beyond the range of effective coupling with the C–O bending mode, which then appears together with the second C–O mode at *ca.* 676 cm.$^{-1}$. The *uncoupled* Mn–H bending frequency is thus fixed at *ca.* 665 cm.$^{-1}$!

Thus both Mn–H stretching and bending frequencies are established. They are consistent with the *metal-hydrogen bonding limit* of the model of Edgell, Magee and Gallup,[1] and with those of Hieber[5] and Cotton and Wilkinson.[3] While not definitely proven, the above findings imply that the bonding of the hydrogen in $HCo(CO)_4$ and $H_2Fe(CO)_4$ is similar to that in $HMn(CO)_5$ with greater hydrogen–CO coupling.

(5) W. Hieber and F. Leutert, *Z. anorg. Chem.*, **204**, 745 (1932); *Die Chemie*, **55**, 25 (1942).

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$D_{\infty h}$ LIGAND FIELDS AND "SANDWICH" COMPLEXES[1]

Sir:

Numerous molecular orbital treatments of ferrocene and its analogs have been published.[2–7] There is presented here a strong-field, ligand-field model for sandwich-type complexes with the general formula $M^{\mu}(R^{\nu})_2$. Here M^{μ} is a transition metal atom in its μth valence state and R^{ν} is a planar ring carrying a charge ν. The field on M^{μ} from rings R^{ν} is due to the formal charges on the ring and/or virtual charges arising from mutual polarization of M and R. It is assumed that the actual field is adequately reproduced by one of $D_{\infty h}$ symmetry and that the field uncouples the d electrons on the transition metal atom.[8] Since the field is axially symmetric, m remains a good quantum number, the d functions of different |m| are not mixed, and the five d orbitals have at most three different energies. Let $a = r \sin \theta$ be the coördinate perpendicular, and $z = r \cos \theta$ the coordinate parallel to the symmetry axis. The perturbing field contains no odd powers in z because of the symmetry plane through M^{μ}. The field is assumed to be continuous at the origin so that it contains no first power in a. To the second power

$$\begin{aligned} V &= V_0 + V_a a^2 + V_z z^2 \\ &= \{V_0 + V_a(a^2 + z^2)\} - (V_a - V_z)z^2 \end{aligned}$$

The portion of the perturbation in braces is spherically symmetric, produces no d splitting, and is neglected. With hydrogenic orbitals of effective charge Z, $E(e_{2g}) = -3Dd$, $E(e_{1g}) = -9Dd$, and $E(a_{1g}) = -11Dd$, where $Dd = 6(V_a - V_z)(Z/a_0)^2$ is the $D_{\infty h}$ ligand field strength. In Table I are listed the $D_{\infty h}$ electron configurations of some ferrocene analogs assuming $V_a > V_z$ and a formal charge of -1 on each ring. Also listed are the observed paramagnetic moments expressed as number of unpaired electrons.

TABLE I

Species[a]	Assignment ($D_{\infty h}$ field)	Unpaired electrons (obs.)[b]
$(Cy)_2Ti$	$(a_{1g})^2$	0
$[(Cy)_2Mo]^{+2}$	$(a_{1g})^2$	0
$(Cy)_2V$	$(a_{1g})^2(e_{1g})^1$	3
$[(Cy)_2Cr]^+$	$(a_{1g})^2(e_{1g})^1$	3
$(Cy)_2Cr$	$(a_{1g})^2(e_{1g})^2$	2
$[(Cy)_2Fe]^+$	$(a_{1g})^2(e_{1g})^3$	1
$(Cy)_2Mn$	$(a_{1g})^2(e_{1g})^3$	5
$(Cy)_2Fe$	$(a_{1g})^2(e_{1g})^4$	0
$[(Cy)_2Co]^+$	$(a_{1g})^2(e_{1g})^4$	0
$[(Cy)_2Rh]^+$	$(a_{1g})^2(e_{1g})^4$	0
$[(Cy)_2Ir]^+$	$(a_{1g})^2(e_{1g})^4$	0
$(Cy)_2Ru$	$(a_{1g})^2(e_{1g})^4$	0
$(Cy)_2Co$	$(a_{1g})^2(e_{1g})^4(e_{2g})^1$	1
$(Cy)_2Ni$	$(a_{1g})^2(e_{1g})^4(e_{2g})^2$	2

[a] Cy = C_5H_5. [b] Bibliography is given in reference 7.

The predictions agree with experiment except for $(Cy)_2V$, $(Cy)_2Cr^+$, and $(Cy)_2Mn$ which suggest that a weak field treatment may be required. The considerations given here should apply also to the benzene metal complexes. The author is indebted to Professor G. W. Watt for the suggestion of a field theory approach to the problem and for a preliminary correlation of the data.

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(1) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society.

(2) H. H. Jaffé, *J. Chem. Phys.*, **21**, 156 (1953).

(3) W. Moffitt, THIS JOURNAL, **76**, 3386 (1954).

(4) J. D. Dunitz and L. E. Orgel, *J. Chem. Phys.*, **23**, 954 (1955).

(5) E. Ruch, *Rec. Trav. Chim.*, **75**, 638 (1956).

(6) M. Yamazaki, *J. Chem. Phys.*, **24**, 1260 (1956).

(7) A. D. Liehr and C. J. Ballhausen, *Acta Chem. Scand.*, **11**, 207 (1957).

(8) See, for example, W. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, **7**, 107 (1956).

SYNTHETIC STUDIES ON SPHINGOLIPIDS. V. THE SYNTHESIS OF DIHYDROCEREBROSIDES

Sir:

The structure of the cerebrosides has been established by Carter and co-workers[1–3] as Va, in which R is a long-chain fatty acid residue. We wish to report the synthesis of palmitoyl- and stearoyl-dihydrocerebrosides (Vb and Vc).

As key intermediate we employed the substituted *cis*-oxazoline I ($R^1 = CH_3(CH_2)_{14}$).[4] Hydrolysis with diluted hydrochloric acid gave *erythro*-3-O-benzoyldihydrosphinogosine (II), which was not isolated, but was acylated directly in the presence of sodium acetate to give the *erythro* form of the amidoester III. (IIIb: m.p. 74–75.5°; found: C, 76.8; H, 11.8; N, 2.2; IIIc: m.p. 73–75°; found: C, 76.9; H, 11.35; N, 2.0.)

When a benzene solution of III was shaken with tetraacetyl-α-D-galactosyl bromide[5] in the presence of freshly-prepared silver carbonate,[6] a 60% yield of IV was obtained. (IVb: m.p. 43–45°; found: C, 67.9; H, 9.7; N, 1.8; IVc: m.p. 43–45°; found: C, 67.9; H, 9.3; N, 1.6). Saponification

(1) H. E. Carter, O. Nalbandov and P. A. Tavormina, *J. Biol. Chem.*, **192**, 197 (1951).

(2) H. E. Carter and F. L. Greenwood, *ibid.*, **199**, 283 (1952).

(3) H. E. Carter and Y. Fujino, *ibid.*, **221**, 879 (1956).

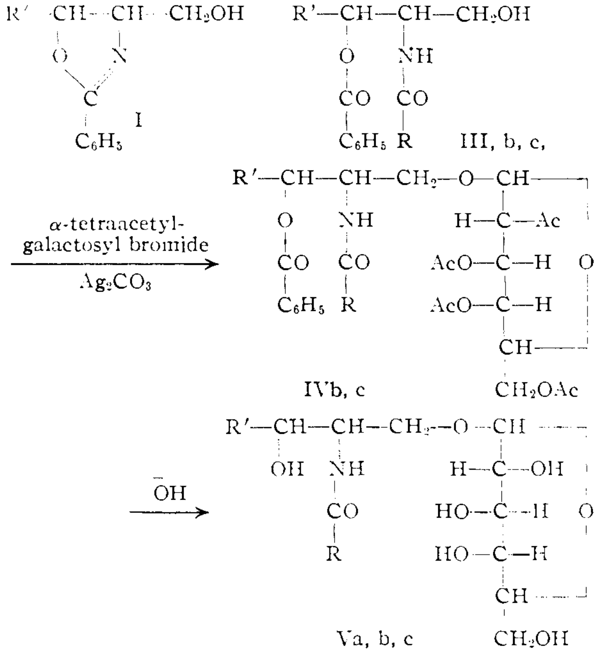
(4) D. Shapiro, H. M. Flowers and S. Spector-Shefer, THIS JOURNAL, in press.

(5) A. Robertson, *J. Chem. Soc.*, 1820 (1929).

(6) W. Koenigs and E. Knorr, *Ber.*, **34**, 957 (1901).

with catalytic amounts of sodium methylate[7] gave a fairly good yield of the dihydrocerebrosides (Vb, c) which were purified by crystallization from either butyl acetate or anhydrous methanol. On heating, both glycosides sintered at about 100° and turned liquid at 125–130°.[8] (Vb: found: C, 68.1; H, 11.4; N, 2.2; galactose (anthrone[9]): 23.9–24.5%; Vc: found: C, 69.1; H, 11.5; N, 2.2).

The infrared spectra of Vb and Vc (pressed in KBr) were essentially identical and showed bands at 3.0, 3.42, 3.52, 6.10, 6.46, 6.80, 7.26, 8.10, 8.56, 8.80, 8.90, 9.30, 9.44, 9.64, 11.18, 11.46, 12.72 and 13.92 μ. This is in good agreement with the spectrum of phrenosin (in KBr) published recently.[10]



a, $R' = CH_3(CH_2)_{12}—CH{=}CH—$
b, $R' = R = CH_3(CH_2)_{14}$
c, $R' = CH_3(CH_2)_{14}$; $R = CH_3(CH_2)_{16}$

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(7) G. Zemplén, *Ber.*, **59**, 1254 (1926).

(8) This relatively low melting point may be due to the presence of a conglomerate of the enantiomorphs rather than a racemic compound, owing to the effect of the D-galactose moiety.

(9) F. A. Loewus, *Anal. Chem.*, **24**, 219 (1952).

(10) A. Rosenberg and E. Chargaff, *J. Biol. Chem.*, **233**, 1323 (1958).

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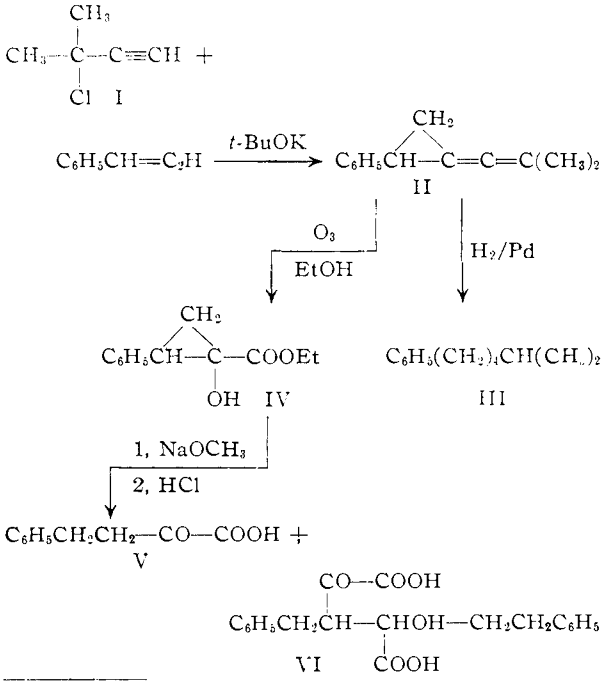
CARBENES FROM *t*-ACETYLENIC CHLORIDES. SYNTHESIS OF ALKENYLIDENECYCLOPROPANES

Sir:

Reactions of ethynyldialkyl carbinyl chlorides with nucleophilic reagents have been investigated.[1,2] Kinetics[1a,b,2] and products[1] of these reactions are rationalized by the formation of an intermediate alkenylidene carbene ($R_2C{=}C{=}C:$).[1] Additional evidence for the carbene intermediate has been obtained by the synthesis of alkenylidenecyclopropanes from reactions of olefins, 2-chloro-2-methyl-3-butyne (I), and base.

Addition of I to a stirred slurry of alcohol-free potassium *t*-butoxide in styrene resulted in a 48% yield of 1-(2-methylpropenylidene)-2-phenylcyclopropane (II). Found: C, 91.71; H, 8.29. The infrared spectrum of II showed the absence of an isolated or conjugated double bond, but exhibited strong absorption at 2050 cm.$^{-1}$, a position intermediate to the normal absorption of allenes and acetylenes.[3] Strong absorption at 1027 cm.$^{-1}$ suggests the presence of the cyclopropane ring.[4] The styrene chromophore was absent in the ultraviolet spectrum. The nuclear magnetic resonance spectrum of II was similar to that of styrene oxide[5] with superposition of the strong methyl absorption.

Hydrogenation of II gave 1-phenyl-5-methylhexane (III). Found: C, 88.05; H, 11.74; diacetamido derivative, m.p. 205–206°. Found: C, 70.21; H, 8.87; N, 9.49. An independent synthesis of III gave a product with identical infrared spectrum and diacetamido derivative. Ozonolysis of II in ethanol yielded acetone (65%), carbon dioxide (3%), a hydroxyester (40%), and a tarry residue. The hydroxyester (IV) is believed to be ethyl 1-hydroxy-2-phenylcyclopropanecarboxylate. Found: C, 70.19; H, 6.89. IV with sodium methoxide at room temperature for two hours gave after acidification benzylpyruvic acid (V) and its aldol condensation product (VI) (76%). Found: C, 67.56; H, 5.74. V (m.p. 36–40°) was oxidized with hydrogen peroxide to β-phenylpropionic acid. VI (m.p. 167–168° dec.) was synthesized independently[6] (mixed m.p. 167–168° dec.); IV would be expected to undergo ring opening readily to give V.[7]



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(1) (a) G. F. Hennion and K. W. Nelson, THIS JOURNAL, **79**, 2142 (1957); (b) G. F. Hennion and D. E. Maloney, *ibid.*, **73**, 4735 (1951); (c) G. F. Hennion and E. G. Teach, *ibid.*, **75**, 1653 (1953).

(2) A. Burawoy and E. Spinner, *J. Chem. Soc.*, 3752 (1954).

(3) L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 48–53.

(4) *Ibid.*, pp. 27–28.

(5) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 48–49.

(6) J. Bougalt, *Compt. rend.*, **155**, 477 (1912).

(7) L. Skattebøl and J. D. Roberts, THIS JOURNAL, **80**, 4085 (1958).