

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<sup>2,8</sup> (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<sup>+</sup> group with a benzene ring (see VIIIId). In this extreme, there are six equivalent carbon atoms.<sup>9</sup>

In 96% sulfuric acid, 7-norbornadienol (III) gives a yellow solution, with an ultraviolet absorption band at 350 m $\mu$  ( $\epsilon = ca. 5 \times 10^3$ ), most probably<sup>10</sup> 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

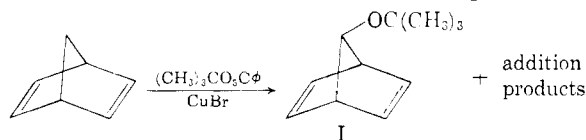
S. WINSTEIN  
C. ORDONNEAU

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#### 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,<sup>1</sup> the *t*-butyl ether (I), rather than the benzoate, was obtained as the sole substitution product.



*t*-Butyl perbenzoate has been reported to react with olefins in the presence of CuBr to yield allylic benzoates without rearrangement.<sup>1</sup> Denney, *et al.*,<sup>2</sup> suggested an intermediate complex of *t*-butoxy and benzyloxy radicals with Cu<sup>++</sup> 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.*<sup>1</sup> After removal of solvent and extraction of 4.9 g. (32%) of benzoic acid, the re-

(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).

action mixture was distilled to yield 5.4 g. (26%) of 7-*t*-butoxynorbornadiene (I), b.p. 57° (7 mm.),  $\lambda_{\text{max}}^{\text{hex}}$  214 m $\mu$  (2000). *Anal.* Calcd. for C<sub>11</sub>H<sub>16</sub>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 13.7 $\mu$ .<sup>3</sup> Even more characteristic of the norbornadiene nucleus was the observed absorption at 6.5 $\mu$  due to double bond stretching.

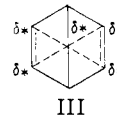
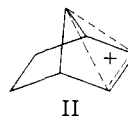
N.M.R. SPECTRA OF NORBORNADIENE<sup>4</sup> AND I<sup>5</sup> IN CCl<sub>4</sub>

H	Norbornadiene <sup>a</sup>	I <sup>a</sup>	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
<i>t</i> -Butyl		8.94	9

<sup>a</sup> 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 anachimerically assisted hydrogen abstraction to produce a radical at C.7. In view of the structure (II) proposed for the 7-norbornenyl cation,<sup>6</sup> the 7-norbornadienyl radical, assuming sp<sup>2</sup> hybridization, may be represented by III. This con-



cept 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.<sup>7</sup> Using the same procedure, III has a delocalization energy of 6.7 kcal.<sup>8</sup>

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

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(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.