cyclization procedures,[21,22] furnished authentic N-(1-methoxycyclohexylmethyl)-pyrrolidine in 52% yield, b.p. 130–131° (14 mm.), $n^{25}D$ 1.4806 perchlorate identical with the product (VIa) from V by m.p., mixture m.p., infrared spectrum and paper chromatography. Ethanolysis of 2,2-pentamethylene-1,1-tetramethyleneaziridinium perchlorate (V) by the same procedure yielded (55%) N-(1-ethoxycyclohexylmethyl)-pyrrolidine perchlorate (VIb), m.p. 93–94° (Calcd. for $C_{13}H_{26}ClNO_5$: C, 50.07; H, 8.41; N, 4.49. Found: C, 50.15; H, 8.65; N, 4.44). By reaction of V with ethylenechlorohydrin, and then treatment of the product with sodium hydroxide in water, extraction with ether, and refluxing of the ether extract for 24 hours, the hygroscopic 2,2-pentamethylene-4,4-tetramethylenemorpholinium chloride was obtained and was converted to the perchlorate (VII), m.p. 190–191°, yield 45% (Calcd. for $C_{13}H_{24}ClNO_5$: C, 50.42; H, 7.81; N, 4.52. Found: C, 50.50; H, 7.71; N, 4.48).

By contrast to the alcoholysis of V, the catalytic reduction with platinum oxide in methanol produces major cleavage (70%) at the bond between the quaternary nitrogen and the methylene carbon, giving rise to N-(1-methylcyclohexyl)-pyrrolidine perchlorate (VIII), m.p. 122–123° (Calcd. for $C_{11}H_{22}ClNO_4$: C, 49.33; H, 8.29; N, 5.23. Found: C, 49.45, H, 8.37, N, 5.23), identical with the salt of the compound obtained from methylmagnesium iodide and IV.

In summary, a new route to aziridinium salts has been provided; three-membered rings varying in degree of substitution and reactivity now become readily available; and the chemistry of aziridinium compounds can be studied systematically, with the attendant benefit of wide synthetic utility. Subsequent publications will present these features with detailed examples.

[21] R. C. Elderfield and H. A. Hagemann, *J. Org. Chem.*, **14**, 605 (1949).

[22] A. T. Bottini and J. D. Roberts, THIS JOURNAL, **80**, 5203 (1958).

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A NEW REARRANGEMENT: CATALYTIC ISOMERIZATION OF *m*-DIOXANES TO β-ALKOXY ALDEHYDES

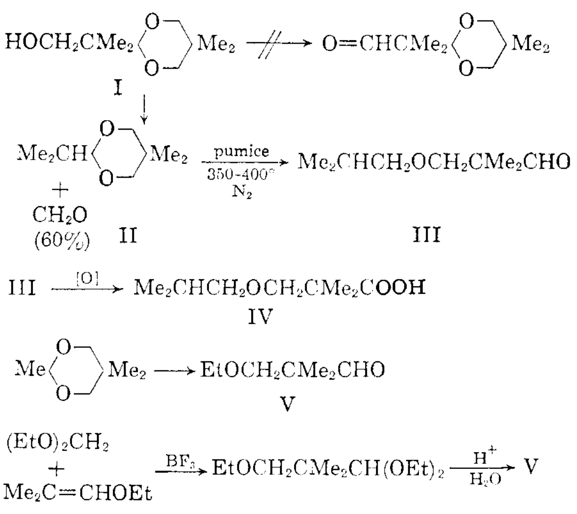
Sir:

2-(Hydroxy-*t*-butyl)-5,5-dimethyl-*m*-dioxane (I) was vaporized through a silver–copper on pumice catalyst[1] in the presence of air at 350° to oxidize the hydroxymethyl group to aldehyde. The expected product was not formed, and I instead was dealdolized to formaldehyde and the known[2] 2-isopropyl-5,5-dimethyl-*m*-dioxane (II). A new compound, isobutoxypivalaldehyde (III) (b.p. 80° (30 mm.), $n^{25}D$ 1.4078), was a significant component of the pyrolyzate. Under the same conditions, pure II was isomerized to III in 56% conversion (90% yield). Use of pumice without metallic additives in a nitrogen atmosphere gave identical results with II, and at higher temperatures conversion became more nearly complete.

The structure of III was demonstrated by analysis (Calcd. for $C_9H_{18}O_2$: C, 68.4; H, 11.4. Found: C, 68.5; H, 11.5), by conversion to the 2,4-dinitrophenylhydrazone (m.p. 124°) (*Anal.* Calcd. for $C_{15}H_{22}N_4O_5$: C, 53.2; H, 6.6; N, 16.5. Found: C, 53.2; H, 6.6; N, 16.4) and the semicarbazone (m.p. 134°) (*Anal.* Calcd. for $C_{10}H_{21}N_3O_3$: C, 55.8; H, 9.8; N, 19.5. Found: C, 56.3; H, 9.7; N, 19.3), and by permanganate or air oxidation to isobutoxypivalic acid (IV) (b.p. 84° (0.7 mm.), $n^{25}D$ 1.4207) (isobutoxypivalamide, m.p. 36°). The acid IV and its amide were identical to independently synthesized samples.

Ethyl hydroxypivalate was alkylated with methallyl chloride[3] in the presence of sodium hydride to generate ethyl methallyloxypivalate (b.p. 94° (16 mm.), $n^{25}D$ 1.4268. *Anal.* Calcd. for $C_{11}H_{20}O_3$: C, 66.0; H, 10.0. Found: C, 65.9; H, 10.2). Reduction of the double bond and hydrolysis yielded IV (b.p. 78° (0.9 mm.), $n^{25}D$ 1.4200. *Anal.* Calcd. for $C_9H_{18}O_3$: C, 62.1; H, 10.3; neut. equiv., 174. Found: C, 62.2; H, 10.3; neut. equiv., 173). Its amide was prepared, m.p. 37°, mixture m.p. with above amide 36–37° (*Anal.* Calcd. for $C_9H_{19}NO_2$: N, 8.1. Found: N, 8.0).

2,5,5-Trimethyl-*m*-dioxane (b.p. 130°, $n^{25}D$ 1.4134. *Anal.* Calcd. for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.6; H, 10.8) was converted by pumice at 390° to 66% of ethoxypivalaldehyde (V) (b.p. 146°, $n^{25}D$ 1.4037. *Anal.* Calcd. for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.0; H, 10.3), which yielded a 2,4-dinitrophenylhydrazone, m.p. 128° (*Anal.* Calcd. for $C_{13}H_{18}N_4O_5$: C, 50.32; H, 5.85; N, 18.06. Found: C, 50.4; H, 5.9; N, 18.0). The aldehyde V was synthesized independently by the boron trifluoride-catalyzed addition of diethyl formal to ethyl isobutenyl ether,[4] which formed 1,1,3-triethoxy-2,2-dimethylpropane (b.p. 100° (33 mm.), $n^{25}D$ 1.4100. *Anal.* Calcd. for $C_{11}H_{24}O_3$: C, 64.66; H, 11.84.



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[1] R. R. Davies and H. H. Hodgson, *J. Chem. Soc.*, 282 (1943).

[2] R. Dworzak and T. M. Lasch, *Monatsh.*, **51**, 67 (1929).

[3] Use of isobutyl iodide in the procedure of L. Marcilly, *Bull. soc. chim. France*, [3] **31**, 119 (1904), for preparing ethoxypivalic acid led to isobutylene by dehydroiodination.

[4] See for example K. C. Brannock, *J. Org. Chem.*, **25**, 258 (1960).

Found: C, 64.7; H, 11.6). Hydrolysis yielded V, the infrared spectrum and dinitrophenylhydrazone of which were identical to those of V prepared by the rearrangement.

An extensive study of the scope of this unusual rearrangement[5] has shown that 5,5-disubstituted *m*-dioxanes are in general converted to α,α-disubstituted-β-alkoxypropionaldehydes in usually excellent yields. Hydrogen atoms at the 5-position are not permissible, since the product of isomerization dissociates to an alcohol and a (substituted) acrolein. The ease of rearrangement depends strongly upon the nature of the groups at C-2 in a manner usually predictable from a mechanism involving acid-catalyzed induction of a positive charge at the acetal carbon followed by intramolecular migration of hydride from C-6 to C-2 and concomitant ring opening. Five- and seven-membered ring acetals do not rearrange but are cleaved to two fragments.

Examination of catalysts other than pumice has shown that weakly acidic substances are active. In particular, a low-surface silica[6] has been most useful in rearranging acetals inert to pumice.

This novel internal oxidation–reduction has provided an efficient synthesis of β-alkoxyaldehydes with no α-hydrogen atoms, a class of compounds hitherto unknown. The chemistry of these new products will be explored.

[5] C. S. Rondestvedt, Jr., THIS JOURNAL, manuscript in preparation.

[6] Davison Chemical Co., Grade 70 silica gel.

CONTRIBUTION NO. 296
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EXCHANGE OF $N^{15}H_3$ BETWEEN SOLVENT AND LIGANDS IN COMPLEX METAL AMMINES[1]

Sir:

Data have been reported for the slow (solvent NH_3)–(ligand NH_3) exchange for chromium and cobalt ammines.[2] As part of a general program of such studies we have investigated the same reactions and others and wish to report preliminary results on some relatively rapid exchanges. Analogous work on the H_2O system has appeared recently.[3]

We have employed a simple flow apparatus for studying the exchange reactions. It consists basically of two hypodermic syringes driven by a synchronous motor, the solutions from each syringe mixing in a "T" stopcock and flowing through variable lengths of glass tubing to the "quencher." All runs were made at −35° or below and quenching was accomplished by allowing the mixed solution to contact glass helices at −190°. Mixing times for similar apparatus have been found by various authors to be *ca.* 0.01 sec. This was confirmed by measurements on the heat evolved in diluting 9 *N* H_2SO_4. The critical velocity for turbulent flow was always exceeded in the runs reported here. N^{15}-Enriched liquid NH_3 was placed in one syringe and an unenriched solution of the metal salt in liquid NH_3 in the other. The entire apparatus was placed in a cold-bath for the run. Care was taken to exclude moisture. Samples for mass spectrometer analysis were obtained by subliming off solvent NH_3 from the "quenched" mixture. Upon removal of all the solvent ammonia from the ammine salt, the salt was treated by the Kjeldahl method and the resulting NH_4^+ converted to nitrogen using a standard hypobromite oxidation. The nitrogen was analyzed isotopically by mass spectrograph in the Chemistry Department of the University of Chicago through the courtesy of Professor H. Taube.

The data reported in the table refer to a reaction of the type

$$\mathrm{M(NH_3)}_x^{+y} + X\mathrm{N^{15}H_3} \rightleftarrows \mathrm{M(N^{15}H_3)}_x^{+y} + X\mathrm{NH_3}$$

The values for X have not as yet been determined in solution so that only half-times for the isotopic exchange of X NH_3 can be given.

TABLE I
$N^{15}H_3$ EXCHANGE RESULTS

Salt used	Salt molality	Temp. (°C.)	$t_{1/2}$ (sec.)
$Cu(NH_3)_4(NO_3)_2$	0.30	−41	0.030
$Cu(NH_3)_4(NO_3)_2$	.18	−42.5	.042
$Cu(NH_3)_4(NO_3)_2$	.15	−50	.16
$Ni(NH_3)_6(NO_3)_2$	.090	−50	.025
AlI_3	.085	−37	1
AlI_3	.085	−37	3
$Al(NH_3)_6I_3$	.072	−35	0.6
$Ag(NH_3)_2NO_3$	.50	−44	< .03

The data cannot be regarded as being at all precise but it is felt that they are reliable to at least an order of magnitude. The results indicate the possibility of determining coördination numbers in liquid ammonia and getting rate data for a variety of metal ions for comparison. Such comparisons are of particular current interest because of predictions that can be made on the basis of crystal-field theory. Work is continuing to improve the precision and to investigate effects of ammonium ion concentration and other details.

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[1] This work supported in part by a grant from the Atomic Energy Commission (Contract No. AT(45-1)-1031).

[2] H. U. D. Wiesendanger, W. H. Jones and C. S. Garner, *J. Chem. Phys.*, **27**, 668 (1957).

[3] H. W. Baldwin and H. Taube, *J. Chem. Phys.*, **33**, 206 (1960).

BIS-DUROQUINONE-NICKEL(0)

Sir:

With respect to general problems connected with the existence of bis-acrylonitrile-nickel(0) and related compounds,[1] the reaction of nickel carbonyl with quinones appeared to be of interest.

Whereas the cyclopentadienone-iron-tricarbonyls[2,3,4] are very stable, the corresponding com-

[1] G. N. Schrauzer, THIS JOURNAL, **81**, 5310 (1959); **82**, 1008 (1960); *Chem. Ber.*, in press.

[2] G. N. Schrauzer, *Chemistry and Industry*, 1403, 1404 (1958); THIS JOURNAL, **81**, 5307 (1959).

[3] W. Hübel, E. Braye, A. Clauss, E. Weiss, U. Krüerke, D. A. Brown, G. S. D. King and C. Hoogzand, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959).

[4] F. A. Cotton and J. R. Leto, *Chemistry and Industry*, 1592 (1958).