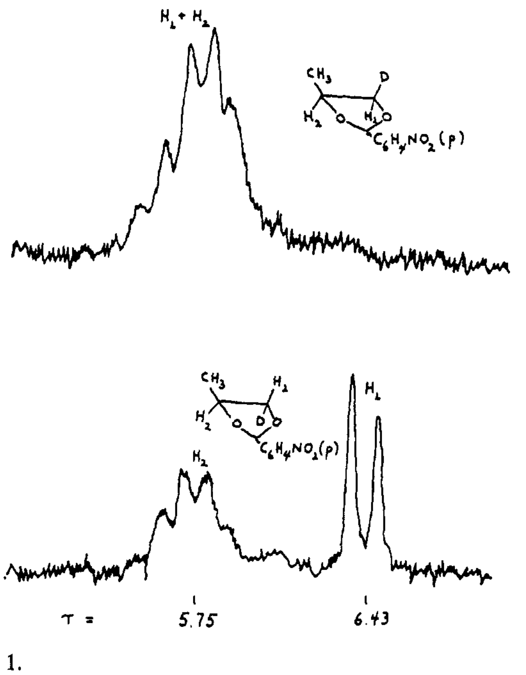
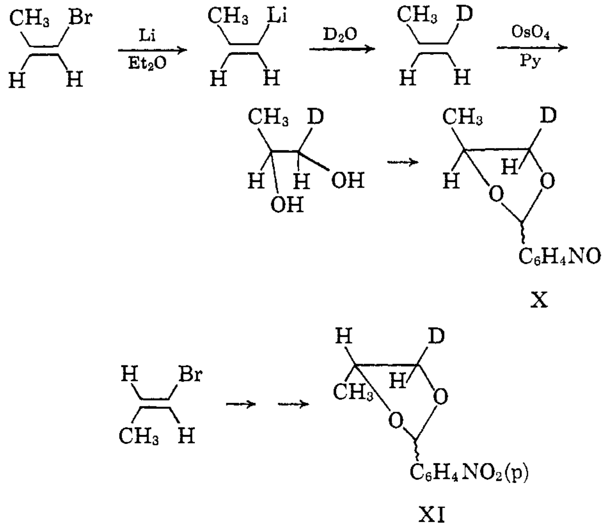


Figure 1.

same as that of VIII′[9] and that of XI as that of IX′, it follows that the absolute configuration at C-1 of VIII and IX is (*R*). As far as product stereospecificity is therefore concerned, lactaldehyde, either D or L, and acetaldehyde have the same substrate–coenzyme relationship (VII and II).



The above results point out the need for further testing the importance of hydrophilic and hydrophobic regions in product stereospecificity control.

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(12) Lubrizol Fellow, 1964–1965.

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A Novel Amination Reaction of Carboxylic Acid Derivatives with Tetrakis(dimethylamino)titanium

Sir:

We wish to report a new reaction in which tetrakis(dimethylamino)titanium (I) converts carboxylic acids and their common derivatives (esters, anhydrides, amides) into orthoamides and ketene N,N-acetals, conveniently and in good yields.

N,N-Dimethylformamide, for example, is converted to the previously unknown[1] tris(dimethylamino)methane ($HC[N(CH_3)_2]_3$, bp 70° (50 mm), $n^{25}\text{D}$ 1.4348), in 83% yield by I at room temperature in ethyl ether in several hours. The structural assignment of the triamine is based on its molecular weight, nmr spectra, and elemental analysis. *Anal.* Calcd for $C_7H_{19}N_3$: C, 57.9; H, 13.2; N, 28.9; mol wt, 145. Found: C, 57.9; H, 13.3; N, 29.3; mol wt (cryoscopy in benzene), 144. The nmr spectrum (benzene solution, TMS internal standard) exhibited sharp singlets at τ 6.98 and 7.69 in the expected ratio of 1:18.

N,N-Dimethylacetamide is converted to 1,1-bis(dimethylamino)ethylene ($CH_2{=}C[N(CH_3)_2]_2$, bp 115° (744 mm), $n^{25}\text{D}$ 1.4500, lit.[2] $n^{20}\text{D}$ 1.4518) in 87% yield under essentially the same conditions as above. *Anal.* Calcd for $C_6H_{14}N_2$: C, 63.1; H, 12.4; N, 24.5; mol wt, 114. Found: C, 62.7; H, 12.1; N, 24.3; mol wt (mass spectroscopy), 114. The nmr spectrum (benzene solvent, TMS internal standard) exhibited sharp singlets at τ 6.60 and 7.53 in the expected ratio of 1:6.

The titanium is converted in both examples to insoluble oxide.

Experiments are in progress to determine the generality of the reaction as a synthetic tool, and a detailed description of this and further work will be reported shortly.

(1) The first authentic member of this series, N,N′,N′′-triphenyl-N,N′,N′′-trimethyltriaminomethane, was reported by D. H. Clemens, E. Y. Shropshire, and W. D. Emmons, *J. Org. Chem.*, 27, 3664 (1962).
(2) H. Bredereck, F. Effenberger, and H. P. Beyerlin, *Chem. Ber.*, 97, 3081 (1964).

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The Oxidation of Water Coordinated to Cobalt(III)

Sir:

Until recently, there have been few systematic investigations of the oxidation of water by metal ion complexes. Some ideas on the mechanism of the oxidation taking account of existing kinetic and thermodynamic data were recently advanced,[1] but the data leave much latitude in the interpretations based on them. In this communication we report the results of some tracer experiments which prove that the water in the first coordination sphere of $(NH_3)_5CoOH_2^{3+}$ can be oxidized. The observations thus fix an important feature of the mechanism, at least in this case.

When, at 50°, a solution of $AgNO_3$ is added to an acidic solution of $K_2S_2O_8$ and $(NH_3)_5CoOH_2(ClO_4)_3$, a small percentage of the Co(III) complex is reduced to

(1) H. Taube, *J. Gen. Physiol.*, 49, 29 (1965).