents (nmr analysis) of 10, 12, and 11 were 58, 36, and 6, respectively. A reference sample of 11 was available, but identification of 10 and 12 was based on the clean multiplets observed in early and late platinum spinning band distillation fractions (yield of distillate, 38%), exhibiting increased proportions of 12 and 10, respectively. (*Cf.* nmr data, eq 3.) Gas chromatography of the distillate using stainless steel columns failed. Tentatively, the formation of 12 is ascribed to the rearrangement shown in eq 4.[5]



9 10 (3)

11, s = sextet 12, q = quintet



13 14 → 12 (4)

The time-averaged nmr spectrum (100 MHz) of the products of solvolysis of 3-chloro-1-butyl triflate indicated the presence of only approximately 5% of primary chlorides, possibly a mixture of compounds analogous to 5 and 7. According to the results we have given, the relative halogen reactivity in 1,3 participation is intermediate between that for 1,2 participation (I >> Br >> Cl)[6] and that for 1,4 participation (I ≥ Br ≥ Cl).[7]

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[4] (a) M. M. Avram, I. Pogany, F. Badea, I. G. Dinulescu, and C. D. Nenitzescu, *Tetrahedron Lett.*, 3851 (1969); (b) R. T. Lalonde, *J. Amer. Chem. Soc.*, **87**, 4217 (1965).

[5] For a related case see ref 1c.

[6] (a) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **70**, 821 (1948); (b) E. Grunwald, *ibid.*, **73**, 5458 (1951).

[7] For references see (a) P. E. Peterson, R. J. Bopp, and M. M. Ajo, *ibid.*, **92**, 2834 (1970); (b) P. E. Peterson, *Accounts Chem. Res.*, in press.

[8] (a) Address correspondence to this author after Sept 1, 1971 at: Department of Chemistry, University of South Carolina, Columbia, S.C. 29208. (b) A. B., June 1971.

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Synthesis and Decarbonylation of Pyruvoylpentacarbonylmanganese

Sir:

The carbonylation of $CH_3Mn(CO)_5$ to give $CH_3COMn(CO)_5$ has been extensively studied[1,2] and shown

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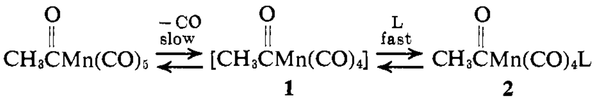
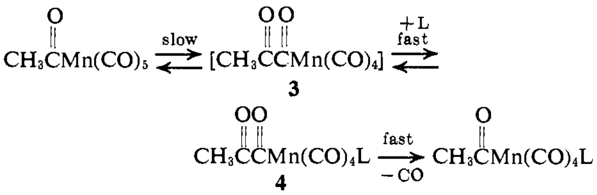
[1] K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10**, 101 (1967).

[2] K. Noack, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, **7**, 345 (1968), and references therein.

to occur by a methyl-migration mechanism.[1] Presumably, the reaction of other nucleophiles with $CH_3Mn(CO)_5$ to give $CH_3COMn(CO)_4L$ (**2**) also proceeds by a methyl-migration mechanism. On the other hand, reaction of triphenylphosphine with $CH_3COMn(CO)_5$, which follows first-order kinetics, has been proposed to occur by a dissociative mechanism, (1), involving the coordinately unsaturated intermediate **1**.[2] However, an acetyl migration mechanism, (2), analogous to the methyl-migration mechanism and involving the unsaturated pyruvoyl species **3**, is also in agreement with previous data.[1,3,4] The observation that $CH_3{}^{13}COMn(CO)_5$ reacts with $P(C_6H_5)_3$ to give $CH_3{}^{13}COMn(CO)_4P(C_6H_5)_3$ rules out a mechanism involving slow decarbonylation to give $CH_3Mn(CO)_5$ which then rapidly reacts with ligand to give $CH_3COMn(CO)_4L$. The direct displacement of CO by the entering ligand is, of course, inconsistent with the observed first-order kinetics.



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}Mn(CO)_5} \underset{\text{slow}}{\overset{-\text{CO}}{\rightleftarrows}} \underset{\mathbf{1}}{[\mathrm{CH_3\overset{\overset{O}{\|}}{C}Mn(CO)_4}]} \underset{\text{fast}}{\overset{\text{L}}{\rightleftarrows}} \underset{\mathbf{2}}{\mathrm{CH_3\overset{\overset{O}{\|}}{C}Mn(CO)_4L}} \quad (1)$$



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}Mn(CO)_5} \overset{\text{slow}}{\rightleftarrows} \underset{\mathbf{3}}{[\mathrm{CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}Mn(CO)_4}]} \underset{\text{fast}}{\overset{+\text{L}}{\rightleftarrows}}$$

$$\underset{\mathbf{4}}{\mathrm{CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}Mn(CO)_4L}} \xrightarrow[-\text{CO}]{\text{fast}} \mathrm{CH_3\overset{\overset{O}{\|}}{C}Mn(CO)_4L} \quad (2)$$

In studying the possibility of mechanism 2, we have prepared $CH_3COCOMn(CO)_5$ (**4**, L = CO). Pyruvoyl chloride[5] (6.4 g, 60 mmol) reacted with $NaMn(CO)_5$ (95 ml, 0.62 *M*, 60 mmol) at 0° in tetrahydrofuran under a nitrogen atmosphere to produce a red solution. Evaporation of the solution to dryness followed by sublimation at 25° (0.2 mm) gave a red solid which was further purified by recrystallization from pentane–ether at −78°. The red solid is shown to be pyruvoylpentacarbonylmanganese (**4**, L = CO) (5.27 g, 33% yield, mp 76–77°) by spectral data. The ir spectrum in heptane has three metal carbonyl bands at 2116 (m), 2021 (s), and 2006 cm^{-1} (s) expected for a $Mn(CO)_5$ fragment and two carbonyl bands at 1718 and 1640 cm^{-1} attributed to the two carbonyls of the pyruvoyl group. The nmr spectrum in benzene is a single sharp singlet at δ 1.63. The uv–visible spectrum contains three maxima at 218 (ϵ 31,200), 255 (shoulder, ϵ 12,000), and 477 mμ (ϵ 62). The red color is apparently due to the pyruvoyl chromophore since $CH_3COMn(CO)_5$ shows no long-wavelength absorption, but biacetyl, a yellow compound, has a λ_{max} at 420 mμ (ϵ 19).[6] The mass spectrum (70 eV) contained no parent ion; the most intense peaks in the spectrum were *m/e* (relative intensity) 223 (12), 195 (17), 167 (13), 139 (23), 111 (28), 98 (21), 83 (35), 70 (11), 55 (98), 43 (30), 28 (100). *Anal.* Calcd for $C_8H_3O_7Mn$: C, 36.09; H, 1.13; Mn, 20.68. Found: C, 36.38; H, 1.38; Mn, 20.3

The thermal decomposition of $CH_3COCOMn(CO)_5$ in benzene has been studied by nmr using *p*-di-*tert*-butylbenzene as an internal standard. When the decomposition is carried out in a sealed tube, the products of the reaction are an equilibrium mixture of $CH_3COMn(CO)_5$ and $CH_3Mn(CO)_5$. The decomposition of $CH_3COCOMn(CO)_5$ follows first-order kinetics to over 87% reaction. At 75°, the rate of decomposition of $CH_3COCOMn(CO)_5$ is 21 times slower than the rate of decarbonylation of $CH_3COMn(CO)_5$ in benzene (Table I). The isolation of $CH_3COCOMn(CO)_5$ as a stable compound indicates that structures of this type cannot be intermediates in the substitution reactions of $CH_3COMn(CO)_5$.

Table I. Decarbonylation of Pyruvoylpentacarbonylmanganese[a]

Compound	Rate constant, sec^{-1}	Temp, °C[b]
$CH_3COCOMn(CO)_5$[c]	8.63×10^{-5}	69.0
$CH_3COCOMn(CO)_5$[c]	1.05×10^{-4}	73.0
$CH_3COCOMn(CO)_5$[c]	2.05×10^{-4}	79.5
$CH_3COCOMn(CO)_5$[c]	5.56×10^{-4}	88.0
$CH_3COMn(CO)_5$[d]	2.88×10^{-3}	75.0

[a] All rates were measured in benzene. [b] Temperatures were estimated from the nmr peak separations of ethylene glycol and are accurate to ±0.5°. [c] $\Delta H^{\ddagger} = 25.5 \pm 1$ kcal, $\Delta S^{\ddagger} = -3.4 \pm 2.9$ eu at 79.5°. [d] Rate determined by nmr analysis of aliquots taken from an open system periodically flushed with nitrogen.

An attempt to prepare $CH_3COCOMn(CO)_5$ by carbonylation of $CH_3COMn(CO)_5$ at 258 atm of CO and 80° for 9 hr failed.

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[4] F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, **1**, 118 (1966).

[5] The solution of pyruvoyl chloride in ether was prepared from pyruvic acid and thionyl chloride and contained a small amount of thionyl chloride: P. Carré and P. Jullien, *C. R. Acad. Sci.*, **202**, 1521 (1936).

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A Convenient General Synthesis of Alkyl Hydroperoxides *via* Autoxidation of Organoboranes

Sir:

The low-temperature autoxidation of organoboranes in tetrahydrofuran (THF) solution leads to a diperoxyborate. Following treatment with aqueous hydrogen peroxide, the corresponding alkyl hydroperoxides can be obtained in excellent yield.

Organoboranes undergo a facile autoxidation which may be stoichiometrically controlled to give essentially quantitative conversion into alcohols.[1] The reaction proceeds through the chain-carrying alkylperoxy radicals[2] (eq 1–3). This initial oxidation produces a peroxide, which may either react with a second mole of oxygen (eq 4) or undergo an intermolecular redox reaction[3] (eq 5). In concentrated solutions (~0.5 *M*)

$$R_3B + O_2 \longrightarrow R\cdot + R_2BO_2\cdot \quad (1)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \quad (2)$$

$$RO_2\cdot + R_3B \longrightarrow RO_2BR_2 + R\cdot \quad (3)$$

$$RO_2BR_2 + O_2 \longrightarrow (RO_2)_2BR \quad (4)$$

$$RO_2BR_2 + R_3B \longrightarrow 2ROBR_2 \quad (5)$$

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[3] S. B. Mirviss, *J. Org. Chem.*, **32**, 1713 (1967).