

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 rearrangement⁵ 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 silica⁶ 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 AMMINES¹

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

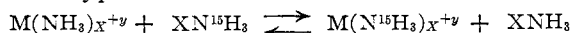
(1) This work supported in part by a grant from the Atomic Energy Commission (Contract No. AT(45-1)-1031).

(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).

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



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. ($^\circ C.$)	$t_{1/2}$ (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 coordination 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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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).

plex of duroquinone⁵ has a comparatively low decomposition temperature. Attempts to prepare a similar complex with *p*-benzoquinone so far were unsuccessful.⁶ The nature of bonding in these complexes has been discussed in terms of molecular orbital theory.⁷

We wish to report the synthesis of the first member of a class of nickel(0)complexes containing quinones as ligands. If duroquinone is refluxed with nickel carbonyl in benzene under nitrogen a red, crystalline substance is formed in good yields. According to analysis, this is bis-duroquinone-nickel, (I): Calcd. for Ni(C₂₀H₂₄O₄): Ni, 15.18; C, 62.05; H, 6.25, mol. wt., 387. Found: Ni, 15.01; C, 61.87; H, 6.28; mol. wt. (ebullioscopic in CH₂Cl₂), 364.

I is completely stable to air and to dilute non-oxidizing acids. It is sparingly soluble in alcohol, benzene, hexane and acetone; moderate solubility permits recrystallization from chloroform and methylene chloride. When heated under the Kofler microscope it remains unchanged up to a temperature of 205°, above which it decomposes without previous melting. When heated in a high vacuum, slow decomposition with partial sublimation starts at temperatures above 160° producing metallic nickel and duroquinone.

The observed diamagnetism ($\chi_m = -176 \cdot 10^{-6}$ cm.³ g.⁻¹)⁸ is in accord with the proposed sandwich-type structure. The infrared spectrum of I shows the C=O absorption at 6.34 μ (KBr).⁹ As in the cyclopentadienone complexes the lowering of the carbonyl frequency is attributed to the presence of dative π -bonds between the metal d-orbitals and the low-lying, unoccupied molecular orbitals of the organic ligands. When *p*-benzoquinone was treated with nickel carbonyl a black, non-crystalline substance of composition Ni(Quinone)₂, (II), was obtained (*anal.* Calcd.: Ni, 21.34. Found: Ni, 21.4). This material starts to decompose at about 150°, yielding nickel and benzoquinone. In contrast to the properties of I, II was found to be insoluble, hygroscopic and paramagnetic (3.31 Bohr magneton). With dilute acids it immediately decomposed, forming Ni((II)-ion and quinhydrone. Consequently, II is to be regarded as a metallic quinhydrone-type compound.¹⁰ Products similar to II were isolated from the reaction of *p*-xyloquinone and naphthoquinone-1,4 with nickel carbonyl. The behavior of these quinones as compared to duroquinone is related to their electron affinities and π -electron densities. Whereas *p*-benzoquinone causes the oxidation of the nickel atom, the introduction of the methyl groups lowers the electron affinity and increases the π -electron densities to such an extent that π -complex formation becomes possible. A detailed de-

scription of this work which currently is being extended will be published elsewhere.

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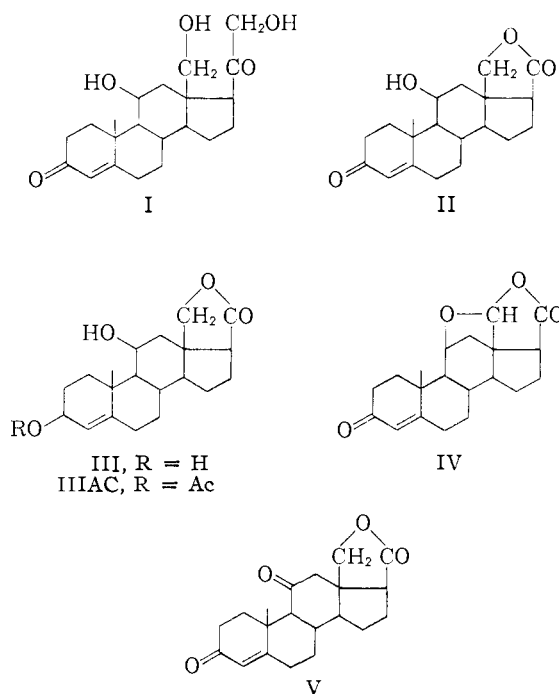
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A NEW C-18 OXYGENATED CORTICOSTEROID FROM BULLFROG ADRENALS

Sir:

The incubation of C¹⁴-progesterone with bullfrog adrenals yielded, in addition to aldosterone,^{1,2} an unknown radioactive substance I, which was considerably more polar ($R_{Aldo} = 0.24$ in toluene-propylene glycol).³ The possibility that the unknown substance might be another C-18 oxygenated corticosteroid was suggested by the quantitative conversion of I to a less polar neutral product (II) with periodic acid.



Compound I (1.2×10^6 c.p.m.) (less than 0.02 mg.) was obtained from the incubation of 4.0×10^7 c.p.m. of progesterone-4-C¹⁴ (0.45 mg.) with adrenal slices from nine bullfrogs (*Rana catesbeiana*), according to the procedure previously described.¹ Oxidation with periodic acid yielded substance II ($R_B = 1.05$ in toluene-formamide). Substance II could not be acetylated with acetic anhydride in pyridine. The reduction of II with excess 0.1 M NaBH₄ in 80% aqueous tertiary butyl

(1) S. Ulick and S. Solomon, *THIS JOURNAL*, **82**, 249 (1960).

(2) In addition to substance I and aldosterone (5% yield) the other products of the incubation were desoxycorticosterone and corticosterone. There was no evidence of 17 α -hydroxylation in this tissue. To be published, S. Ulick, K. Kusch and S. Solomon.

(3) *R* values refer to the distance migrated by the sample on paper chromatograms (run at room temperature) relative to the reference steroid. Radioactive steroids were located with a windowless paper strip scanner and reference steroids with ultraviolet light. Abbreviations for reference steroids: Aldo = aldosterone, B = corticosterone, F = cortisol, DOCA = desoxycorticosterone acetate.

(5) H. W. Sternberg, R. Markby and I. Wender, *THIS JOURNAL*, **80**, 1009 (1958); *Chemistry and Industry*, 1381 (1959).

(6) E. Weiss and W. Hübel, *J. Inorg. Nucl. Chem.*, **11**, 42 (1959).

(7) D. A. Brown, *ibid.*, **10**, 39, 49 (1959).

(8) The magnetic measurements were performed by Mr. A. Sepp, Technische Hochschule at Munich.

(9) The C=C— stretching frequency overlaps with the C=O absorption of duroquinone (6.14 μ); it could not yet be assigned with certainty.

(10) Fe₂(CO)₁₂ also reacts with quinone to produce a black powder of composition Fe(Quinone) ~ 21. Calcd.: Fe, 20.52. Found: Fe, 22.6.