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

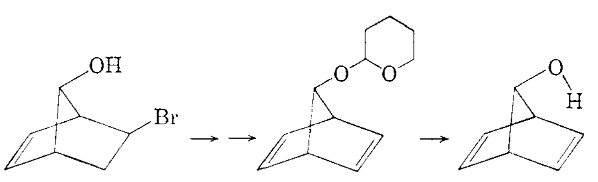
RECEIVED JANUARY 18, 1960

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.

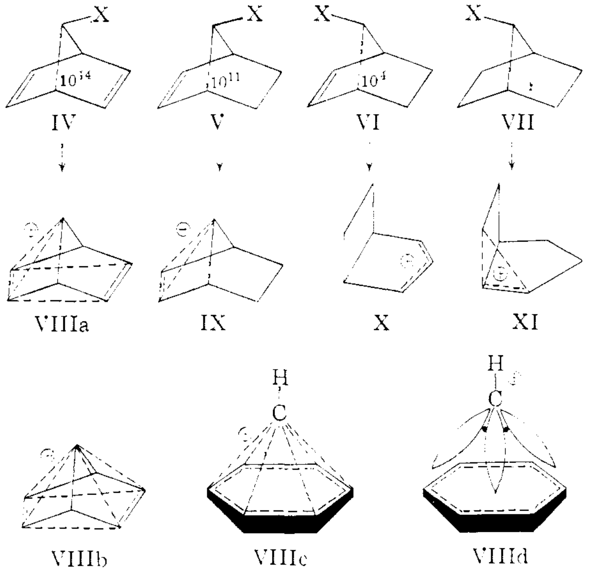
The norbornadienol III was prepared from bromohydrin[2] I, m.p. 48°, previously employed in the synthesis of *anti*-7-norbornenol. Treatment of the crude tetrahydropyranyl ether of bromohydrin I with potassium *t*-butoxide in refluxing toluene led to 7-norbornadienyl tetrahydropyranyl ether[4] (II), 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}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.



I II III

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}D 1.5087, and the trifluoroacetate, b.p. 85° (66 mm.), n^{25}D 1.4095. The 7-norbornadienyl chloride, b.p. 77.5° (63 mm.), n^{25}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).

acetate in 80% aqueous acetone in the presence of sodium bicarbonate at 50°.

It is obvious that the 7-norbornadienyl cation is highly stabilized by non-classical electron delocalization, but it is not yet clear whether it should be depicted as VIIIa, somewhat unsymmetrical and analogous to the *anti*-7-norbornenyl cation[2,8] (IX) except for some electron delocalization from the second olefinic group, or as a symmetrical cation VIIIb. Further, it is not yet clear to what extent the 1,7- and 4,7-bonding electrons are delocalized, with the 7-norbornadienyl cation partaking of the character of VIIIc. In the extreme, the cation could be regarded as a delocalized eight-electron system resulting from the interaction of an approximately tetrahedrally hybridized HC^+: group with a benzene ring (see VIIId). In this extreme, there are six equivalent carbon atoms.[9]

In 96% sulfuric acid, 7-norbornadienol (III) gives a yellow solution, with an ultraviolet absorption band at 350 mμ (ε = *ca.* 5 × 10^3), most probably[10] due to the non-classical cation VIII.

[9] The possibility of this type of geometry, but with different atomic orbital hybridization at the HC:group, was independently suggested by Dr. A. Streitwieser.

[10] *E.g.*, (a) J. A. Grace and M. C. R. Symons, *J. Chem. Soc.*, 958 (1959); (b) G. Leal and R. Pettit, THIS JOURNAL, **81**, 3160 (1959).

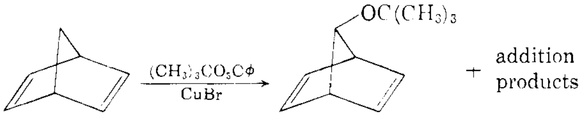
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
LOS ANGELES 24, CALIFORNIA
S. WINSTEIN
C. ORDRONNEAU

RECEIVED MARCH 7, 1960

7-*t*-BUTOXYNORBORNADIENE. A UNIQUE HOMOALLYLIC SUBSTITUTION

Sir:

In the course of experiments designed to study radical formation at C.7 in norbornadiene, *t*-butyl perbenzoate was investigated as a possible radical substitution agent and found to provide a unique reaction. (1) The reaction product is the first reported example of a 7-substituted norbornadiene. (2) In contrast to reactions of *t*-butyl perbenzoate with other olefins in the presence of CuBr,[1] the *t*-butyl ether (I), rather than the benzoate, was obtained as the sole substitution product.



I

t-Butyl perbenzoate has been reported to react with olefins in the presence of CuBr to yield allylic benzoates without rearrangement.[1] Denney, *et al.*,[2] suggested an intermediate complex of *t*-butoxy and benzoyloxy radicals with Cu^{++} and the olefin. The available evidence, however, has not eliminated a possible ionic intermediate.

t-Butyl perbenzoate (24.5 g.) was added to a mixture of norbornadiene (29.8 g.) and CuBr (0.064 g.) in benzene using the general technique of Kharasch, *et al.*[1] After removal of solvent and extraction of 4.9 g. (32%) of benzoic acid, the reaction mixture was distilled to yield 5.4 g. (26%) of 7-*t*-butoxynorbornadiene (I), b.p. 57° (7 mm.), λ_{max}^{hex} 214 mμ (2000). *Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.44; H, 9.78. I also was isolated from the reaction mixture by chromatography on alumina and by vapor phase chromatography.

A viscous oil, whose infrared spectrum indicated a saturated *t*-butoxy benzoate, was isolated from both the distillation residue and the crude reaction mixture by chromatography on alumina.

The infrared spectrum of I was characteristic of the norbornadiene nucleus with an intense absorption at 13.7μ.[3] Even more characteristic of the norbornadiene nucleus was the observed absorption at 6.5μ due to double bond stretching.

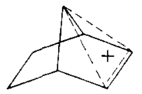
N.M.R. SPECTRA OF NORBORNADIENE[4] AND I[5] IN CCl_4

H	Norbornadiene[a]	I[a]	Peak area ratio, I
Olefinic	3.35	3.56 3.70	4
Bridgehead	6.53	6.77 (essentially unsplit)	2
Bridge	8.05	6.38 (singlet)	1
t-Butyl		8.94	9

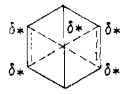
[a] Chemical shift values in p.p.m. relative to tetramethylsilane as 10.00.

I rapidly absorbed 2 molar equivalents of hydrogen to yield a saturated *t*-butyl ether and, like norbornadiene, absorbed oxygen upon standing in air.

It is very likely that the formation of I proceeds by anchimerically assisted hydrogen abstraction to produce a radical at C.7. In view of the structure (II) proposed for the 7-norbornenyl cation,[6] the 7-norbornadienyl radical, assuming sp^2 hybridization, may be represented by III. This concept of the radical is supported by a comparison of the delocalization energies of II and III. The delocalization energy of II has a calculated value of 7.7 kcal.[7] Using the same procedure, III has a delocalization energy of 6.7 kcal.[8]



II



III

Extensions of this reaction are under investigation and, along with more detailed LCAO calculations, will be presented later.

BELL TELEPHONE LABORATORIES
MURRAY HILL, N. J.
PAUL R. STORY

RECEIVED FEBRUARY 19, 1960

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[1] M. S. Kharasch, G. Sosnovsky and N. C. Yang, THIS JOURNAL, **81**, 5819 (1959).

[2] D. B. Denney, D. Z. Denney and G. Feig, *Tetrahedron Letters*, No. 15, 19 (1959).

[3] L. Schmerling, J. P. Luvisi and R. W. Welch, THIS JOURNAL, **78**, 2819 (1956).

[4] G. V. D. Tiers, Minnesota Mining and Manufacturing Co., St. Paul, Minn., compilation of n.m.r. data to be published.

[5] N.m.r. spectrum by Dr. Martin Saunders, Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

[6] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, THIS JOURNAL, **77**, 4183 (1955).

[7] If molecular distortions are considered, the maximum stabilization energy equals 10.5 kcal.; W. G. Woods, R. A. Carboni and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

[8] This value is based on the norbornadiene model. The maximum stabilization energy will be somewhat higher. Unpublished work of Dr. L. C. Snyder, Bell Telephone Laboratories, Murray Hill, N. J.