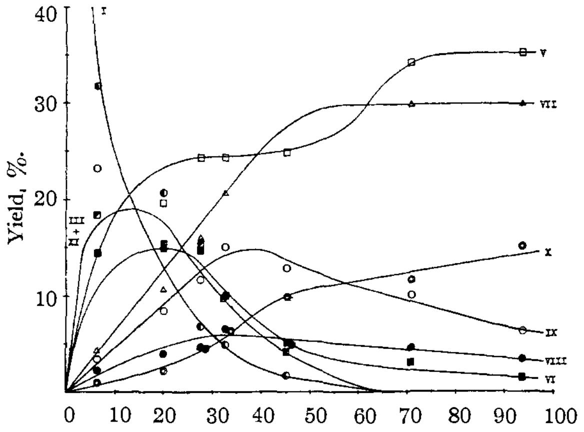

Fig. 1.[11]

(proposed to be (IV)) and α-chigadmarene[6] (proposed to have the constitution of (V)), bulnesol (I) is an attractive biogenetic precursor for these structurally related sesquiterpenoids. Of particular interest is the transannular reaction to yield patchouli alcohol (II), for which there is a laboratory precedent.[7]

We have tried to duplicate these proposed biosynthetic conversions of bulnesol (I) in the laboratory, without enzymes.

To get two bulnesenes by an unambigous route, bulnesyl acetate was pyrolyzed at 275°, giving α-bulnesene (V, 84%) and β-bulnesene (VI, 7%). α-Bulnesene (V, $[\alpha]^{25}D$ 0°) was not identical with α-chigadmarene[6] ($[\alpha]^{28}D$ −150°), but proved to be the same (infrared spectrum, refractive index, optical rotation) as the compound from patchouly oil called "δ-guaiene"[5,8] ($[\alpha]^{20}D$ + 0.3°). The finding that V occurs in the same plant as II lends some credence to the hypothesis that II is formed in nature from bulnesyl carbonium ion.

Bulnesol (I) was treated under a variety of conditions which should favor carbonium ion formation: When bulnesol (I) was refluxed with *p*-toluenesulfonyl chloride in 2,6-lutidine, a mixture of α- and β-bulnesenes (V, 31% and VI, 13%) was obtained. Bulnesol (I) was heated with alumina and pyridine,[9] yielding β-bulnesene (VI, 10%) and β-patchoulene[3] (VII, 60%), the latter identical (infrared, n.m.r., optical rotation, refractive index, vapor phase chromatographic retention time) with an authentic sample from the degradation of patchouli alcohol (II).[10] When bulnesol (I) in acetic acid was treated with a drop of sulfuric acid at room temperature, some double bond migrations were observed; the yields of the major products are shown in Fig. 1. α-Guaiene (VIII) and IX, which we now name β-guaiene, have been described previously[12]; γ-guaiene (X, λ_{max}^{EtOH} 256, ε 8900) and 10-epiguaiol (XI) are new compounds. All three guaienes from this reaction probably are mixtures of epimers at carbon 10.

Thus bulnesol (I) can be converted in the laboratory directly into guaiol (III) and "δ-guaiene" (V), and, since VII has been converted into II,[13] indirectly into patchouli alcohol (II).

A reaction similar to that shown in Fig. 1 was run in AcOD to gain information about double bond migrations during the reaction. The major components of samples withdrawn occasionally were analyzed by combustion (to give % deuterium incorporated) and by n.m.r. (to give information about the location of the deuterium). The guaiol (III) and 10-epiguaiol (XI) isolated after 14 hours contained slightly more than one deuterium each, located (as expected) almost exclusively at C_{10}, since in place of a doublet centered at 9.0 τ for the C_{10} methyl group in each undeuterated alcohol, a single peak at 9.0 τ was observed in each deuterated alcohol. Clearly, the configurations at C_4 and C_7 are largely unchanged in these conversions of I to III and XI. The β-patchoulene (VII) isolated after 14 hours contained 1.4 deuteriums, all but 0.3 of which were in methyl groups; undoubtedly most of the deuterium in this sample is in the *gem*-dimethyl group, and under these conditions the asymmetry at C_4 and C_7 is largely preserved in the I → VII reaction. These experiments, coupled with the demonstration that VII has the same configurations as II at C_4 and C_7,[13] confirm that bulnesol (I), patchouli alcohol (II) and guaiol (III) possess the same configurations at C_4 and C_7.[14]

(4) E. J. Eisenbraun, T. George, B. Riniker and C. Djerassi, *ibid.*, **82**, 3648 (1960); K. Takeda and H. Minato, *Tetrahedron Letters*, **22**, 33 (1960).

(5) F. Šorm, L. Dolejš, O. Knessl and J. Plíva, *Coll. Czech. Chem. Comm.*, **15**, 82 (1950).

(6) A. S. Rao, K. B. Dutt, S. Dev and P. C. Guha, *J. Indian Chem. Soc.*, **29**, 604, 620 (1952); the structure of α-chigadmarene is being reinvestigated (private communication with Dr. S. Dev).

(7) G. Le Ny, *Compt. rend.*, **251**, 1526 (1960).

(8) It is possible that "δ-guaiene" is the enantiomorph of V, but since an overwhelming majority of sesquiterpenoids have the configuration shown in V at their carbon corresponding to C_7 in I, this is quite unlikely.

(9) E. von Rudloff, *Canadian J. Chem.*, **39**, 1860 (1961).

(10) We are grateful to Dr. G. Büchi for authentic samples of II and VII.

(11) Yields were calculated from areas under vapor phase chromatography peaks; each component which was identified was characterized by n.m.r. and infrared. III and XI were not well resolved by vapor phase chromatography, and thus are included together; careful vapor phase chromatography of a sample of the mixture isolated after 14 hours indicated it to contain nearly equal amounts of III and XI.

(12) K. Takeda, H. Minato and S. Nosaka, *Tetrahedron*, **13**, 308 (1961).

(13) Private communication with Dr. G. Büchi and Mr. W. MacLeod.

(14) We gratefully acknowledge the financial support of the Public Health Service (RG-7689).

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RECEIVED FEBRUARY 1, 1962

MAGNETIC ANISOTROPY OF FERROCENE

Sir:

The anisotropy measurements were made by the method of maximum torque originally developed by Krishnan, in which a number of modifications, including those suggested by Gordon,[1] were inincluded. The torsion fibers used in the measurements on the ferrocene crystals were calibrated by means of the known principal susceptibilities and crystal structure of naphthalene and acenaphthene. The field strength of the electromagnet ranged from about 4,000 to 9,000 oersteds.

(1) D. A. Gordon, *Rev. Sci. Instruments*, **29**, 929 (1958).

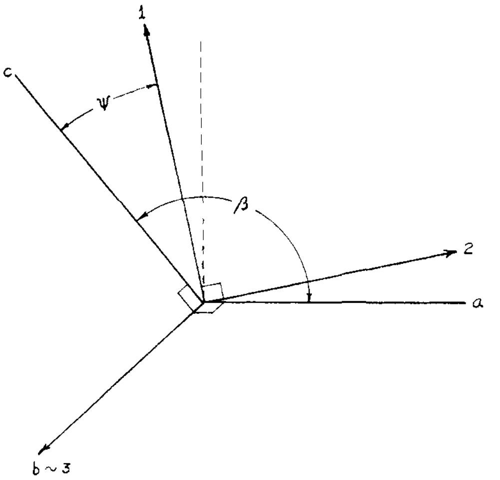

Fig. 1.—Relationship of the crystal axes *a*, *b*, *c*, to the principal magnetic axes: 1, 2, 3.

Single crystals of ferrocene were grown by slow evaporation from appropriate solvents.[2] The crystals were extremely well formed and the mountings were made by sight based on the morphology and X-ray data of the crystals.[3] The size of the crystals used for the measurement varied from about 25 to 165 mg. Measurements were made on fourteen ferrocene crystals using four different quartz fibers. The anisotropies obtained for ferrocene in terms of molar susceptibilities times 10^{-6} c.g.s. units are: $\chi_1 - \chi_2 = 37.0 \pm 0.4$, $\chi_1 - \chi_3 = 40.9 \pm 0.3$, $\chi_2 - \chi_3 = 3.9 \pm 0.3$, $\psi = 24.0° \pm 1°$, where ψ is the angle between the *c*-crystal axis and the direction of χ_1 (Fig. 1). Using the average susceptibility as reported by Wilkinson, *et al.*,[4] the principal susceptibilities are found to be in units of 10^{-6}, $\chi_1 = -99.0$, $\chi_2 = -136.0$, $\chi_3 = -139.9$.

The uncertainties in the anisotropies are average deviations and reflect the internal consistency of the results. Any systematic errors in the calibration of the magnet and of the torsion fibers will add to the absolute error in the final values. The diamagnetic susceptibility of ferrocene is under further investigation in our laboratories.

A preliminary calculation of the principal molecular susceptibilities has been made on the basis of these susceptibility values and crystal structure according to the method worked out by Lonsdale and Krishnan[5] for monoclinic crystals. The molecular axes have been chosen as shown in Fig. 2. All the values are expressed in 10^{-6} c.g.s. units:

$$\begin{array}{lll} K_1 = -105 & K_1 - K_2 = 7 & \\ K_2 = -112 & K_2 - K_3 = 46 & \psi = 22° \\ K_3 = -158 & K_1 - K_3 = 53 & \end{array}$$

The agreement in the ψ values may be regarded as a check on the determined values of the molecular direction cosines and the crystal susceptibilities.

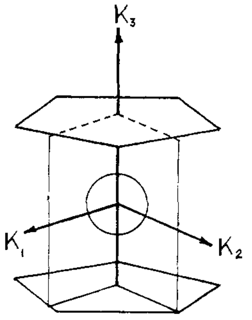

Fig. 2.—Molecular axes for the magnetic anisotropy of ferrocene.

The results clearly show that the contribution to susceptibility at right angles to the plane of the cyclopentadienyl ring (along the K_3 direction) is quite large and may be attributed to the circulation of π electrons in this ring; the anisotropy $\Delta K = 49.5 \times 10^{-6}$. The situation is reminiscent of the large susceptibility at right angles to the plane of the benzene ring, for which $\Delta K = 54 \times 10^{-6}$.

While ferrocene would involve a total of eight π electrons in two different rings,[6] nevertheless the radius of their circulation in each ring probably is reduced. The distance from the K_3 axis to the carbon atoms of ferrocene is approximately 1.2 Å. while in benzene it is 1.39 Å.

According to preliminary calculations the theoretical susceptibility arising from the π electrons in the cyclopentadienyl ring shows the same order of magnitude as the experimental value. However, it appears that the "π-electron current" approach[7,8] in benzene cannot be simply applied to the cyclopentadienyl ring in spite of its aromaticity in the ferrocene molecule. It may be noted that in the ferrocene molecule K_1 is not equal to K_2. While this is generally found to be the case of aromatic systems, the situation is given little attention. However, several factors suggest themselves as possible reasons for this anisotropy: (1) The symmetry of the molecule about the K_2 axis is much greater than about the K_1 axis. (2) The only condition under which K_1 is identical with K_2 is that the ferrocene molecule can be treated as a spherically symmetrical system of atoms together with a non-interacting system of mobile π electrons, which are constrained in orbits of cylindrical symmetry defined roughly by the contour of the rings. This does not seem likely; it is more probable that there is some distortion[9] of the localized electron distribution, which accounts for the anisotropy in the K_1–K_2 plane. It may be noted that in ferrocene the C–C distances are not equal,[3] which is also true of the C–Fe distances.

The experimental values of anisotropy have been used to explain the observed n.m.r. chemical shifts for protons in some derivatives of ferrocene.[10]

(2) Sr. M. E. Fox and L. N. Mulay, *Rev. Sci. Instruments*, **33**, 119 (1962).

(3) J. D. Dunitz, L. E. Orgel and A. Rich, *Acta Cryst.*, **9**, 373 (1956).

(4) G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *J. Am. Chem. Soc.*, **74**, 2125 (1952).

(5) K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc.* (*London*), **156A**, 597 (1936).

(6) W. Moffitt, *J. Am. Chem. Soc.*, **76**, 3386 (1954).

(7) Linus Pauling, *J. Chem. Phys.*, **4**, 673 (1936).

(8) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(9) *Cf.* L. Singh, *Trans. Farad. Soc.*, **54**, 1117 (1958).

(10) This will be published separately.

The details of the experimental method, calculations and a complete discussion of their bearing on the concepts of chemical bonding in ferrocene proposed and discussed by various workers[6,11–13] will be published elsewhere.

The author wishes to thank the Research Corporation and the Monsanto Chemical Co. for supporting this work.

(11) E. O. Fischer, *Rec. Trav. Chim. Pays-Bas*, **75**, 629 (1956); Int. Conf. Coord. Chem. Publication of Chem. Soc., London, 1959, p. 73.

(12) A. Cotton and G. Wilkinson, *Z. Naturforsch.*, **9b**, 453 (1954).

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

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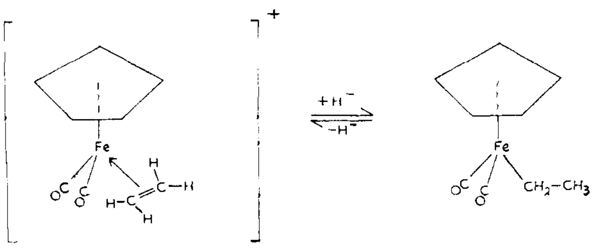
RECEIVED FEBRUARY 5, 1962

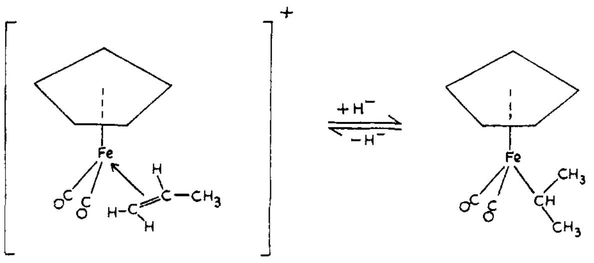
HYDRIDE ADDITION TO SOME π-BONDED OLEFIN-IRON COMPLEXES

Sir:

We have noted previously the abstraction of a hydride ion from some σ-bonded iron–alkyl complexes.[1] We now report that this reaction is *reversible* and that reduction with sodium borohydride of tetrahydrofuran solutions of the cation perchlorates, $[\pi\text{-}C_5H_5Fe(CO)_2CH_2{=}CHR]^+ClO_4^-$ where R = H,Me,[1,2,3] forms σ-alkyl complexes. The cation (I), R = H, gives the ethyl complex (II) in good yields. The product was identified by comparison of the infrared and proton magnetic resonance spectra with those of a sample of the ethyl compound prepared as previously reported.[4] Reduction of the cation (III), R = Me, gives the isopropyl complex (IV) in high yield. The isopropyl complex was identified by the comparison of the spectra with those of characterized samples of the isopropyl and n-propyl complexes prepared by the reaction of the sodium salt, $Na^+[\pi\text{-}C_5H_5\text{-}Fe(CO)_2]^-$ with the propyl halides.[5] No n-propyl isomer was found in the reaction products. The major product of the reduction of the cation $[Mn(CO)_5.\text{propene}]^+$,[5] under similar conditions, was manganese carbonyl. When the reduction of the cation (III) was carried out in the presence of a large excess of 1-hexene and also of butadiene only the isopropyl complex (IV) was formed. It therefore seems reasonable that the reaction proceeds by an internal mechanism rather than by the prior formation of the hydride $\pi\text{-}C_5H_5Fe(CO)_2H$[6] and expulsion of the propene, followed by the addition of the Fe-H across the olefinic double bond. This latter reaction has been shown separately.[5] The reaction may proceed by hydride ion attack either on the metal, as suggested for the reduction of the related cobalticinium cation,[7] or on the cyclopentadienyl group, with transfer from the intermediate cyclopentadiene complex to the ethylenic group,[6] or directly on the ethylenic group.



I II



III IV

Since the propene cation (III) may be prepared readily from the n-propyl complex, $\pi\text{-}C_5H_5Fe\text{-}(CO)_2n\text{-propyl}$,[1] and its reduction gives high yields of the isopropyl complex (IV), the isomerization of the n-propyl to isopropyl may be understood as a simple, two-step hydride removal and addition process. This mechanism is very similar to that put forward recently for the isomerization of olefins on metal surfaces.[8] Also this reversible conversion of alkyl to olefin complexes very clearly bears a strong relationship to the intermediate steps postulated to occur in the hydroformylation, Fischer–Tropsch and related reactions.[8]

Acknowledgments.—We thank the International Nickel Company (Mond) Ltd. for a gift of iron carbonyl, the Ethyl Corporation for a gift of manganese carbonyl and the Hungarian Relief Fund for financial support to P.L.I.N.

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(2) E. O. Fischer and K. Fichtel, *Chem. Ber.*, 1200 (1961).

(3) M. L. H. Green and P. L. I. Nagy, *Proc. Chem. Soc.*, 378 (1961).

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(8) H. W. Sternberg and I. Wender, Int. Conf. Co-ordination Chem. London, 1959. Chem. Soc. Special Publ., No. 13, p. 35, and references therein.

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RECEIVED FEBRUARY 1, 1962

A NEW SYNTHESIS OF BARBITURIC ACIDS

Sir:

We wish to report that the reaction of carbodiimides with substituted malonic acids leads to barbiturates in many instances. Thus, when malonic acid and two moles of N,N′-dicyclohexylcarbodiimide were brought together in tetrahydrofuran solution, an exothermic reaction ensued with the separation of crystalline N,N′-dicyclohexylurea. On filtering off the urea and evaporating the tetrahydrofuran solution, a colorless crystalline compound I, m.p. 200–201°, was obtained in 65% yield (based on the malonic acid). *Anal.* Calcd. for $C_{16}H_{24}N_2O_3$: C, 65.72; H, 8.27; N, 9.58. Found: C, 66.00; H, 8.19; N, 9.39.

Partly on the basis of n.m.r. and infrared spectra, the barbituric acid structure I was assigned to this compound. The correctness of this assignment was later proved by the synthesis of I by the action of malonyl chloride on N,N′-dicyclohexylurea.