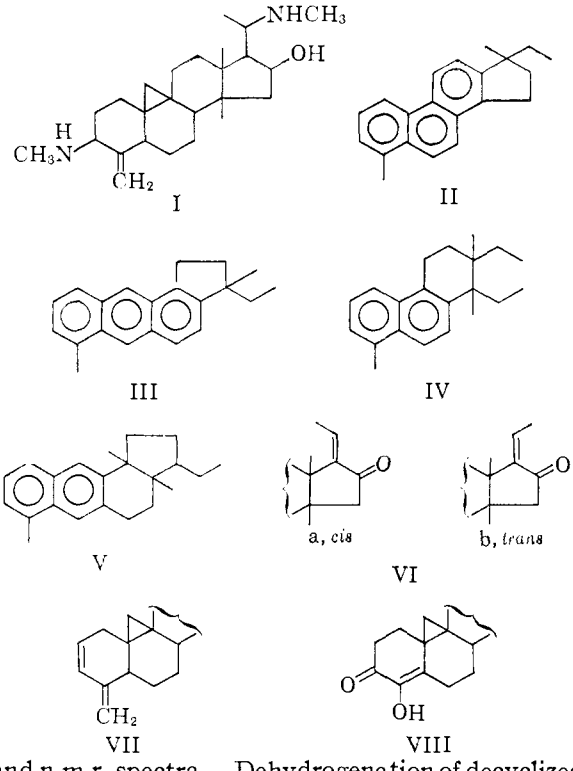

and n.m.r. spectra. Dehydrogenation of decyclized material (in which the cyclopropane had been opened in the usual manner) gave *only phenanthrene-related products.*

Ozonolysis of N,N′-diacyl derivatives[10] gave α-acylamino-ketones which had lost one carbon atom and which gave negative Zimmermann tests.[11] Decyclization of cyclobuxine and various derivatives with hydrogen chloride in chloroform gave mixtures showing n.m.r. peaks for a new tertiary methyl group and a new vinyl hydrogen; the new double bonds resisted hydrogenation. Chromic acid or manganese dioxide oxidation of N,N′-diacyl derivatives of dihydrocyclobuxine gave cyclopentanones (λ_{max} 5.78 μ) showing positive Zimmermann tests. It was not possible to move the double bonds produced by decyclization into conjugation with the keto-groups produced by manganese dioxide oxidation. The oxidation product of dihydrocyclobuxine[12] (N,N′-dibenzoyl derivative, $C_{39}H_{50}O_3N_2$, m.p. 281–283° dec., $[\alpha]^{21}D$ — 53°) rapidly eliminated methylamine in basic solution to give two *cisoid* cyclopentenones (VIa and VIb): λ_{max} 5.85, 6.09 μ; λ_{max}^{EtOH} 244 mμ (ε 7,700); n.m.r. peaks for *cis*[13] isomer, VIa, m.p. 149–152°, 3.53 (1H, quadruplet, *J* 7.5 c./s.; vinyl proton coupled with CH_3), 7.60 (3H, NCH_3), 8.19 (3H, doublet, *J* 7.5 c./s.; vinyl CH_3), 8.68, 9.05 (6H, 2 tertiary CH_3), 9.19 (3H, doublet, *J* 7 c./s.; secondary CH_3), and 9.34 and 9.67 τ (2H, cyclopropyl methylene); n.m.r. peaks for *trans* isomer, VIb, m.p. 134–137°, 4.35 (1H, quadruplet, *J* 7 c./s.), 7.62 (3H), 7.92 (3H, doublet, *J* 7 c./s.), 8.77 (3H), 9.08 (3H), 9.21 (3H, doublet, *J* 7 c./s.), and 9.33 and 9.69 τ (2H)[14]; dihydro-N-benzoyl derivative, $C_{31}H_{43}O_2N$, m.p. 220–223°. The ketones still gave positive Zimmermann tests.

Hofmann degradation of N,N′-dimethylcyclobuxine monomethiodide,[3] $C_{28}H_{49}ON_2I$, m.p. 224–227° dec., yielded N,N′-dimethylcyclobuxine (10–20%) and VII[3] (70%), $C_{25}H_{39}ON$, m.p. 169–170°, $[\alpha]^{22}D$ + 170°; λ_{max} 3.00, 6.10, 6.25, 11.15, 11.30 μ; λ_{max}^{EtOH} 229.5 mμ (ε 16,600), shoulders at 225, 238 mμ; n.m.r. peaks at 3.60–4.60 (2H, complex splitting; vinyl protons), 5.34 (2H, terminal methylene), 6.06 (1H, octuplet; CHOH), 6.80 (1H, OH), 7.73 (6H, $N(CH_3)_2$), 8.87, 9.03, 9.14 (9H, 3 CH_3, as in N,N′-dimethylcyclobuxine), 9.72 and 9.90 τ (2H, doublets, *J* 4 c./s.; cyclopropyl methylene); *O*-monoacetate, λ_{max} 5.80 μ; tetrahydro derivative,[3] $C_{25}H_{43}ON$, m.p. 161–164°, $[\alpha]^{23}D$ + 36°. VII showed no tendency to aromatize upon chloranil dehydrogenation.

Base treatment of the ozonolysis product of cyclobuxine[12] (dihydrochloride, $C_{24}H_{40}O_2N_2 \cdot 2HCl \cdot H_2O$, dec. > 225°) yielded VIII, a diosphenol showing additional conjugation, λ_{max} 2.91 (strong), 6.04, 6.18 μ; λ_{max}^{EtOH} 296.5 mμ (ε 9,000), $\lambda_{max}^{0.1\,N\,NaOH}$ 343.5 mμ (ε 6,500); triacetate, $C_{29}H_{41}O_6N$, m.p. 245–250° dec., λ_{max} 5.67, 5.78, 5.97, 6.14 μ; λ_{max}^{EtOH} 277 mμ (ε 12,600). The corresponding diosphenol from decyclized cyclobuxine showed λ_{max} 2.91, 6.00 μ; λ_{max}^{EtOH} 277 mμ (base, 322 mμ); triacetate, λ_{max} 5.68, 5.78, 5.96, 6.13 μ, λ_{max}^{EtOH} 247 mμ (ε 12,500).[15,16,17]

(10) Non-acylated derivatives were not attacked by ozone or peracid, indicating the close proximity of an amino function to the double bond.

(11) W. Zimmermann, *Z. physiol. Chem.*, **300**, 141 (1955).

(12) Obtained *via* the N,N′-di-*p*-nitrobenzylcarbamate.

(13) *Cf.* L. F. Fieser and M. Fieser, *Experientia*, **4**, 285 (1948).

(14) The configurations of VIa and VIb were assigned on the basis of the n.m.r. spectra; *cf.* L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960).

(15) *Cf.* the analogous diosphenol from cholesterol, λ_{max}^{EtOH} 278 mμ; acetate, λ_{max}^{EtOH} 247 mμ (L. F. Fieser and R. Stevenson, *J. Am. Chem. Soc.*, **76**, 1728 (1954)), and that from cevagenine, λ_{max}^{EtOH} 278 mμ (base, 320 mμ) (E. Sundt, O. Jeger and V. Prelog, *Chem. and Ind.*, 1365 (1953).

(16) Satisfactory analyses have been obtained for products with cited empirical formulas. We thank Mr. Joseph Alicino, Metuchen, N. J., for the analyses.

(17) We gratefully acknowledge the kind assistance of the Ciba Pharmaceutical Company in procurement and large-scale extraction of plant material, and thank especially Drs. Emil Schlittler, Daniel Dickel and Karl Heusler for their kind interest and co-operation. The investigation was supported in part by research grants from the National Institutes of Health (H-2952 and CY-4500).

(18) Cooperative National Science Foundation Predoctoral Fellow in Chemistry, 1960–1962.

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RECEIVED OCTOBER 26, 1962

π-ALLYL-IRON TRICARBONYL CATIONS

Sir:

We wish to report the preparation of a new series of stable salts of π-allyl-iron tricarbonyl cations. The allyl group previously has been found to function as a π-type ligand in complexes of Mn, Co, Ni, and Pd,[1] also in the covalent molecule methylallyl-chloro-iron tricarbonyl[2] and in the per-

(1) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1601 (1961); R. F. Heck and D. S. Breslow, *ibid.*, **83**, 1097 (1961); J. M. Rowe, *Proc. Chem. Soc.*, 66 (1962); G. Wilke and B. Bogdanovic, *Angew. Chem.*, **73**, 756 (1961), and references contained therein.

(2) F. J. Impastato and K. G. Ihrman, *J. Am. Chem. Soc.*, **83**, 3726 (1961).

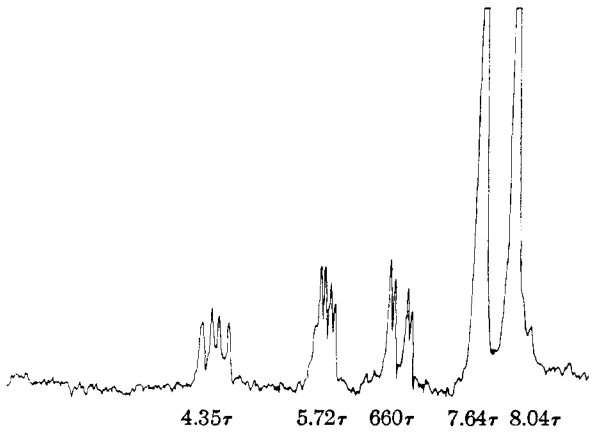
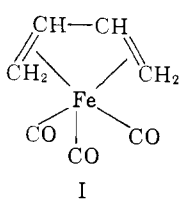


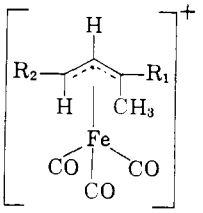
Fig. 1.—N.m.r. spectrum of 1,1-dimethyl-π-allyl-iron tricarbonyl fluoroborate.

fluorocyclohexenyl-iron tricarbonyl anion.[3] In contrast to these latter complexes the effective atomic number of krypton is not attained by iron in the present complexes.

The present series of salts has been obtained by reaction of acyclic diene-iron tricarbonyl complexes with strong acids. Contrary to a recent report,[4] such treatment results in protonation of a double bond already involved in coördination to the metal, rather than protonation on the metal atom. Thus reaction of butadiene-iron tricarbonyl (I) with HBF_4, $HClO_4$, or $HSbCl_6$ in nitromethane gives rise to the corresponding salts of the 1-methyl-π-allyl-iron tricarbonyl cation (II, $R_1 = R_2 = H$). (Analysis of the fluoroborate salt, calcd. for $C_7H_6FeO_3 \cdot HBF_4$: C, 29.83; H, 2.51; B, 3.84. Found: C, 29.66; H, 2.67; B, 3.75.) In a similar way the



I

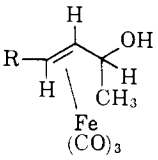


II

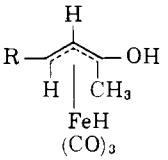
fluoroborate salts of the 1,1-dimethyl-π-allyl-Fe(CO)$_3$ cation (II, $R_1 = CH_3$, $R_2 = H$), the 1,3-dimethyl-π-allyl-Fe(CO)$_3$ cation (II, $R_1 = H$, $R_2 = CH_3$), and the 1-methyl-3-phenyl-π-allyl-Fe(CO)$_3$ cation (II, $R_1 = H$, $R_2 =$ phenyl) have been made from isoprene-iron tricarbonyl, *trans*-piperylene-iron tricarbonyl and 1-phenylbutadiene-iron tricarbonyl, respectively.[5]

All of these salts are pale yellow, crystalline, diamagnetic solids, very soluble in nitromethane and liquid SO_2 but insoluble in non-polar solvents. They each exhibit strong carbonyl absorption frequencies in the infrared at about 2085 and 2150 cm.$^{-1}$, and none at lower frequencies commonly associated with a bridging carbonyl group.[6] Evidence for the structure of the cations is seen in the n.m.r. spectra of the salts taken in SO_2. For example the spectrum of the complex derived from isoprene-iron tricarbonyl is shown in Fig. 1; the two singlet methyl peaks at 764 and 8.04 τ are clearly in accord with structure II ($R_1 = CH_3$, $R_2 = H$) and the other protons are readily assigned from the observed splitting pattern. The methyl group of the complex derived from butadiene-iron tricarbonyl gives rise to a doublet centered at 8.17 τ while those of protonated piperylene-iron tricarbonyl show as two doublets centered at 7.86 and 8.35 τ.[7] This latter result indicates that geometrical inversion does not accompany protonation. The cryoscopic measurements of butadiene-iron tricarbonyl in H_2SO_4 indicate an i-factor of 2.16 ± 0.16. The n.m.r. spectrum of the solution in H_2SO_4 is similar to that of the salt in liquid SO_2 and shows no proton resonance at abnormally high fields indicative of a proton attached to a metal.[4]

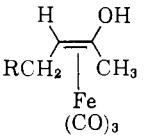
Of further interest are the products obtained after reaction of the salts with water. For example, such treatment of the salt derived from butadiene-Fe(CO)$_3$ gives rise to appreciable quantities of 2-butanone while that derived from *trans*-piperylene-Fe(CO)$_3$ gives 2-pentanone. These products probably result from attack of water to give a substituted allyl alcohol complex (III) and subsequent isomerization, *via* π-allyl-hydroiron tricarbonyl complexes (IV), to enol-Fe(CO)$_3$ complexes (V). The latter are expected to be unstable and would decompose to give the observed products.



III



IV



V

In agreement with this, the salt derived from isoprene-Fe(CO)$_3$ gives mainly dimethylvinylcarbinol; in this instance isomerization cannot occur because of the absence of a hydrogen on the carbon atom bearing the hydroxyl group. Also consistent with this mechanism is the isomerization of allyl alcohol to propionaldehyde observed when the alcohol is heated with Fe(CO)$_5$.

We thank the National Science Foundation and the Robert A. Welch Foundation for financial support.

(3) H. H. Hoehn, L. Pratt, K. F. Watterson and G. Wilkinson, *J. Chem. Soc.*, 2738 (1961).

(4) A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, *Chem. and Ind.*, 553 (1961).

(5) Satisfactory analyses were obtained for these other salts.

(6) Bands observed at 1510–1525 cm.$^{-1}$ may be associated with the π-allyl group; *cf.* reference (1).

(7) N.m.r. spectra were taken at 60 Mc. Peak intensities of olefin and methyl protons, in all cases, were found in the expected ratios.

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RECEIVED SEPTEMBER 4, 1962

THE CONFIGURATION OF CYCLOBUXINE AND ITS INTERRELATION WITH CYCLOEUCALENOL

Sir:

In our previous communication,[1] we proposed structure Ia, exclusive of stereochemistry, for cyclobuxine, the major alkaloid of the acetone-insoluble

(1) K. S. Brown, Jr., and S. M. Kupchan, *J. Am. Chem. Soc.*, **84**, 4590 (1962).