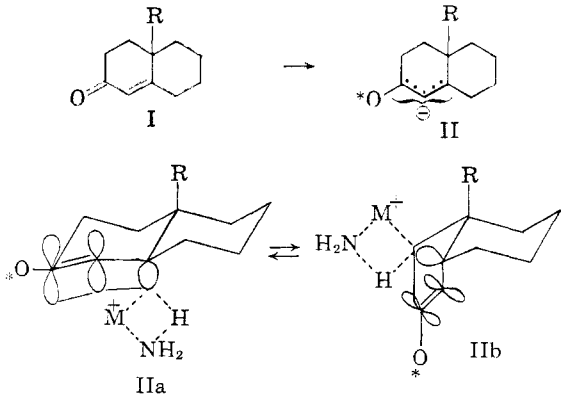
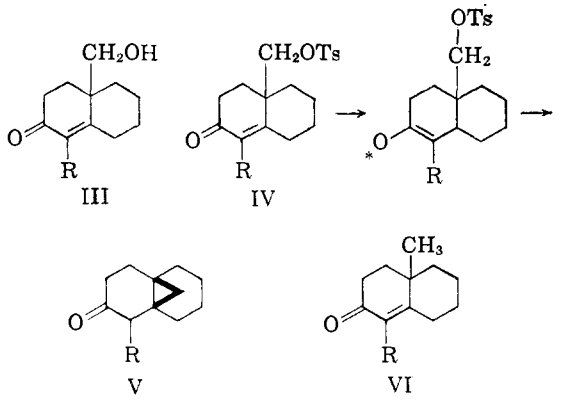


of 10-hydroxymethyl-$\Delta^{1,9}$-2-octalone-2-dioxolane[2] (III, R = H), with toluenesulfonyl chloride in pyridine followed by deketalization with methanolic hydrochloric acid on the steam-bath for fifteen minutes. The tosylate IV thus obtained had m.p. 102–104° after recrystallization from hexane–ethyl acetate (calcd. for $C_{18}H_{22}O_4S$: C, 64.65; H, 6.63. Found: C, 64.67; H, 6.80). Addition of lithium to a solution of IV in tetrahydrofuran and dry liquid ammonia, then addition of ammonium chloride and isolation, gave a 45% yield of V, R = H, b.p. (bath) 75–78° (0.4 mm.). This gave, under mild conditions, the corresponding orange 2,4-dinitrophenylhydrazone, m.p. 155–157°; $\lambda_{max}^{CHCl_3}$ 366 mμ, ε 20,400. (Calcd. for $C_{17}H_{20}N_4O_4$: C, 59.29; H, 5.85. Found: C, 58.91; H, 5.74.) The structure of V follows from its infrared spectrum which shows a saturated carbonyl group,



from the n.m.r. spectrum which shows the expected proton resonance at $\tau \cong 9.7$ and by the acid catalyzed rearrangement of V on heating with aqueous acetic acid containing sulfuric acid. The rearrangement converted V completely into an α,β-unsaturated ketone, as shown by infrared spectra, and the product was identified as 10-methyl-$\Delta^{1,9}$-octalone (VI, R = H) by mixed melting point of its 2,4-dinitrophenylhydrazone, m.p. 168–169°, with a sample made from authentic material (reported[3] m.p. 169°).

In a similar fashion the tosylate of IV (R = CH_3)[4] m.p. 81–82° (calcd. for $C_{19}H_{24}O_4S$: C, 65.50; H, 6.94. Found: C, 65.33; H, 6.88) was reduced with lithium in anhydrous ammonia to give around 50% of V, R = CH_3 identified as its 2,4-dinitrophenylhydrazone, m.p. 125–127°, $\lambda_{max}^{CHCl_3}$ 363 mμ, ε 23,100 (calcd. for $C_{18}H_{22}O_4N_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 60.70; H, 6.31; N, 15.58). The structure of V, R = CH_3, was confirmed as before by its n.m.r. spectrum which showed again the presence of the cyclopropane hydrogens in addition to the split methyl peak. Rearrangement of V, R = CH_3, with acid as above transformed it into the expected 1,10-dimethyl-$\Delta^{1,9}$-2-octalone (VI, R = CH_3) identified as its 2,4-dinitrophenylhydrazone, m.p. 199–200° undepressed by an authentic specimen.[5]

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CARBONYL AND HYDRIDO-CARBONYL COMPLEXES OF IRIDIUM BY REACTION WITH ALCOHOLS. HYDRIDO COMPLEXES BY REACTION WITH ACID

Sir:

Evidence has been presented recently[1] that iridium halides react with triphenylphosphine (or related ligands) in alcohols to yield hydrido complexes, $[IrHX_2L_3]$, and, at higher temperatures, $[IrH_2XL_3]$, rather than simple adducts which might be expected from these environments. We now find that on further treatment of these reaction mixtures the interaction with the solvent proceeds to give hydrido-carbonyl and carbonyl complexes, the subjects of the present communication. The new types of iridium compounds (see Table I) are diamagnetic, non-electrolytes and stable in air.

TABLE I

Compound	Color	M.p., °C. (dec. in vac.)	Infrared spectrum ($cm.^{-1}$)[a] ν_{Ir-H}	$\nu_{C=O}$
$[IrCl(CO)(Ph_3P)_2]$	Lemon yellow	323–325	...	1944
$[IrBr(CO)(Ph_3P)_2]$	Yellow	318–320	...	1947
$[IrHCl_2(CO)(Ph_3P)_2]$	White	315–320	2245[b]	2030
$[IrHBr_2(CO)(Ph_3P)_2]$	Light yellow	348–351	2230	2030
$[IrHCl_2(CO)(Ph_2As)_2]$	Light yellow	249–252[c]	2200	2020

[a] ±5 $cm.^{-1}$, halocarbon mull. [b] Deuteride, 1603 $cm.^{-1}$; ν_{Ir-H}/ν_{Ir-D} = 1.40; calcd., 1.41. [c] In air.

$[IrCl(CO)(Ph_3P)_2]$ has been synthesized from $IrCl_3 \cdot (H_2O)_x$ or $(NH_4)_2IrCl_6$, triphenylphosphine (10–20 moles) and these alcohols (temperature, time and yield refer to best results): aqueous 2-(β-methoxyethoxy)-ethanol, 190°, 2 hr., 86%; ethylene glycol, 190°, 7 hr., 75%; diethylene glycol, 240°, 2 hr., 76%; triethylene glycol, 270°, 4 hr., 83%. (*Anal.* Calcd. for $IrClP_2C_{37}H_{30}O$: Ir, 24.6; Cl, 4.5; P, 7.9; C, 57.0; H, 3.9; O, 2.05. Found: Ir, 25.0; Cl, 4.1; P, 8.2; C, 57.6; H, 4.1; O, 2.2.) Preliminary studies of the mechanism of this peculiar reaction indicate that hydrogen is liberated as one of the by-products. The compound has been obtained also, although in low yield, by treating the reactants with aqueous *butanal* at 70° for 2 hr.

The presence of a coördinated CO is shown by the characteristic strong absorption in the infrared spectrum. Carbon monoxide is given off on pyro-

(1) L. Vaska, *J. Am. Chem. Soc.*, **83**, 756 (1961).

lyzing the compound in vacuum. To confirm the origin of this ligand, the complex was synthesized as above except using ^{14}C-ethylene glycol as solvent. The product, processed as described previously,[2] was found to contain 1.06 ^{14}C per formula weight of the compound.

On treatment with dry HCl in ether, $[Ir^{I}Cl(CO)(Ph_3P)_2]$ is rapidly and quantitatively converted to $[Ir^{III}HCl_2(CO)(Ph_3P)_2]$. (*Anal.* Calcd. for $IrCl_2P_2C_{37}H_{31}O$: Ir, 23.5; Cl, 8.7; P, 7.6; C, 54.4; H, 3.8; O, 2.0. Found: Ir, 23.1; Cl, 8.5; P, 7.6; C, 54.7; H, 4.7; O, 2.4.) $[IrBr(CO)(Ph_3P)_2]$ (prepared as described for the chloride) behaves similarly with HBr. An analogous reaction, with $[PtHCl(Et_3P)_2]$, has been mentioned before,[3] but the product was unstable and not sufficiently characterized. This noteworthy reaction is being tested on other (low valent) transition metal complexes with the view to synthesizing new types of hydrides, including paramagnetic ones.

$[IrHCl_2(CO)(Ph_3P)_2]$ was detected (but not obtained pure) in some of the experiments leading to $[IrCl(CO)(Ph_3P)_2]$, notably when the reactants were refluxed in diethylene or triethylene glycols for longer periods than indicated above. With triphenylarsine, on the other hand, the corresponding compound (Table I) was obtained by heating the reactants in ethylene glycol to 170°.

According to their X-ray diffraction patterns, the carbonyl hydrides (Table I) are isomorphous with each other. The same is true for $[IrX(CO)(Ph_3P)_2]$ which are isomorphous also with $[RhCl(CO)(Ph_3P)_2]$.[4,5] For the latter, a *trans* configuration has been suggested on the basis of dipole moment, 3.15 *D*.[4] Preliminary measurements on $[IrCl(CO)(Ph_3P)_2]$ gave $\mu = 3.9$ *D*, which, altogether, indicates *trans* structures for the iridium compounds.

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NYSTATIN. II. THE STEREOCHEMISTRY OF MYCOSAMINE[1]

Sir:

Mycosamine, the amino-sugar moiety obtained by the hydrolysis of several of the polyene antifungal antibiotics including nystatin,[2] amphotericin B[2] and pimaricin,[3] has been shown to be a 3-amino-3,6-dideoxy-D-aldohexose.[1] Degradative studies as well as the preparation of certain new derivatives[4] have indicated that the stereochemistry of mycosamine is that of D-mannose. Confirmatory evidence for this configurational assignment has now been obtained by the following synthesis of mycosamine derivatives.

Methyl 3-amino-3-deoxy-α-D-mannopyranoside was synthesized from glucose by the ingenious method of Baer and Fischer[5] and converted with acetic anhydride in methanol to methyl 3-acetamido-3-deoxy-α-D-mannopyranoside (I, m.p. 242.5–243.5°, $[\alpha]^{23}D$ +17° (*c*, 1.1 in water); calcd. for $C_9H_{17}O_6N$: C, 45.95; H, 7.29; N, 5.95; OCH_3, 13.19. Found: C, 45.94; H, 7.22; N, 5.93; OCH_3, 13.48). Tosylation of the primary hydroxyl group at C_6 with 1.1 equivalents of tosyl chloride in pyridine and subsequent acetylation with acetic anhydride yielded an amorphous product which was converted in good yield, by heating with sodium iodide in acetone, to the crystalline methyl 2,4-diacetyl-3-acetamido-6-iodo-3,6-dideoxy-α-D-mannopyranoside (II, m.p. 196.5–197.5°, $[\alpha]^{22}D$ +22° (*c*, 1.0 in ethanol); calcd. for $C_{13}H_{20}O_7NI$: C, 36.38; H, 4.70; N, 3.26; I, 29.57; OCH_3, 7.23. Found: C, 36.18; H, 4.82; N, 3.28; I, 29.59; OCH_3, 7.40).

Reductive dehalogenation of II with hydrogen and Raney nickel yielded methyl 2,4-diacetyl-3-acetamido-3,6-dideoxy-α-D-mannopyranoside (III, m.p. 139–141°, $[\alpha]^{23}D$ +31 ± 2° (*c* 1.0 in ethanol): calcd. for $C_{13}H_{21}O_7N$: C, 51.48; H, 6.98; N, 4.62; OCH_3, 10.23. Found: C, 51.42; H, 6.79; N, 4.32; OCH_3, 10.36).

The properties of this compound, including the infrared spectrum, proved to be identical with those of methyl 2,4,N-triacetylmycosaminide (m.p. 140–141°, $[\alpha]^{23}D$ +33 ± 2° (*c*, 1.0 in ethanol); calcd. for $C_{13}H_{21}O_7N$: C, 51.48; H, 6.98; N, 4.62; OCH_3, 10.23. Found: C, 51.32; H, 6.86; N, 4.46; OCH_3, 10.44) prepared from the known methyl-N-acetylmycosaminide[1] by acetylation with acetic anhydride in pyridine.

O-Deacetylation of synthetic III with sodium methoxide in methanol afforded methyl 3-acetamido-3,6-dideoxy-α-D-mannopyranoside (m.p. 168–170°, $[\alpha]^{23}D$ +45 ±2° (*c*, 1.1 in ethanol); calcd. for $C_9H_{17}O_5N$: OCH_3, 14.15. Found: OCH_3, 14.51) identical in every respect with methyl-N-acetylmycosaminide (m.p. 168–170°, $[\alpha]^{23}D$ +47° (*c*, 0.9 in ethanol) prepared from mycosamine.[1]

In view of the incontestable evidence adduced by Baer and Fischer[5] for the stereochemistry of their synthetic product, and of the unequivocal nature of the above conversion to the 6-deoxy product, the assignment of the D-mannose configuration to mycosamine is secure. The synthetic route also furnishes proof that the methyl mycosaminide derivatives are the α-anomers. It furthermore follows that the 2-acetamido-2,5-dideoxypentose obtained from N-acetyl-mycosamine by periodate oxidation[1] is 2-acetamido-2,5-dideoxy-D-arabinose.

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