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7-Substituted Norbornadienes[1]

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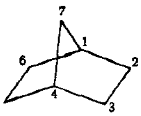
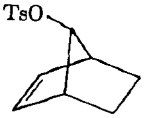
Several 7-norbornadienyl derivatives have been synthesized utilizing the reaction of norbornadiene and *t*-butyl perbenzoate. In addition, *anti*-7-norbornenol and 7-norborneol have been synthesized by a new and shorter route. The possibility of anchimerically assisted hydrogen abstraction from norbornadiene to give an intermediate homoallylic, nonclassical radical is discussed.

In the past few years a number of norbornane derivatives have received wide attention, primarily because the special fixed stereochemistry of the norbornane ring system I allows unusual interactions of functional groups. For example, the ultraviolet spectrum of dehydronorcamphor has been used to demonstrate transannular interaction of the double bond and the carbonyl.[2]

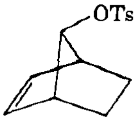
One of the most elegant and extensive investigations involving the norbornane system is that of Winstein. Of particular interest is the demonstration of anchimeric assistance to ionization in the 7-norbornenyl system II.[3] The solvolysis of 7-norbornadienyl derivatives III, which contain the elements of both the *anti* (IIa) and *syn* (IIb) isomers of the 7-norbornenyl system, was of obvious interest and a logical extension of the previous work. Until very recently, however, these compounds were not at all available. 7-Norbornadienyl derivatives were also of interest in connection with their possible thermal isomerization to cycloheptatrienyl analogs. Because of such wide theoretical and synthetic interest the synthesis of these compounds was undertaken.



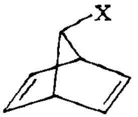
I



IIb

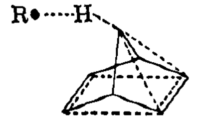


IIa

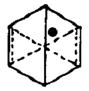


III

A very appealing and direct synthetic method was suggested by the phenomenon of anchimeric assistance to ionization, demonstrated so convincingly in the *anti*-7-norbornenyl case.[3a] If such anchimeric assistance will promote ionization, will it not then promote hydrogen abstraction to give a homoallylic radical? Anchimerically assisted hydrogen abstraction in norbornadiene could proceed as shown in IV. The structure of the resultant radical is still unclear. However, one representation is depicted in V.



IV



V

Although formation of the 7-norbornadienyl radical appeared to be quite reasonable,[1] the problem remained to find a suitable radical initiator which would abstract a hydrogen at C_7 but would not add to the highly strained olefinic system. The two most promising reagents appeared to be *t*-butyl hypochlorite and *t*-butyl perbenzoate. *t*-Butyl hypochlorite has been observed to react quite selectively with allylic systems with little addition to the double bond.[4] *t*-Butyl perbenzoate, in the presence

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[1] A portion of this work, the preparation of 7-*t*-butoxynorbornadiene, has appeared as a preliminary communication. P. R. Story, *J. Am. Chem. Soc.*, **82**, 2085 (1960).

[2] R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).

[3] (a) S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, **78**, 592 (1956). (b) S. Winstein and E. T. Stafford, *J. Am. Chem. Soc.*, **79**, 505 (1957).

[4] C. Walling, B. B. Jacknow, and W. Thaler, Abstracts of Papers, 136th National Meeting, American Chemical Society, Atlantic City, N. J., Sept., 1959, p. 54P.

of cuprous salts, is reported to give good yields of allylic benzoates without addition to the double bond and without rearrangement.[5]

These considerations have led to a new reaction which may prove to be of general application in homoallylic substitution. In this particular case, previously unreported 7-norbornadienyl derivatives have been synthesized.[1] 7-Norbornadienol, recently prepared by a fairly arduous procedure,[6] has also been synthesized. This reaction further provides a shorter route to *anti*-7-norbornenol and 7-norborneol.

RESULTS AND DISCUSSION

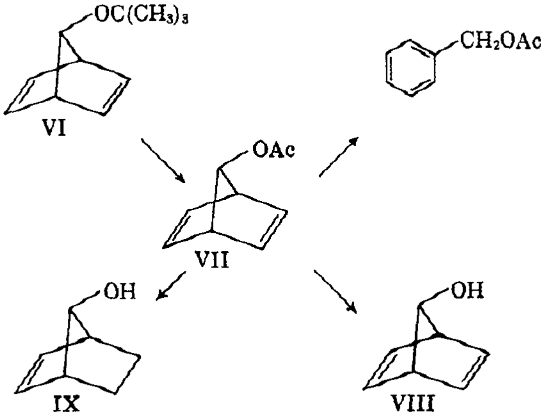
The reaction of *t*-butyl hypochlorite and norbornadiene in benzene resulted only in *t*-butoxy addition products. Possible reaction conditions were by no means exhaustively investigated, however.

t-Butyl perbenzoate and norbornadiene in benzene in the presence of cuprous bromide gave a 25% yield of 7-*t*-butoxynorbornadiene (VI) as the sole substitution product. This product was somewhat surprising since, in all previously reported cases, only the allylic *benzoate* was isolated.[5] There is as yet insufficient evidence to distinguish between several possible mechanisms. Nonetheless, it is quite reasonable to propose that the product arises by anchimerically assisted hydrogen abstraction at C_7. Experiments designed to test this thesis are in progress. It is possible, although reaction conditions make it seem unlikely, that the ether (VI) may not be the initial product but may result from the reaction of 7-norbornadienyl benzoate with *t*-butyl alcohol. Other less likely mechanisms to be considered involve addition of a radical moiety followed by, or concomitant with, rearrangement.

The ether (VI), in concentrated sulfuric acid, gave a yellow solution with maxima at 350 $m\mu$ (ϵ 4200) and 464 $m\mu$ (ϵ 300). The latter absorption accounts for the red color of concentrated solutions. Even though the ether was apparently cleaved in 50–100% sulfuric acid solutions, the corresponding 7-norbornadienol (VIII) could not be isolated on addition of water. On the other hand, perchloric acid cleavage of VI in acetic acid yielded (73%) 7-norbornadienyl acetate (VII). The acetate (VII) was identified by hydrogenation and hydrolysis to the known 7-norborneol and by its NMR spectrum.

VII could be pyrolyzed to benzyl acetate in either the sample inlet of a Beckman GC-2 Gas Chromatograph at 225° or in a 9 in. column packed with glass helices at 375°. Neither benzene nor the expected tropylium acetate could be detected in the pyrolysate. Conditions which will isomerize 7-norbornadienyl derivatives to their cycloheptatrienyl analogs are being sought. Even though no evidence of a carbene intermediate could be detected in the pyrolysis of norbornadiene,[7] the more stable carbenes obtainable from substituted norbornadienes may make such a reaction path more attractive.

The acetate (VII) could not be hydrolyzed to the corresponding alcohol (VIII) by dilute acid or base. Lithium aluminum hydride reduced VII in good yield to the known *anti*-7-norbornenol (IX). Quite analogously, *anti*-7-benznorbornadienyl acetate was reduced by lithium aluminum hydride to *anti*-7-benznorbornenol.[8] Methylmagnesium iodide was successfully used[8] to reduce acetate (VII) to the dienol (VIII) whose structure was established by NMR and by hydrogenation to the known 7-norborneol. The dienol (VIII) appeared to be even more thermally labile than the acetate but could be purified by vapor phase chromatography using a column of Ucon polar on Fluoropak (*vide infra*).



The intramolecular hydrogen bonding in VIII observed by Winstein[6] is dramatically demonstrated by a comparison of the retention times[9] of the dienol (VIII) and IX. Under identical conditions *anti*-7-norbornenol (IX) gave a retention time of fifty-eight minutes compared to fifteen minutes for 7-norbornadienol (VIII); *a factor of nearly 4!*

In summary, the reaction of *t*-butyl perbenzoate and norbornadiene has provided a facile path to a series of compounds of considerable synthetic and theoretical significance. Of no less importance is the question, posed by the reaction product, of the plausibility of homoallylic hydrogen abstraction to give a nonclassical radical intermediate.

EXPERIMENTAL

All melting and boiling points are uncorrected. Microanalyses were performed by Midwest Microlab, Indianapolis,

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[5] M. S. Kharasch, G. Sosnovsky, and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 5819 (1959).

[6] S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960).

[7] W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).

[8] P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).

[9] C. H. DePuy and P. R. Story, *Tetrahedron Letters*, No. 6, 20 (1959).

Ind. Vapor phase chromatographic analyses were performed on a Beckman GC-2 Gas Chromatograph using a 10 ft. × 5/8 in. preparative column packed with 10% by weight Ucon 50-HB-2000[10] on Celite, except in the instance of 7-norbornadienol (VIII), which was purified on a 40 in. × 5/8 in. column packed with 10% Ucon polar on Fluoropak.

TABLE I

NMR Spectra in CCl_4[a]

H	Ether (VI)	Acetate (VII)	Dienol (VIII)
Olefinic	3.56 (m) 3.70 (m)	3.56 (3) 3.72 (m)	3.47 (m)
Bridgehead	6.77 (m)	6.46 (6)	6.62 (m)
Bridge	6.38 (s)	5.55 (s)	6.26 (s)
Other	8.94 (s)	8.14 (s)	conc. dep.

[a] NMR spectra are by Dr. M. Saunders, Department of Chemistry, Yale University, New Haven, Conn. Chemical shift values are in p.p.m. relative to tetramethylsilane as 10.00. Peaks are designated as follows: (s), singlet or unresolved multiplets; (m), multiplet but incompletely resolved; (2), doublet, etc.

Norbornadiene. The Shell Chemical Co. product was carefully fractionated *immediately before use*, b.p. 89.5–90°.

t-Butyl perbenzoate was obtained from the Lucidol Division of Wallace and Tiernan Co. and used without further purification.

t-Butyl hypochlorite was prepared by the method of Teeter and Bell.[11]

Reaction of t-butyl hypochlorite and norbornadiene. A mixture of 5.0 g. (0.054 mole) of freshly fractionated norbornadiene and 6.5 g. (0.06 mole) of *t*-butyl hypochlorite in 100 ml. of benzene under a nitrogen atmosphere was irradiated with an ordinary 100 watt light bulb for 1.5 hr. The yellow color of *t*-butyl hypochlorite was dissipated after 45 min. reaction time. Gradual disappearance of the characteristic double bond stretching absorption of the norbornadiene nucleus and the appearance of bands indicative of a *t*-butyl ether were followed by infrared. Infrared analysis of the product indicated the absence of substituted norbornadienes. The product appeared to be chiefly *t*-butoxy addition compounds.

7-t-Butoxynorbornadiene (VI). To a stirred refluxing mixture of 149 g. (1.62 moles) of freshly fractionated norbornadiene and 0.325 g. (2.3 mmoles) of cuprous bromide in 500 ml. of benzene was added, in a nitrogen atmosphere, a solution of 122.5 g. (0.63 mole) of *t*-butyl perbenzoate in 100 ml. of benzene over a period of 1 hr. After addition was complete, stirring and refluxing were continued for an additional 30 min. The infrared of the reaction mixture indicated that no *t*-butyl perbenzoate remained after this time. After cooling to room temperature, the reaction mixture was extracted with 10% sodium carbonate to remove 23 g. (30%) of benzoic acid, washed with water, and dried. Careful removal of benzene at reduced pressure and distillation of the crude product yielded 26.0 g. (25%) of 7-*t*-butoxynorbornadiene (VI), b.p. 70–72°/14 mm. Variation in addition rate of *t*- butyl perbenzoate and reflux time had no effect on the yield of ether (VI). Infrared (carbon tetrachloride): 6.48 (w), 7.20 (m), 7.35 (s), 7.61 (m), 9.05 (s), 13.7 (s).

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.44; H, 9.78.

VI could also be isolated from the reaction mixture by vapor phase chromatography and by chromatography on alumina. The remainder of the product was a viscous oil, b.p. 127–130°/0.2 mm., whose infrared strongly indicated one or more isomeric *t*-butoxy benzoates.

7-Norbornadienyl acetate (VII). After standing at room temperature for 30 min., a solution of 15 g. (0.092 mole) of ether (VI) in a mixture of 150 ml. of glacial acetic acid and 30 ml. of acetic anhydride was cooled in an ice bath and quickly added to 20.3 g. (0.14 mole) of 70% perchloric acid previously cooled to 0° and placed in an ice bath. The deep red mixture was swirled and allowed to stand in the ice bath for exactly 1 min. It was then poured into a separatory funnel containing about 500 ml. of ice and water. If necessary, more water was added to dissipate the red color. The product, which has a raspberry-like odor, was extracted with dichloromethane. The combined dichloromethane extracts were washed with saturated sodium bicarbonate, water, saturated sodium chloride, and dried over anhydrous sodium sulfate. Infrared and vapor phase chromatographic analysis indicated no starting material remained. Distillation yielded 10.0 g. (73%) of 7-norbornadienyl acetate (VII), b.p. 65°/8 mm. Infrared (neat): 5.74 (s), 6.48 (w), 8.02 (s), 9.57 (s), 13.6 (s).

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.98; h, 6.71. Found: C, 72.18; H, 6.87.

The NMR spectrum was consistent with the structure proposed. The acetate (VII) rapidly absorbed two molar-equivalents of hydrogen over 5% palladium-charcoal in 95% ethanol to yield a saturated acetate. This material was hydrolyzed by dilute potassium hydroxide/ethanol overnight at room temperature and gave an overall 80% yield of 7-norborneol, m.p. 149.5–151° after one purification by vapor phase chromatography. A second purification by vapor phase chromatography gave material melting at 152–153°. The literature[3a] m.p. is 150–151° (from pentane). The *p*-toluenesulfonate of 7-norborneol, prepared in the usual way, melted at 54–55°. The literature[3a] m.p. is 54–55°.

7-Norbornadienol (VIII). To a Grignard reagent, prepared from 2.63 g. (0.11 g.-atom) of magnesium and 14.2 g. (0.1 mole) of methyl iodide in 100 ml. of anhydrous ether, 5.0 g. (0.033 mole) of VII in 100 ml. of ether was added over a period of 15 min. under a nitrogen atmosphere. After addition, the reaction mixture was allowed to stir at room temperature for 1 hr. Water and wet sodium sulfate were added and the ether solution decanted. The remaining salts were washed thoroughly with ether. The ether extracts were combined, washed, and dried. The ether was carefully removed and the product distilled to yield 3.1 g. (86%), b.p. 79°/57 mm., of 7-norbornadienol (VIII). Vapor phase chromatographic analysis at 105° (*vide supra*) indicated the product to be homogeneous. Infrared (carbon tetrachloride) 2.79 (m), 6.48 (w), 7.18 (s), 8.40 (s), 9.25 (s), 13.7 (s).

Anal. Calcd. for C_7H_8O: C, 77.75; H, 7.46. Found: C, 77.99; H, 7.74.

The NMR spectrum was consistent with structure VIII. Pure dienol (VIII) (0.1214 g., 0.0011 mole) rapidly absorbed 1.99 molar-equivalents of hydrogen over 0.1009 g. of 5% palladium-charcoal in 30 ml. of 95% ethanol. Worked up in the usual way, the product, 7-norborneol, was purified by vapor phase chromatography and shown by infrared, vapor phase chromatography and melting point to be identical with the alcohol obtained from VII by hydrogenation and hydrolysis. The *p*-nitrobenzoate of VIII was prepared by a standard method, m.p. 101–102°; reported[6] m.p. is 101–102°.

anti-7-Norbornenol (IX). To a stirred solution of 0.7 g. (0.019 mole) of lithium aluminum hydride in 40 ml. of anhydrous ether under a nitrogen atmosphere was added 2.0 g. (0.013 mole) of VII in 40 ml. of ether over a period of 15 min. After stirring at room temperature for 30 min., water and wet sodium sulfate were added and the product extracted with ether. The combined ether extracts were washed and dried in the usual way. Slow removal of ether

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(10) This material is called Ucon polar. It is available from Union Carbide Chemical Co. and described as a water soluble monoalkyl ether of a mixed polyoxyethylene-oxypropylene.

(11) H. M. Teeter and E. W. Bell, *Org. Syntheses*, **32**, 20 (1952).

yielded 1.40 g. (95%) of solid *anti*-7-norbornenol (IX), m.p. after vapor phase chromatographic purification, 117–118°; reported[8a] m.p. is 117–118°. This material was hydrogenated to 7-norborneol, identical with the 7-norborneol obtained from VII and VIII above.

Pyrolysis of the acetate (VII). Pyrolysis of the acetate (VII) was effected by injecting a sample into the sample inlet of a Beckman GC-2 heated at 225° with a column temperature of 130°. No benzene could be detected among the many volatile products. The chief product, as shown by vapor phase chromatography, infrared and ultraviolet comparison with an authentic sample, was benzyl acetate.

The acetate (VII) could also be pyrolyzed at 375° in a 9 in. column packed with glass helices to give good yields of benzyl acetate. With this apparatus the acetate (VII) was not pyrolyzed at 275°. Pyrolysis at a lower temperature in the gas chromatograph was probably promoted by carbonized materials known to be present in the inlet tube.

Hydrolysis of 7-norbornadienyl acetate (VII). Hydrolysis of the acetate (VII) was attempted under the following conditions with uniformly negative results. In every instance the acetate was hydrolyzed but did not give the alcohol (VIII). In most cases infrared analysis indicated ring opening.

(1) 1*N* hydrochloric acid/50% aqueous methanol at room temperature for 3 hr.

(2) 2*N* hydrochloric acid/H_2O at room temperature overnight.

(3) 1*N* potassium hydroxide/75% aqueous methanol overnight at room temperature under nitrogen.

(4) 1*N* sodium methoxide/methanol at room temperature for 2 hr. under nitrogen.

Acid hydrolysis of the ether (VI) A solution of 0.5 g. (0.003 mole) of ether (VI) in 1 ml. of 50% sulfuric acid (0.018 mole) was allowed to stand at room temperature for 1 hr. Ice and water were added and the product was extracted with dichloromethane. None of the alcohol (VIII) could be detected in the product which appeared to consist chiefly of a saturated diol.

Acknowledgment. The author is deeply grateful to several members of the Chemistry Department and especially to Dr. R. W. Murray for many stimulating discussions and suggestions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SOUTHERN ILLINOIS UNIVERSITY]

Mechanism of the Meerwein-Ponndorf-Verley Reduction[1]

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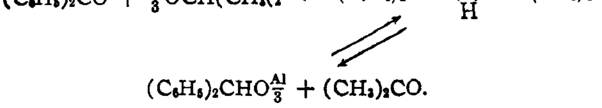
The rate of reduction of benzophenone by aluminum isopropoxide in isopropyl alcohol has been measured at three temperatures and three catalyst concentrations. The reaction is first order in benzophenone and approximately 1.5 order in aluminum isopropoxide. It is suggested that the reaction may proceed by two mechanisms, one the accepted mechanism which involves a cyclic transition state and one mole of aluminum isopropoxide, and a second mechanism which involves a noncyclic transition state and two moles of alkoxide.

The metal alkoxide-catalyzed equilibration of an alcohol and a carbonyl compound (Meerwein-Ponndorf-Verley reduction,[2] Oppenhauer oxidation[3]) has been generally thought to involve a cyclic transition,[4,5] which in the case of benzophenone and isopropyl alcohol can be formulated in the following way:



In support of this mechanism deuterium tracer studies indicate that hydrogen transferred to the carbonyl does come from the carbinol carbon.[6,7] Pickkart and Hancock[8] found a Hammett *rho* constant of 1.296 for the equilibrium between substituted benzophenone and diethylcarbinol. Thus increased positive character of the carbonyl group facilitates the reaction, which is evidence for hydride ion transfer. Doering and Young[9] have used the cyclic transition state to explain their observation that an optically active reductant gives a partially active product.

The evidence to date does not preclude a mechanism in which two molecules of aluminum isopropoxide would be involved, one to complex with the carbonyl oxygen and a second to serve as hydride ion donor. A choice between these two mechanisms should be possible on the basis of kinetic

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[1] Taken in part from the M.A. thesis of R. R. Ruch. This work was supported by grants from the Research Corporation and the Graduate School of Southern Illinois University.

[2] H. Meerwein and R. Schmidt, *Ann.*, **444**, 221 (1925); W. Ponndorf, *Z. angew. Chem.*, **39**, 138 (1926); M. Verley, *Bull. soc. chim.*, [4] **37**, 537 (1925).

[3] R. V. Oppenauer, *Rec. trav. chim.*, **56**, 137 (1937).

[4] R. E. Lutz and J. S. Gillespie, Jr., *J. Am. Chem. Soc.*, **72**, 344 (1950).

[5] R. B. Woodward, N. L. Wendler, and F. J. Brutschy, *J. Am. Chem. Soc.*, **67**, 1425 (1945).

[6] W. von E. Doering and T. C. Ashner, *J. Am. Chem. Soc.*, **75**, 393 (1953).

[7] E. D. Williams, K. A. Krieger, and A. R. Day, *J. Am. Chem. Soc.*, **75**, 2404 (1953).

[8] D. E. Pickkart and C. K. Hancock, *J. Am. Chem. Soc.*, **77**, 4642 (1955).

[9] W. von E. Doering and R. W. Young, *J. Am. Chem. Soc.*, **72**, 631 (1950).