by independent synthesis. Diferrocenyl ketone, m.p. 210–211°,[7] was treated with methylmagnesium iodide and the product dehydrated to give *unsym*-diferrocenylethylene, m.p. 162–164° [*Anal.* Found: C, 66.70; H, 5.18], λ_{max} 252 mμ, ϵ_{max} 18,700. The olefin then was hydrogenated to authentic 1,1-diferrocenylethane, whose m.p. (144–146°) showed no depression with the dichloroethane–aluminum chloride product, and whose infrared spectrum was identical to that of the Friedel–Crafts material.

The rearrangement presumably proceeds by the path shown, involving the very stable intermediate cation (II),[8] and is unusual in that the reaction of benzene with 1,2-dichloroethane is reported to proceed, without rearrangement, to give bibenzyl.[9] The great stability of the cation (II) presumably supplies the driving force for the different path taken in the present study.

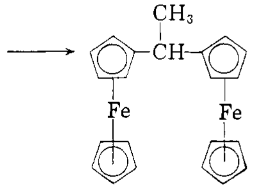
This demonstration of the structure (I) of the simple Friedel–Crafts product renders still more implausible the recently proposed[10] structure (III) for the polycondensate from the same reaction.

$$C_{10}H_{10}Fe + ClCH_2CH_2Cl \xrightarrow{AlCl_3}$$

$$C_{10}H_9Fe{-}CH_2CH_2Cl \xrightarrow{AlCl_3}$$

$$C_{10}H_9Fe{-}CH_2CH_2{}^+AlCl_4{}^- \longrightarrow$$

$$\underset{\text{II}}{C_{10}H_9Fe{-}C^+HCH_3AlCl_4{}^-} \longrightarrow$$



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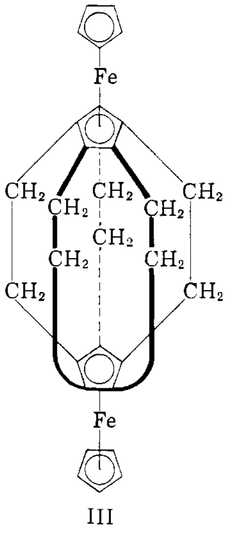

III

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(7) Prepared in 31% yield by an earlier method (R. B. Woodward and E. Csendes, personal communication), from ferrocene, phosgene and aluminum chloride. Woodward and Csendes found m.p. 206–208°.

(8) J. H. Richards and E. A. Hill, THIS JOURNAL, **81**, 3484 (1959).

(9) (a) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, N. Y., 1941, pp. 110, 815; (b) G. S. Kolesnikov, V. V. Korshak and T. V. Smirnova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 172 (1955).

(10) A. N. Nesmeyanov and N. S. Kochetkova, *Doklady Akad. Nauk S.S.S.R.*, **126**, 307 (1959).

(11) Undergraduate Research Participant, supported by a grant (NSF G-8521) from the National Science Foundation.

DEPARTMENT OF CHEMISTRY AND
CHEMICAL ENGINEERING KENNETH L. RINEHART, JR.
UNIVERSITY OF ILLINOIS PAUL A. KITTLE[11]
URBANA, ILLINOIS ALAN F. ELLIS

RECEIVED MARCH 7, 1960

THE π-π* PHOSPHORESCENCE OF CHLOROPHYLLS *a* AND *b*[1]

Sir:

Although the phosphorescence of chlorophyll *b* has been obtained,[2,3] attempts to photograph the phosphorescence spectrum of chlorophyll *a* have not been successful.

Recently, Fernandez and Becker[4] observed the long-lived emission spectra of solutions of dry chlorophylls *a* and *b* at 7550 Å. and 7330 Å., respectively. On the basis of solvent studies concerning both the absorption and emission spectra, the emissions were assigned as phosphorescences arising from transitions from n-π* triplet states.

The present investigation employed both 3-methylpentane and ether–ethanol–hydrocarbon (EPA) solvents. The 3-methylpentane was purified by distillation and chromatography but not dried as by Fernandez and Becker.[4] The chlorophylls *a* and *b* were crystalline, spectroscopically pure samples[5] prepared and analyzed according to Stoll and Wiedemann.[6] The concentrations employed were approximately 2 × 10^{-5} *M*. All samples were degassed and sealed *in vacuo* to prevent air or photoöxidation. Studies were carried out at 77°K. employing two different spectrographs and hyper-sensitized Kodak spectroscopic plates, types M, N and Q. Special attention was given to hyper-sensitization of the plates regarding temperature and ammonia concentration. That is, the temperatures of all solutions were kept at or below 4° and the percentage ammonia was approximately 0.5. This procedure both improves plate sensitivity and decreases background. The improvement is particularly noticeable in plate types M and Q. Light sources were either a high pressure 1 kw. Xe–Hg lamp or a 500-watt projection lamp. Excitation light was selected by means of glass and solution filters or a grating monochromator.

The emission spectrum of chlorophyll *b* consists of two rather poorly resolved bands in the near-infrared region. One band occurs at 8750 ± 50 Å. and the other at 9150 ± 50 Å. The location of the first band differs by approximately 100 Å. from that previously reported.[2] The second band is a new one. The emission extends to approximately 9800 Å. The lifetime of the emission has been determined to be $\geqslant 5 \times 10^{-4}$ second.

The emission spectrum of chlorophyll *a* also appears to consist of two bands but these are even less resolved than for chlorophyll *b*. The first band occurs at 8850 ± 50 Å. and the second band at 9250 ± 50 Å. The emission extends to approximately 10,000 Å. The lifetime of the emission has been determined to be $\geqslant 5 \times 10^{-4}$ second.

It has not been possible to decide whether the two band system represents transitions between different electronic states or between different vibrational states. However, the low energy spacing strongly indicates that the bands are vibrational in origin. The emission intensity of the

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(1) Supported by the Robert A. Welch Foundation.

(2) R. S. Becker and M. Kasha, THIS JOURNAL, **77**, 3669 (1955).

(3) N. Calvin and G. Dorough, *ibid.*, **70**, 699 (1948).

(4) J. Fernandez and R. S. Becker, *J. Chem. Phys.*, **31**, 467 (1959).

(5) Kindly provided by Sandoz Ltd., Basle, Switzerland.

(6) A. Stoll and E. Wiedemann, *Helv. Chim. Acta*, **42**, 679 (1959).

chlorophyll *a* is greater than that of chlorophyll *b*. Moreover, the intensities of the n,π^* phosphorescence[4] and the usual fluorescence are approximately 50 times greater than is the π-π^* phosphorescence reported herein.

In view of these and previous results,[2,4] Franck's[7] assignment of the earlier observed phosphorescence spectrum of chlorophyll b^2 to the n,π^* system does not appear to be valid. We agree with the assignment of Fernandez and Becker[4] and assign the present emissions as phosphorescences arising from transitions from π,π^* triplet states. Further discussion of these and other molecules will appear in the near future.

[7] J. Franck, *Proc. Nat. Acad. Sci.*, **44**, 951 (1958).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF HOUSTON
HOUSTON, TEXAS
INDRA S. SINGH
RALPH S. BECKER

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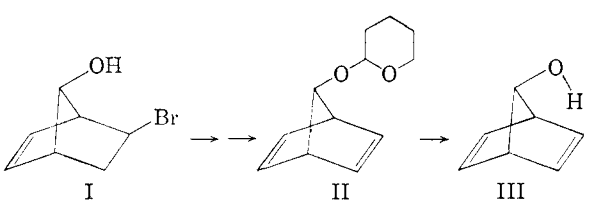
THE 7-NORBORNADIENYL NON-CLASSICAL CATION[1]

Sir:

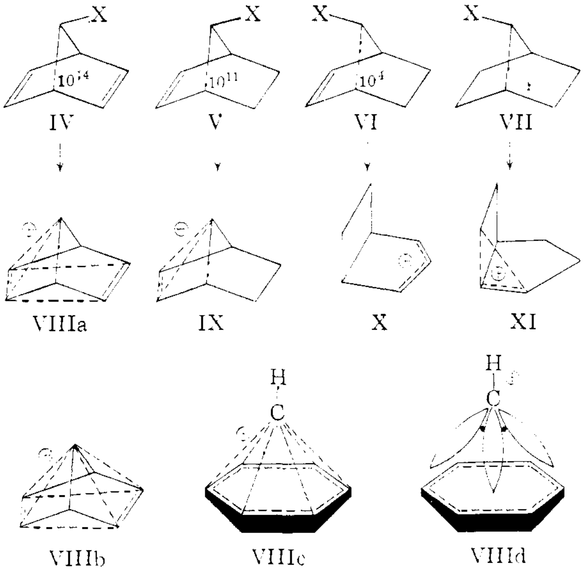
The *anti*- and *syn*-7-norbornenyl systems V[2] and VI[3] represent interesting and instructive examples of neighboring carbon participation in solvolysis. *anti*-7-Norbornenyl *p*-toluenesulfonate[2] (V) is more reactive than the related 7-norbornyl derivative VII in acetolysis by a factor of 10^{11}, the anchimerically assisted ionization leading to cation IX. The isomeric *syn*-isomer[3] VI is more reactive than the 7-norbornyl analog by a factor of 10^4, the allylic cation X being formed. In this connection, 7-norbornadienyl derivatives IV with both *syn*- and *anti*-olefinic groups were obviously of interest, and we have now prepared 7-norbornadienol (III) and have observed the behavior of its derivatives in solvolysis.

The norbornadienol III was prepared from bromohydrin[2] I, m.p. 48°, previously employed in the synthesis of *anti*-7-norbornenol. Treatment of the crude tetrahydropyranyl ether of bromohydrin I with potassium *t*-butoxide in refluxing toluene led to 7-norbornadienyl tetrahydropyranyl ether[4] (II), b.p. 89–90° (1.5 mm.), in high yield. Careful hydrolysis of this material gave rise to 7-norbornadienol (III), b.p. 76° (52 mm.), $n^{25}\text{D}$ 1.5060, homogeneous in vapor phase chromatographic analysis. On hydrogenation the tetrahydropyranyl ether II consumed 1.99 moles, and the 7-norbornadienol (III) 2.00 moles, of hydrogen. This led to a homogeneous alcohol, m.p. 144–145°, identified as 7-norborneol by melting point, vapor phase chromatographic analysis and infrared spectrum.



By standard methods, the 7-norbornadienol was converted to the *p*-nitrobenzoate, m.p. 101–102°, the trichloroacetate, b.p. 112° (3.5 mm.), $n^{25}\text{D}$ 1.5087, and the trifluoroacetate, b.p. 85° (66 mm.), $n^{25}\text{D}$ 1.4095. The 7-norbornadienyl chloride, b.p. 77.5° (63 mm.), $n^{25}\text{D}$ 1.5050, was obtained from treatment of the dienol with thionyl chloride in ether. The infrared spectra of all the 7-norbornadienyl derivatives confirmed the fact that they possessed the IV-structure.

In dilute solution in carbon tetrachloride, 7-norbornadienol (III) displays doublet monomeric O–H absorption in the first overtone region,[5] the two bands[6] being at 1.4110 and 1.4434 μ. The band at longer wave length is probably to be associated with π-hydrogen bonding,[7] and it is noteworthy that the frequency shift is the largest observed in these Laboratories for any analogous cases.



In solvolytic reactivity, the 7-norbornadienyl derivatives have proven to be *ca.* 10^3 times as reactive as the *anti*-7-norbornenyl analogs.[2,8] Thus, the first order rate constant for hydrolysis of 7-norbornadienyl chloride in 80% aqueous acetone at 25.0° is $(6.12 \pm 0.08) \times 10^{-4}$ sec.$^{-1}$, compared to a value of $(8.1 \pm 0.2) \times 10^{-7}$ for a sample of *anti*-7-norbornenyl chloride[8] kindly supplied by Robert Hansen. On this basis, the 7-norbornadienyl system is *ca.* 10^{14} times as reactive as the 7-norbornyl analog! As regards products of solvolysis of 7-norbornadienyl derivatives, only unrearranged 7-norbornadienol (III) in *ca.* 90% yield has been observed as the product from hydrolysis of 7-norbornadienyl chloride or trifluoro-

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[1] This research was supported by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] (a) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, THIS JOURNAL, **77**, 4183 (1955); (b) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

[3] S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

[4] Satisfactory carbon and hydrogen analyses were obtained for the new compounds here mentioned.

[5] R. Piccolini and S. Winstein, *Tetrahedron Letters*, **13**, 4 (1959).

[6] R. Piccolini, unpublished work.

[7] *E.g.*, P. Schleyer, D. S. Trifan and R. Bacskai, THIS JOURNAL, **80**, 6691 (1958).

[8] W. G. Woods, R. A. Carboni and J. D. Roberts, THIS JOURNAL, **78**, 5653 (1956).