The Copper-Catalyzed Reaction of Benznorbornadiene with Benzoyl Peroxide and *t*-Butyl Perbenzoate. Nuclear Magnetic Resonance Spectra of *anti*-7-Benznorbornadiene Derivatives

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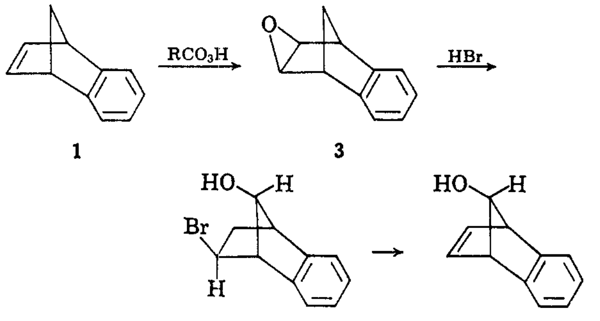
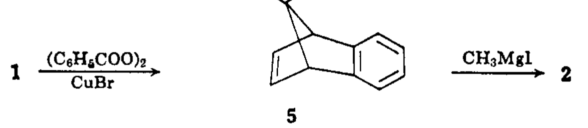
The Cu(I) salt catalyzed reaction of benzoyl peroxide with benznorbornadiene leads to the expected substitution product *anti*-7-benzoyloxybenznorbornadiene, although in lower yield than a previous reported. In addition, the reaction yields up to 10% of a heretofore unknown hydrocarbon which has been identified as a phenylation product of benznorbornadiene. The structure of the phenylation product is shown to be *anti*-7-phenylbenznorbornadiene by means of spectral evidence and an independent synthesis. The Cu(I) salt promoted reaction of *t*-butyl perbenzoate and benznorbornadiene affords a 40% yield of *anti*-7-*t*-butoxybenznorbornadiene, which, upon treatment with aqueous sulfuric acid, is quantitatively converted to *anti*-7-benznorbornadienol. The latter sequence represents a more convenient and higher yield route to *anti*-7-benznorbornadienol. The chemical reactivity of *anti*-7-*t*-butoxybenznorbornadiene is contrasted to that of its 7-norbornadienyl counterpart. The nmr spectra of a number of *anti*-7-benznorbornadienyl and *anti*-7-benznorbornenyl derivatives are presented and discussed with reference to unequivocal assignment of configuration.

The synthesis of benznorbornadiene (**1**) by the 1,4-cycloaddition reaction of cyclopentadiene and benzyne, was described in 1958.[1] Shortly afterward, Bartlett reported the preparation of *anti*-7-benznorbornadienol (**2**) from diene **1** by a multistep synthesis (eq 1).[2] Oxidation of **1** with monoperphthalic acid afforded the *exo* epoxide **3** which on treatment with HBr gave the rearranged bromohydrin **4**. After formation of the dihydropyran derivative of **4**, base-catalyzed elimination of HBr and subsequent hydrolysis led to *anti*-7-benznorbornadienol (**2**) in an over-all yield of 23%. Alcohol **2** is the key compound in the *anti*-7-benznorbornadienyl series since other derivatives, such as the acetate or brosylate, may be easily prepared from **2** by standard procedures. However, the complexity of the above sequence and the low yield for the conversion of diene **1** into alcohol **2** are major disadvantages.



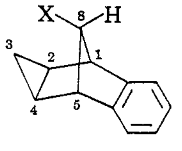
(1)

In 1963 Tanida and Tsuji reported that the Cu(I) bromide catalyzed reaction of benzoyl peroxide with benznorbornadiene (**1**) afforded *anti*-7-benzoyloxybenznorbornadiene (**5**) as the sole substitution product in *ca.* 34% yield (eq 2).[3] This reaction was extensively studied by these workers under a wide variety of reaction conditions, and a radical–ionic mechanism was established.[3b] The benzoate **5** may be directly converted to *anti*-7-benznorbornadienol (**2**) by treatment with methylmagnesium iodide, the over-all yield for the conversion of **1** to **2** being 26%.[3b] Thus this reaction appeared to provide a relatively facile two-step synthesis of alcohol **2**, and, consequently, a stereospecific entry to other *anti*-7-benznorbornadienyl derivatives.



(2)

In conjunction with a study of homoconjugative effects of the fused cyclopropane ring in 8-substituted derivatives of the tricyclo[3.2.1.0^{2,4}]octane ring system,[4] we required a number of *anti*-7-benznorbornadienyl derivatives as synthetic precursors of the *anti*-8-substituted benztricyclo[3.2.1.0^{2,4}]octene (**6**) system.



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Consequently, it was necessary to reexamine the previously reported preparative routes to derivatives of **2**. The results from a reinvestigation of the Cu(I) salt promoted reaction of benzoyl peroxide with benznorbornadiene (**1**), reported earlier in preliminary form,[5] are now described in full detail. In addition, the related synthesis of *anti*-7-*t*-butoxybenznorbornadiene by Cu(I) ion catalyzed reaction of *t*-butyl perbenzoate with **1** and its quantitative hydrolysis to benznorbornadienol (**2**) are reported. The nmr spectra of a number of *anti*-7-benznorbornadienyl and *anti*-7-benznorbornenyl derivatives are also recorded and discussed with reference to assignment of configuration in these systems. Observation of a small long-range stereospecific coupling between the *syn*-7

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[1] G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

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

[3] (a) H. Tanida and T. Tsuji, *Chem. Ind.* (London), 211 (1963); (b) H. Tanida and T. Tsuji, *J. Org. Chem.*, **29**, 849 (1964).

[4] M. E. Brennan, M. S. Thesis, University of Florida, Gainesville, Fla., June 1965. M. A. Battiste and M. E. Brennan, *Tetrahedron Letters*, 5857 (1966); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *J. Am. Chem. Soc.*, **89**, 1954 (1967).

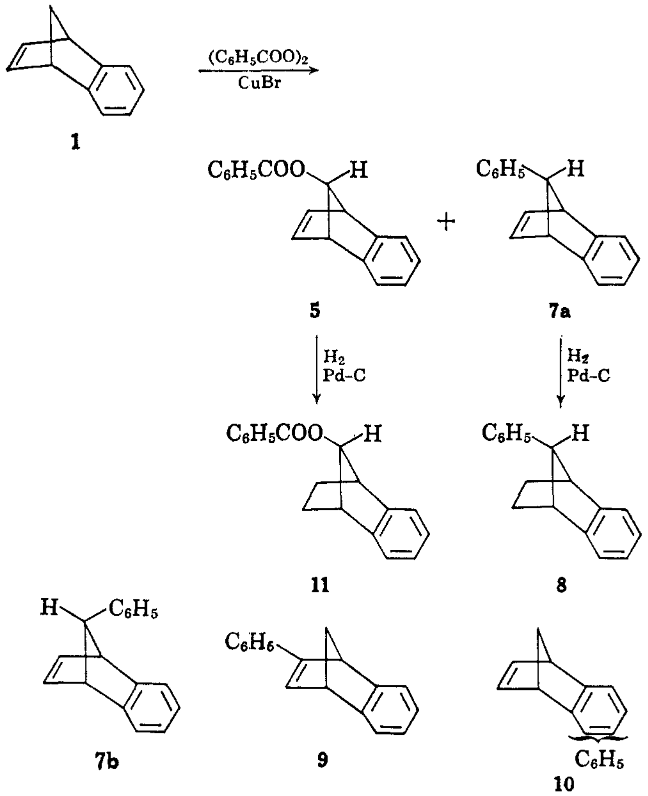
[5] M. A. Battiste and M. E. Brennan, *Chem. Ind.* (London), 1494 (1966).

bridge proton and the olefinic $H_{2,3}$ or *endo* $H_{2,3}$ hydrogens respectively, was found to be particularly useful in these assignments.

Results and Discussion

Cu(I) Salt Catalyzed Reaction of Benzoyl Peroxide with Benznorbornadiene (1).—The Cu(I) bromide catalyzed reactions of benzoyl peroxide with benznorbornadiene (**1**) were carried out in benzene solution as previously described,[3] using molar diene/peroxide ratios of 3.9:1.0 and 1.3:1.0. Distillation at reduced pressure (see Experimental Section) gave a forerun of starting diene **1** and a crude product fraction, which was shown to consist of four components by thin layer chromatography. By the use of authentic control samples this technique identified three of the components as benznorbornadiene (**1**), biphenyl, and the expected *anti*-7-benzoate **5** (Chart I). The fourth component, a relatively nonpolar compound with respect to **5**, was unknown at this time, although it was thought to be a product of phenylation as suggested by the detection of biphenyl in the crude product mixture. Further purification of the crude distillate by column chromatography on standard alumina gave a small amount of starting diene **1**, 8–10% of biphenyl, up to 10% of the unknown component, and 20–25% of *anti*-7-benzoyloxybenznorbornadiene (**5**), mp 94–96° (all yields based on benzoyl peroxide).

CHART I



The unknown component, a crystalline hydrocarbon, mp 92–94°, was analyzed as $C_{17}H_{14}$ with a molecular weight of 218 (mass spectrum). In the infrared the unknown hydrocarbon showed absorptions characteristic of the benznorbornadienyl system[2] and bands for a monosubstituted phenyl. Thus this hydrocarbon component was obviously a phenylation product of **1**.

There are five possible isomeric structures for a phenylation product of **1**. These are the *anti*-7 and *syn*-7-phenyl configurational isomers **7a** and **7b**, the conjugated 2-phenyl isomer **9**, and the conjugated 3'- and 4'-phenyl isomers shown as **10** in Chart I. The conjugated styrenyl and biphenyl like isomers **9** and **10** were excluded from further speculation by virtue of the ultraviolet spectrum of the phenylation product which was nearly identical with that reported[6] for benznorbornadiene (**1**).

The nmr spectrum of the $C_{17}H_{14}$ hydrocarbon clearly establishes the 7-phenylbenznorbornadiene (**7**) structure, and further allows a choice to be made between *anti* and *syn* configurational isomers **7a** and **7b**. Thus the nmr spectrum of **7** showed a nine-proton aromatic multiplet consisting of a sharp phenyl spike superimposed on an obvious A_2B_2 pattern at τ 2.91, a doublet of triplets at 3.51 corresponding to two olefinic protons virtually coupled[7,8] to two bridgehead protons and further coupled to the C-7 bridge proton[7] ($J_{2,7}$ = 0.55–0.60 cps), a two-proton quartet ($J_{1,7}$ = 1.80 cps) at 5.89 assigned to the bridgehead protons, and a broad ($W_{1/2}$ = 3.8 cps) one-proton singlet at 6.08 corresponding to the C-7 benzylic bridge hydrogen. The doublet of triplets observed for the olefinic protons of **7** is due to further splitting of the usual vinyl "triplet" by a small stereospecific coupling ($J_{2,7}$ = 0.55–0.60 cps) of these protons with the C-7 bridge proton, which must be *syn* to the fused benzene ring in order to have the requisite transoid relationship to the vinyl protons (see nmr discussion). Thus the structure of the phenylation product is established as *anti*-7-phenylbenznorbornadiene (**7a**). It has been further demonstrated (Table I) that the observance of this small stereospecific coupling is general for *anti*-7-benznorbornadienyl derivatives and is a valuable tool for assignment of configuration in this system (*vide infra*).

On catalytic hydrogenation **7a** absorbed 1 molar equiv of hydrogen to give nearly a quantitative yield of *anti*-7-phenylbenznorbornene (**8**), mp 78–79°. The nmr spectrum of **8** (Table II) revealed an unresolved two-proton multiplet at τ 6.28, assigned to the bridgehead protons, and a broad ($W_{1/2}$ = 4.56 cps) one-proton singlet at 6.75 corresponding to the C-7 benzylic bridge proton in addition to unresolved multiplets for the 2,3-*exo*, 2,3-*endo*, and aromatic protons. The broad singlet observed for the C-7 bridge proton is again consistent with the *anti*-7-phenyl configuration **8** and is a result of coupling between the 2,3-*endo* protons and the *syn*-C-7 proton in addition to the usual coupling with the bridgehead protons.[8] On the other hand, the *syn*-7-phenyl isomer would be expected to show a clean triplet for the C-7 bridge hydrogen due to coupling with the bridgehead protons only. The broad singlet observed for the C-7 bridge proton of **8** has been found to be general for a number of *anti*-7-benznorbornenyl derivatives (Table II), and is of value

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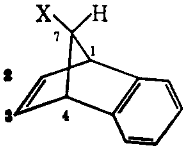
[6] H. Tanida, *et al.*, *Bull. Chem. Soc. Jap.*, **37**, 40 (1964).

[7] E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964), and references cited therein.

[8] (a) P. Laszlo and P. von Schleyer, *ibid.*, **86**, 1171 (1964). (b) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963).

TABLE I

NMR SPECTRAL DATA FOR *anti*-7-BENZNORBORNADIENYL DERIVATIVES[a]

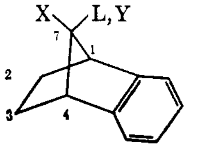


Compound	Chemical shift, τ					J, cps[b]		
X	H-7 Bridge	H-1, H-4 Bridgehead	H-2, H-3 Olefinic	Aromatic[c]	Other	$J_{2,7}$	$J_{1,7}$	$J_{1,2} + J_{1,3}$
H[d]	*syn* 7.79 d-t-t *anti* 7.72 d-t	6.18 qi	3.28 t-d	...	...	...	*syn* 1.80 *anti* 1.50	4.20
$OC(CH_3)_3$	6.07 b[e]	6.18 q	3.36 d-t	2.87	8.83 s	0.95	1.70	3.76
$OOCCH_3$	5.25 hp	5.98 q	3.38 d-t	2.85	8.00 s	0.90	1.80	3.90
OOCPh	4.99 hp	5.86 q	3.32 d-t	1.98[f] 2.78	...	0.95	1.80	3.75
OH	5.88 b[g]	6.12 q	3.32 d-t	2.85	6.72 s	1.00	1.70	3.50
Ph	6.08 b[h]	5.89 q	3.51 d-t	2.91	...	0.55–0.60	1.80	3.90
Cl	5.72 hp	5.88 q	3.30 d-t	2.88	...	0.80	1.75	3.75

[a] Recorded in deuteriochloroform on a Varian A-60A instrument with tetramethylsilane as an internal reference; multiplicities are represented by s(singlet), d(doublet), t(triplet), q(quartet), qi(quintet), hp(heptuplet), and b(broad); for exampl., d-t represents a doublet of triplets; relative peak areas were in accord with assigned structures. [b] $J_{2,7}$ is taken as the doublet separation of the outer members of the observed doublet of triplets; $J_{1,7}$ is estimated to be the separation of successive lines of the observed $H_{1,4}$ irregular quartet; $J_{1,2} + J_{1,3}$ was calculated according to the method of ref 7. [c] A_2B_2 multiplet unless otherwise indicated. [d] Reference 23. [e] Band width at half height, $W_{1/2}$ = 5.30 cps. [f] Ester phenyl *ortho* protons. [g] $W_{1/2}$ = 6.40 cps. [h] $W_{1/2}$ = 3.80 cps.

TABLE II

NMR SPECTRAL DATA FOR *anti*-7 AND *syn*-7-BENZNORBORNENYL DERIVATIVES[a]

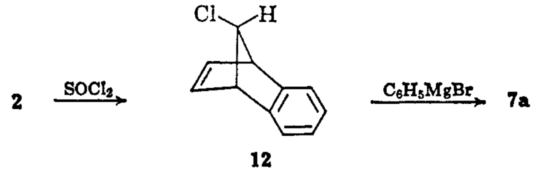


Compound		Chemical shift, τ								
		H-7 Bridge		H-1,H-4	H-2,H-3					H-7[c]
X	Y	*syn*	*anti*	Bridgehead	*exo*	*endo*	Aromatic	Other	$J_{1,7}$[b]	$W_{1/2}$
H	H[d]	8.27 d-qi	8.52 d-t	6.70 qi	8.15 m	8.86 m			*syn* 1.50 *anti* 1.90	
$OC(CH_3)_3$	H	6.44 b		6.97 q	7.88 m	8.94 m[e]	2.89 s	8.82 s	1.85	4.60
$OOCCH_3$	H[d]	5.53 t-t		6.72 q						
H	$OOCCH_3$[d]		5.27 t	6.67 q						
OOCPh	H	5.15 b		6.51 q	7.82 m	8.73 m	1.94[f] 2.66		1.85	4.50
OH	H[d]	6.26 t-m		6.97 q						
H	OH[d]		6.03 t-m	6.92 q						
Ph	H	6.79 b		6.30 q	8.19 m	8.87 m	2.78		1.60	4.56

[a] Recorded in deuteriochloroform on a Varian A-60A instrument with tetramethylsilane as an internal reference; multiplicities are represented by s(singlet), d(doublet), t(triplet), q(quartet), qi(quintet), b(broad), and m(multiplet); for example, t-t represents a triplet of triplets; relative peak areas were in accord with assigned structures. [b] Estimated to be the separation between successive lines of the irregular quartet observed for the H-1,H-4 bridgehead protons. [c] Band width at half height is given in cycles per second. [d] Reference 23. [e] The chemical shift for the *endo* protons is an approximation in that the protons of the *t*-butyl group absorb at very nearly the same position. [f] Ester phenyl *ortho* protons.

in the assignment of configuration in this series (*vide infra*).

The *anti*-7-phenylbenznorbornadiene (**7a**) structure was further established by independent synthesis. Reaction of *anti*-7-chlorobenznorbornadiene (**12**) with phenylmagnesium bromide in refluxing ether gave *anti*-7-phenylbenznorbornadiene, mp 91–93°, identical in all respects with the phenylation product **7a** (eq 3). The *anti*-7-chlorobenznorbornadiene (**12**), mp 44–45°, was prepared in 51% yield from reaction of *anti*-7-benznorbornadienol (**2**) with thionyl chloride in ether. The nmr spectrum of **12** again offered unequivocal evidence for the assigned *anti* configuration, showing a four-proton aromatic A_2B_2 multiplet centered at τ 2.88, two olefinic protons as a doublet of triplets ($J_{2,7}$ = 0.80 cps) at 3.30, a septet at 5.72 corresponding to the *syn* C-7 bridge proton, and a two-proton quartet ($J_{1,7}$ = 1.75 cps) at 5.88 assigned to the bridgehead protons.[9] The treatment of *anti*-7-norbornenol with thionyl choride has also been reported to give chloride of retained configuration.[10]



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(3)

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[9] (a) The bromide related to **12**, *anti*-7-bromobenznorbornadiene, has been recently synthesized by Wilt and coworkers.[9b] The nmr spectrum reported by these authors for this bromo derivative of **1** is virtually identical with that of **12** which was reported in our preliminary communication.[5] (b) J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *J. Org. Chem.*, **32**, 893 (1967).

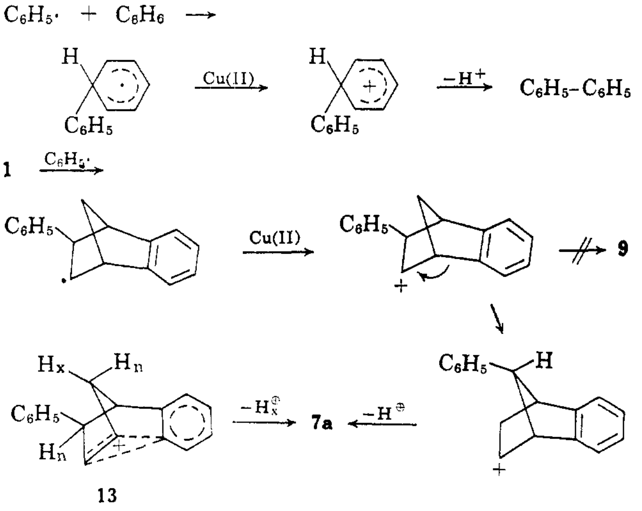
[10] H. Tanida and Y. Hata, *ibid.*, **30**, 977 (1965).

The formation of the phenylation product **7a** from the Cu(I)-catalyzed reaction of benzoyl peroxide with benznorbornadiene (**1**) can be rationalized by the radical–ionic mechanism shown in Chart II. This mechanism is suggested on the basis of the work of Kochi[11] who established the general mechanism for Cu(I)-catalyzed olefin–per ester reactions, and by the results of detailed mechanistic investigations of the Cu(I)-catalyzed reactions of norbornadiene with benzoyl peroxide[3b] and *t*-butyl perbenzoate.[12] Phenyl radicals are evidently formed by thermal decomposition of benzoyloxy radicals. Once formed they either attack solvent molecules (benzene) to give biphenyl or the olefinic bond of **1** from the *exo* direction to give a 2-benznorbornenyl radical. Subsequent oxidation of this radical by Cu(II) followed by Wagner–Meerwein rearrangement of the resulting bridged carbonium ion and loss of a proton leads to the observed product **7a**. However, it is striking that the conjugated 2-phenyl isomer **9** is not formed in this reaction. This observation is perhaps best explained by the preferential loss of an *exo* proton (H_x) from nonclassical ion **13** (Chart II) to give **7a** rather than the 2-phenyl isomer **9** despite the possibility of extra conjugation.

CHART II

$$(C_6H_5COO)_2 + Cu(I) \longrightarrow C_6H_5COO\cdot + C_6H_5COO^- \; Cu(II)$$

$$C_6H_5COO\cdot \longrightarrow C_6H_5\cdot + CO_2$$

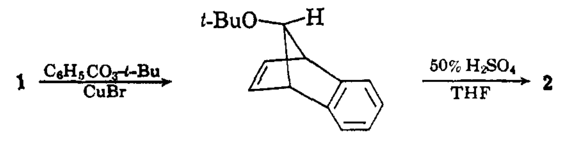


The formation of the phenylation product **7a** is of particular interest in that the production of phenyl radicals from the Cu(I) salt catalyzed decomposition of benzoyl peroxide in the presence of unsaturated hydrocarbons is not generally observed. The relatively long-lived benzoyloxy radicals from benzoyl peroxide have been shown to react mainly by addition to an olefinic bond or by chain transfer with a hydrogen donor in benzene.[13] In his work on the Cu(I)-catalyzed reaction of benzoyl peroxide with the isomeric butenes, Kochi observed very little fragmentation of benzoyloxy radicals.[13] However, he has indicated, without elaboration, that small percentages of phenylated products are formed. In the Cu(I) ion catalyzed reaction of benzoyl peroxide with 1-octene in benzene at 60–80°, Kharasch and Fono have reported a 45% yield of 1-phenyl-1-octene (no 1-phenyl-2-octene) and a 23% yield of isomeric benzoyloxyoctenes.[14] However, in the same reaction with 2-octene less than 5% of phenylated octenes were isolated.[14]

A reinvestigation of the Cu(I)-promoted reaction of benzoyl peroxide with norbornadiene failed to reveal any 7-phenylnorbornadiene[15] in the products, although biphenyl was isolated in 3–4% yield.

Cu(I) Salt Catalyzed Reaction of *t*-Butyl Perbenzoate with Benznorbornadiene (**1**).—The synthetic difficulties encountered in the preparation of *anti*-7-benzoyloxybenznorbornadiene (**5**), a useful precursor of alcohol **2**, have been cited above. It was desirable, therefore, to develop a more convenient route to *anti*-7-benznorbornadienol (**2**).

Story has previously reported that the Cu(I) bromide catalyzed reaction of *t*-butyl perbenzoate with norbornadiene in refluxing benzene affords a 25% yield of 7-*t*-butoxynorbornadiene.[16] In the present study, application of the Cu(I) bromide–*t*-butyl perbenzoate reaction[16] to benznorbornadiene (**1**) resulted in the formation of *anti*-7-*t*-butoxybenznorbornadiene (**14**), mp 48–49°, in up to 40% yields based on *t*-butyl perbenzoate (30% yields based on consumed **1**). The infrared spectrum of this bicyclic ether showed characteristic absorptions for the *t*-butyl ether and benznorbornadienyl groupings while the nmr spectrum (Table I) offered unequivocal evidence for the assigned *anti* configuration. Specifically, **14** showed resonance signals for four aromatic protons as an A_2B_2 pattern centered at τ 2.87, two olefinic protons as a doublet of triplets ($J_{2,7}$ = 0.95 cps) at 3.36, a broad singlet at 6.07 assigned to the *syn*-C-7 bridge proton, a two-proton quartet ($J_{1,7}$ = 1.7 cps) at 6.18 corresponding to the bridgehead protons, and nine *t*-butyl protons as a sharp singlet at 8.83. The appearance of the doublet of triplets for the olefinic protons of **14** is ascribed to the previously mentioned stereospecific coupling with the *syn*-7 bridge proton, thus establishing the configuration as *anti*.



14 (4)

The formation of *anti*-7-*t*-butoxybenznorbornadiene (**14**) in the Cu(I)–*t*-butyl perbenzoate reaction may be mechanistically accounted for by a radical–ionic path similar to that established by Story for the norbornadiene case[12] and by others[3b,12] for similar reactions. The mechanism requires *exo* attack of a *t*-butyloxy radical on the olefinic bond of diene **1** as shown for the analogous phenylation mechanism in Chart II.

Catalytic hydrogentation of **14** afforded a nearly quantitative yield of *anti*-7-*t*-butoxybenznorbornene (**15**). Its nmr spectrum (Table II) was again consistent with the assignment of the *anti* configuration (*vide infra*).

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[11] J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 744 (1962).

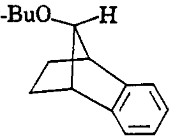
[12] P. R. Story, *Tetrahedron Letters*, 401 (1962).

[13] J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1572 (1962).

[14] M. S. Kharasch and A. Fono, *J. Org. Chem.*, **24**, 606 (1959).

[15] P. R. Story and S. R. Fahrenholtz, *ibid.*, **28**, 1716 (1963).

[16] P. R. Story, *ibid.*, **26**, 287 (1961).



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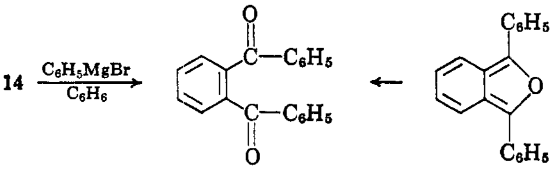
Treatment of the *t*-butyl ether **14** in tetrahydrofuran solution with 50% aqueous sulfuric acid at room temperature afforded an almost quantitative yield of *anti*-7-benznorbornadienol (**2**) identical in all respects with an authentic[2,3] sample. No reaction was observed when **14** was similarly treated with 25% aqueous sulfuric acid. Thus the preparation of *anti*-7-*t*-butoxybenznorbornadiene (**14**) and its subsequent acid hydrolysis constitutes a much more convenient and higher yield (30% over-all from **1**) route to *anti*-7-benznorbornadienol than those previously reported.[2,3]

Story also attempted the acid hydrolysis of 7-*t*-butoxynorbornadiene, but found that treatment with 50% aqueous sulfuric acid did not yield 7-norbornadienol; the product mixture consisted chiefly of a saturated diol.[16] This is yet another example of the contrasting chemical behavior of *anti*-7-benznorbornadienyl derivatives and their 7-norbornadienyl analogs (*vide infra*).

The previous report[15] that reaction of 7-*t*-butoxynorbornadiene with phenylmagnesium bromide in benzene gave a 75% yield of 7-phenylnorbornadiene encouraged us originally to attempt the independent synthesis of *anti*-7-phenylbenznorbornadiene (**7a**) by this method. However, reaction of phenylmagnesium bromide with **14** in benzene gave a fluorescent green oil, which upon attempted purification by crystallization or column chromatography on standard alumina resulted in recovery of starting material and varying amounts of *o*-dibenzoylbenzene (**16**) (eq 5).

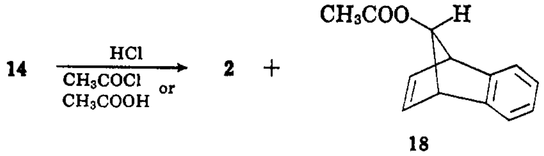


(5)

16 17

The unusual reaction leading to the formation of **16** apparently attests to the difficulty of generating the 7-benznorbornadienyl cation[2] relative to the 7-norbornadienyl cation[17,18] under these conditions. As a result the reaction probably proceeds through attack of phenylmagnesium bromide on the olefinic double bond; however, it is mechanistically very difficult to account for the formation of *o*-dibenzoylbenzene (**16**) without employing several air-oxidation steps. The expected precursor of **16**, 2,5-diphenylisobenzofuran (**17**), a yellow, bluish green fluorescing compound, is known to give *o*-dibenzoylbenzene (**16**) on hydrolysis and/or air oxidation.[19]

Story and Saunders have reported that treatment of 7-*t*-butoxynorbornadiene with anhydrous hydrogen chloride in acetyl chloride leads to a 70% yield of the corresponding 7-chloro compound.[17] Application of these reaction conditions to *anti*-7-*t*-butoxybenznorbornadiene (**14**) gave, instead of the 7-chloro derivative, *anti*-7-benznorbornadienol (**2**) and *anti*-7-benznorbornadienyl acetate (**18**) in 33 and 29% yields, respectively. In the same manner, treatment of **14** with anhydrous hydrogen chloride in glacial acetic acid gave the corresponding alcohol **2** and acetate **18** in 10 and 50% yields, respectively (eq 6).



(6)

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The failure of anhydrous hydrogen chloride to convert **14** into the *anti*-7-chloride **12** again attests to the relative instability of the 7-benznorbornadienyl cation[2] as compared to the 7-norbornadienyl cation.[17,18] In the present case, the hydrogen chloride reactions are easily explained by protonation of the *anti*-7-*t*-butyl ether **14** to give an oxonium ion which then cleaves to the *t*-butyl cation and alcohol **2** rather than *t*-butyl alcohol and the bicyclic cation as in the 7-*t*-butoxynorbornadiene case. Subsequent acetylation of **2** in acetyl chloride or acid-catalyzed esterification in acetic acid affords acetate **18**.

Nmr Spectra.—Several significant points emerge from examination of the chemical shifts and coupling constants of the *anti*-7-benznorbornadienyl and *anti*- and *syn*-7-benznorbornenyl derivatives listed in Tables I and II, respectively. Foremost is the small long-range stereospecific coupling observed between the olefinic and the C-7 bridge proton in the 7-benznorbornadiene derivatives (Table I). In an earlier study Snyder and Franzus noted a differing multiplicity for the two pairs of olefinic protons in norbornadiene derivatives monosubstituted at the C-7 bridge position.[7] Specifically, the nmr spectrum of a typical 7-substituted norbornadiene shows a low-field vinyl triplet (a result of virtual coupling of one pair of the olefinic protons with the bridgehead protons), and a higher field vinyl multiplet approximating a doublet of triplets with a doublet separation of 0.69–0.86 cps. The latter multiplet may be assigned to the olefinic protons situated *syn* to the 7 substituent (*anti*-C-7 bridge proton), and the observed multiplicity may be accounted for by virtual coupling with the bridgehead protons to give a triplet, each line of which is further split into a doublet by long-range stereospecific coupling with the *anti*-C-7 bridge proton. The transoid nature of the long-range coupling with the bridge proton was confirmed by examining the multiplicity of the olefinic protons in isomeric 7-substituted norbornenes.[7] Thus for *anti*-7-norbornene derivatives (*syn*-H_7) the olefinic protons appeared as a triplet whereas in the case of the corresponding *syn* isomers (*anti*-H_7) these protons approximated a doublet of triplets (doublet separation *ca.* 0.8 cps) with considerable broadening of the inner lines. The small stereospecific coupling, postulated to result from the interaction of the backside of the *anti*-C-7 hydrogen's sp^3 bonding orbital with the π-orbital system of the appropriate double bond,[7] is therefore of considerable use in the establishment of the configuration of a 7-substituent in unsaturated bicyclo[2.2.1]heptyl systems.

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[17] P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **84**, 4876 (1962).

[18] S. Winstein and C. Ordonneau, *ibid.*, **82**, 2084 (1960).

[19] G. M. Badger, R. S. Pearce, H. J. Rodda, and I. S. Walker, *J. Chem. Soc.*, 3151 (1954).

The olefinic proton resonance for each of the 7-benznorbornadiene derivatives prepared in this work was observed experimentally as a doublet of triplets with the separation of the outer members of this multiplet ($J_{2,7}$) varying over the range 0.55–1.00 cps (Table I). It follows then, from the above arguments, that the configuration of the 7 substituent in each of these derivatives is *anti* with respect to the fused benzene ring. The magnitude of the long-range coupling constant, $J_{2,7}$, appears to depend to a large extent on the inductive effect of the C-7 bridge substituent, a fact suggesting that increased positive character of the bridge carbon enhances interaction of the olefinic π-orbital system with the back lobe of the H_7 bonding orbital. The report of a 2.7-cps coupling constant between the bridge and vinyl hydrogens of the 7-norbornadienyl cation is in line with this suggestion.[20]

The directly measured values of $J_{2,7}$ were found to be in good agreement with those evaluated for the same coupling constant by the "one and one-half order" analysis method described by Snyder and Franzus.[7] Considering only the separation in cycles per second between the outermost members of the proton multiplets observed for $H_{2,3}$, $H_{1,4}$, and H_7, three equations with three unknowns were obtained which on solution gave values for $J_{2,7}$, $J_{1,7}$, and $J_{1,2} + J_{1,3}$.[21] In this way, for example, the calculated values of $J_{2,7}$ and $J_{1,7}$ for *anti*-7-*t*-butoxybenznorbornadiene (**14**) are 1.00 and 1.65 cps which check quite well with the observed values (Table I) of 0.95 and 1.70 cps, respectively.

For several of the 7-benznorbornadiene derivatives (Table I) the H_7 bridge proton appeared as a heptuplet which is consistent with the coupling of this proton to both bridgehead and olefinic protons. The regular pattern of the heptuplet further suggested that $J_{1,7} \sim 2J_{2,7}$ which agreed quite well with the value of 1.70–1.80 cps for $J_{1,7}$ estimated from the separation of individual lines of the $H_{1,4}$ irregular quartet. Similar observations have been recently reported for 7-norbornadiene and *syn*-7-norbornene derivatives.[7] However, in several cases the H_7 resonance signal appeared as a broad singlet with a band width at half height ($W_{1/2}$) varying from 3.8 to 6.4 cps. This is again consistent with an unresolved multiplet of larger magnitude than the triplet which would result from coupling of this proton with the bridgehead protons only.[8b] As a result of "virtual coupling," a coupling mechanism first described by Musher and Corey,[22] the actual coupling constant of each olefinic proton with the bridgehead protons is effectively averaged so that H_2, H_3, and H_7 appear as magnetically equivalent protons and fortuitously give rise to an irregular quartet for the $H_{1,4}$ resonance signal. This rationale is readily verified, and from Table I it is seen that $J_{1,2} + J_{1,3} \sim 2J_{1,7}$.

The chemical shift of the olefinic protons of the *anti*-7-benznorbornadienyl derivative (Table I) are in every case shifted upfield (0.02–0.23 ppm) relative to these same protons in the parent hydrocarbon benznorbornadiene. This phenomenon is characteristic for the set of olefinic protons in 7-norbornadienyl derivatives which are on the same side of the molecule as the 7-substituent and has been previously ascribed to loss of symmetry about the C_1–C_4–C_7 plane.[7] Thus, although benznorbornadiene is not symmetric about this plane, it is not surprising that its *anti*-7-substituted derivatives show this same relationship as a result of small changes of geometry.

The *syn*-C-7 bridge proton is more efficiently shielded in the *anti*-7-benznorbornenyl derivatives (Table II) than in the corresponding *anti*-7-benznorbornadienyl derivatives (Table I). The shift varies from 0.16 to 0.71 ppm for the compounds examined and is at a minimum for the benzoate and a maximum for the phenyl derivatives; however, there appears to be no general correlation of this result with the inductive effect of the substituent. The observed upfield shift is presumably due to a number of factors, and among these are the change of angle geometry at the bridge, the inductive effects of the double bond and the 7-substituent, and a buttressing effect of the 2,3-*exo* hydrogens of the saturated derivatives resulting in more favorable alignment of the *syn*-C-7 bridge proton with respect to the shielding cone of the benzo group. It should be noted that in comparing the unsubstituted compounds, benznorbornadiene (Table I) and benznorbornene (Table II), the trend is reversed, and the *anti*-C-7 bridge proton in benznorbornene is actually more shielded and shifted farther upfield (0.80 ppm) than the corresponding *syn*-C-7 bridge proton (0.48 ppm). This unexpected result is difficult to rationalize and recently required a reassignment of the chemical shifts of the C-7 bridge protons of norbornene, benznorbornene, and benznorbornadiene.[23] The shifts observed for the unsubstituted compounds are undoubtedly an exception to the general case; for example, in the isomeric *anti*-7- and *syn*-7-benznorbornenols and their corresponding acetates (Table II), the *syn*-C-7 bridge proton appears at higher field than the *anti*-C-7 bridge proton by 0.23 and 0.26 ppm, respectively.[23] It is unfortunate that to date *syn*-7-benznorbornadienyl derivatives have not been available; thus a complete comparison has not been possible.

Laszlo and Schleyer have observed long-range coupling of 2.0–3.1 cps between the *syn*-C-7 bridge proton and the 5,6-*endo* protons for several norbornene derivatives,[8a] and Musher[8b] has reported a similar coupling of 1.4–1.85 cps for a number of norbornane derivatives. An analogous coupling of 3–4 cps has been found for 3-*exo*-halo-2-norbornanones.[24] In the present work, the *syn*-C-7 bridge hydrogen and the 2,3-*endo* hydrogens of the *anti*-7-benznorbornenyl derivatives have the same "transoid" relationship, and thus long-range coupling of these protons is to be expected. As revealed in Table II, the H_7 resonance signal for the 7-benznorbornenyl derivatives examined appeared as an unresolved broad singlet with a band width ($W_{1/2}$) of 4.5–4.6 cps. The breadth of the H_7 band suggests an unresolved multiplet of greater complexity than

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[20] P. R. Story, L. C. Snyder, D. C. Douglas, E. W. Anderson, and R. L. Kornegay, *J. Am. Chem. Soc.*, **85**, 3630 (1963).

[21] In cases where the H_7 resonance signal was a broad unresolved multiplet rather than the expected heptuplet, the separation of the outermost members was taken as the band width at one-half height in cycles per second.

[22] J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

[23] K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Letters*, 9 (1966); K. Tori, R. Muneyuki, and H. Tanida, *Can. J. Chem.*, **41**, 3142 (1963).

[24] J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1964).

would result from exclusive coupling of the bridge proton with the bridgehead protons; therefore, this observation is taken as evidence for assignment of the *anti* configuration in this series. However, the lack of resolution of the *syn*-C-7 bridge proton signal and the complexity of the 2,3-*exo* and -*endo* proton multiplets prevented determination of $J_{2n,7s}$, although the similar coupling in 7-norbornanol has been estimated to be about 1.5 cps on the basis of a band width for the H_7 resonance signal of *ca.* 4 cps.[8b]

The bridgehead protons of the *anti*-7-benznorbornenyl derivatives appear as an irregular quartet due to "virtual coupling" with the 2,3-*exo* protons and additional coupling to the *syn*-C-7 bridge proton. The observed coupling constant $J_{1,7}$, estimated to be the observed separation between consecutive lines of the irregular quartet, varies from 1.60–1.85 cps and agrees well with the values reported for analogous couplings in related systems.[7,8a] According to Musher and Corey, the separation between the outer lines of this irregular quartet should be equal to the sum of $J_{1,2e} + J_{1,3e}$ and $J_{1,7}$.[22] This separation is *ca.* 5.7 cps for the *anti*-7-phenyl and *anti*-7-*t*-butoxybenznorbornenyl derivatives, and since the coupling between the bridgehead and the *exo* protons of the ethylenic bridge of various norbornene derivatives have been reported to be about 3–4 cps,[8a] the observed values of $J_{1,7}$ reported here are quite reasonable.

Experimental Section[25]

Benznorbornadiene (**1**).—The procedure reported by Wittig and Knauss,[1] involving the 1,4-cycloaddition of benzyne to cyclopentadiene, was followed. Distillation through a spinning band column gave a colorless liquid, bp 81.5–82.5° (12 mm), $n^{20}D$ 1.5659–1.5663 (lit.[1] bp 82.5–83.0° (12 mm), $n^{20}D$ 1.5654–1.5668). The infrared[1] and the nmr[23] spectra (see Table I) of **1** were in agreement with the reported spectra; the diene was shown by vpc to be homogeneous at 150° on a 0.25 in. × 5 ft 20% SF-96 on 60/80 firebrick column.

Cu(I) Bromide Catalyzed Reaction of Benzoyl Peroxide with Benznorboraniene (**1**).—The procedure of Tanida and Tsuji was used with modifications in isolation and purification as outlined below.[3] To a well-stirred mixture of 71.0 g (0.50 mole) of benznorbornadiene (**1**) and 0.250 g (1.75 mmoles) of Cu(I) bromide in 250 ml of benzene at 40°, there was added, in an argon atmosphere, a solution of 30.3 g (0.13 mole) of benzoyl peroxide in 200 ml of benzene over a period of 1 hr. After addition was complete, the reaction mixture was heated gradually to reflux and maintained at this temperature for an additional 14 hr. At the end of this time, qualitative analysis by potassium iodide–starch paper showed that no peroxide remained. During the course of the reaction, a gradual color change of the solution from blue to green was observed. After cooling to room temperature, the benzene solution was washed with aqueous 10% sodium carbonate solution (to remove benzoic acid), 5% ferrous sulfate solution, 10% sodium carbonate solution again, and, finally, distilled water. The benzene solution was dried over anhydrous sodium sulfate and filtered, and the benzene was removed. Distillation of the residue at reduced pressure gave a forerun (41.8 g or 59%) of starting diene 1 (infrared spectrum identical to an authentic sample), bp 63–66° (3.45–3.65 mm), and a main fraction collected at 145–155° (0.20–0.25 mm), lit.[3] 150° (0.25 mm). The latter fraction solidified on standing and was chromatographed on standard alumina to give 7.1 g (20.8% based on benzoyl peroxide) of *anti*-7-benzoyloxybenznorbornadiene (**5**) as colorless needles, mp 94–96° (lit.[3] 33.6%; mp 95–96°), 1.6 g (8%) of biphenyl, and 1.6 g (5.6%) of another hydrocarbon, mp 87–91°, subsequently identified as *anti*-7-phenylbenznorbornadiene (**7a**). The infrared spectrum (KBr) of benzoate **5** showed absorption at 3.30 (w), 5.84 (s), 6.25 (m), 6.90 (s), 9.74 (s), 12.78 (s), 13.73 (s) and 14.25 (m)μ; the nmr spectrum of **5** is listed in Table I. The hydrocarbon **7a** was also isolated in 5–6% yield from a similar reaction in which the molar ratio of diene **1** to peroxide was 1.31 rather than the 3.85 molar ratio used above. A reflux time of 3 days was employed in this second reaction. The hydrocarbon **7a**, mp 87–91°, was recrystallized once from benzene and twice from hexane to give colorless prisms, mp 92–94°, as an analytical sample.

Anal. Calcd for $C_{17}H_{14}$: C, 93.53; H, 6.47. Found: C, 93.31; H, 6.31.

The infrared spectrum (KBr) of **7a** showed absorption at 3.28 (w), 3.42 (w), 6.28 (w), 6.71 (m), 6.92 (s), 7.72 (m), 9.95 (m), 12.72 (s), 13.40 (s), 13.65 (s), and 14.40 (s)μ; the nmr spectrum is given in Table I. The ultraviolet spectrum of **7a** in isooctane showed absorption at λ_{max}, mμ(log ε): 261 (2.99), 263 sh, 267 sh, 269 (2.94), and 276 (2.76) along with strong end absorption.[26]

In an additional experiment, employing 9.90 g (0.0697 mole) of pure (by vpc) benznorbornadiene (**1**) in 35.0 ml of benzene, 0.040 g (0.28 mmole) of Cu(I) bromide, 4.38 g (0.0181 mole) of benzoyl peroxide in 35.0 ml of benzene, and a reflux time of 20 hr, there was obtained, after the usual work-up and removal of benzene, 13.0 g of an oily residue. Distillation of this oil gave 5.80 g (58.5%) of recovered diene, 3.00 g of reaction products, bp 150–165° (0.25–0.35 mm), and a polymeric residue of *ca.* 2.10 g. Thin layer chromatography of the crude distillate on silica gel HF_{254} revealed four components after two successive developments with hexane. In order of decreasing mobility these were benznorbornadiene (**1**), biphenyl, *anti*-7-phenylbenznorbornadiene (**7a**), and *anti*-7-benzoyloxybenznorbornadiene (**5**). Column chromatography of the same distillate on standard alumina gave 1.23 g of a mixture of diene **1** and biphenyl, 0.42 g (10.6%) of **7a**, mp 88–92°, and 1.05 g (22.2%) of **5**, mp 88–93°. A small sample of each of the crystalline fractions was recrystallized to give pure samples of **7a** and **5**, mp 92–94° and 94–96°, respectively.

***anti*-7-Phenylbenznorbornene** (**8**).—A 0.300-g (1.37 mmoles) sample of *anti*-7-phenylbenznorbornadiene (**7a**), mp 92–94°, in 50.0 ml of ethyl acetate was hydrogenated at room temperature with 0.050 g of 10% Pd–C as the catalyst. After 5–10 min 1 equiv of hydrogen was absorbed, and the reduction was allowed to proceed for an additional 10 min. The reaction solution was filtered through Celite, and on removal of the solvent, 0.236 g (78.2%) of slightly yellow-brown needles, mp 73–76°, were obtained. Two recrystallizations from hexane gave analytically pure *anti*-7-phenylbenznorbornene (**8**) as white needles, mp 78–79°.

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.47; H, 7.30.

The infrared spectrum (KBr) of **8** showed absorption at 3.33 (m), 6.68 (m), 6.86 (m), 6.92 (m), 8.96 (m), 11.92 (m), 13.28 (s), 14.08 (m), and 14.42 (m) μ; the nmr spectrum is listed in Table II.

***anti*-7-Benzoyloxybenznorbornene** (**11**).—A solution of 0.300 g (1.14 mmoles) of *anti*-7-benzoyloxybenznorbornadiene (**5**), mp 95–97°, in 50.0 ml of ethyl acetate, containing 0.050 g of 10% Pd–C as catalyst, was subjected to hydrogenation as described above. After 1 hr of reaction, 1 equiv of hydrogen had been absorbed. Filtration through Celite and removal of solvent gave 0.300 g (quantitative yield) of nearly white prisms, mp 104–107°. Recrystallization from hexane gave analytically pure *anti*-7-benzoyloxybenznorbornene (**11**), mp 110–111°.

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.57; H, 6.15.

The infrared spectrum (KBr) of **11** showed absorption at 3.33 (m), 5.84 (s), 6.90 (s), 8.98 (s), 9.78 (s), 11.42 (m), 13.20 (s), and 14.15 (s) μ; the nmr spectrum is given in Table II.

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(25) Melting points were determined with a Thomas–Hoover apparatus. All melting and boiling points were uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Vapor phase chromatographic analyses were performed with an Aerograph Model 600-D instrument equipped with a hydrogen flame ionization detector. Infrared spectra were recorded on either a Perkin-Elmer 137 or Beckman IR-10 instrument. Solid samples were examined in potassium bromide disks while liquid samples were examined neat on sodium chloride plates. Ultraviolet spectra were determined on a Cary Model 14 recording spectrophotometer. Nmr spectra were obtained on a Varian A-60A instrument using tetramethylsilane as an internal reference.

(26) Benznorbornadiene is reported to show ultraviolet absorption (cyclohexane) in λ_{max}, mμ (log ε), at 216 (4.00), 231 (3.06), 262 (2.66), 269 (2.76), and 277 (2.72).

***anti*-7-Chlorobenznorbornadiene (12).**—To a well-stirred solution of 1.0 g (6.53 mmoles) of *anti*-7-benznorbornadienol (**2**), mp 105–107°, in 12 ml of anhydrous ether, there was added a solution of 1.2 g (0.01 mole) of thionyl chloride in 10 ml of anhydrous ether over a period of 10 min. The whole was then allowed to stir at reflux for *ca.* 3 hr. After cooling to room temperature, the ether and excess thionyl chloride were removed under partial vacuum to afford a brown oil. Chromatography of this oil on standard alumina using hexane gave 0.590 g (51.3%) of **12** as white needles, mp 42–44°, which were shown to be homogeneous by vpc analysis on a $^1/_8$ in. × 5 ft, 5% SE-30 on 60/80 Chromosorb W column at 178°. One recrystallization from hexane gave analytically pure material, mp 44–45°.

Anal. Calcd for $C_{11}H_9Cl$: C, 74.77; H, 5.14. Found: C, 74.71; H, 5.14.

The infrared spectrum (KBr) of *anti*-7-chlorobenznorbornadiene (**12**) showed absorption at 3.25 (s), 6.20 (w), 6.87 (s), 7.68 (s), 8.15 (s), 10.65 (s), 12.60 (s), 13.45 (s), and 14.25 (s) μ; the nmr spectrum of **12** is listed in Table I.

Independent Synthesis of *anti*-7-Phenylbenznorbornadiene (7a).—To a solution of phenylmagnesium bromide prepared from 0.74 g (4.7 mmoles) of bromobenzene and 0.115 g (4.7 mg-atoms) of magnesium turnings in 10 ml of dry ether, there was added dropwise under an inert atmosphere a solution of 9.415 g (2.35 mmoles) of *anti*-7-chlorobenznorbornadiene (**12**), mp 42–44°, in 10 ml of dry ether over a period of 10 min. The reaction mixture was then allowed to stir at reflux for 55 hr, after which the excess Grignard reagent was destroyed by addition of water. The ether phase was separated, washed with several portions of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. Removal of the ether gave a yellow oil which was chromatographed on standard alumina using hexane to give a liquid fraction and several solid fractions. The first fraction, the liquid, was distilled through a micro Hickman still to give 0.077 g of a clear oil, bath temperature *ca.* 125° (0.20–0.25 mm). Analysis of this oil by vpc (SE-30 column, 178°) indicated the presence of starting chloride **12**, *anti*-7-phenylbenznorbornadiene (**7a**), and a third unidentified component. The nmr spectrum of the three-component mixture indicated resonance signals for the unidentified component at τ 3.84 and 4.30 in addition to the expected signals for **7a** and **12**. The several solid fractions totaled 0.140 g and melted variously from 80–85°. Infrared, vpc (SE-30 column, 178°), and thin layer chromatography analyses established the identity of this crystalline material with that of hydrocarbon **7a** isolated from the reaction of Cu(I) bromide–benzoyl peroxide with benznorbornadiene (**1**). A small sample of the above solid was recrystallized to give pure *anti*-7-phenylbenznorbornadiene (**7a**), mp 91–93°.

Cu(I) Bromide Catalyzed Reaction of Benzoyl Peroxide with Norbornadiene.—A reinvestigation of this Cu(I)-catalyzed reaction was carried out in benzene solution as previously described, employing a molar diene:peroxide ratio of 1.3:1.0.[3] Careful and patient distillation of the crude reaction mixture failed to reveal the presence of 7-phenylnorbornadiene.[15] Examination of the crude distillate by thin layer chromatography indicated only two components which were identified as biphenyl and the expected 7-benzoyloxynorbornadiene, mp 52–54° (lit.[3] mp 53–54°). Biphenyl was isolated in 3–4% yield by chromatography and subsequent sublimation.

Cu(I) Bromide Catalyzed Reaction of *t*-Butyl Perbenzoate with Benznorbornadiene (1).—To a stirred refluxing mixture of 33.5 g (0.236 mole) of redistilled, pure (by vpc) benznorbornadiene (**1**) and 0.150 g (1.05 mmole) of Cu(I) bromide in 100 ml of benzene, there was added, in an inert atmosphere, a solution of 17.85 g (0.0920 mole) of *t*-butyl perbenzoate (10.8 g of 95% practical) in 15 ml of benzene over a period of 30 min. The reaction mixture turned a deep green color upon addition of several drops of the *t*-butyl perbenzoate solution and this color persisted throughout an additional reflux period of 3.5 hr. At this time a qualitative test with potassium iodide–starch paper showed that no perester remained. After cooling to room temperature, the green benzene solution was washed successively with 10% aqueous sodium carbonate solution and distilled water and then dried over anhydrous magnesium sulfate. The benzene was removed by distillation through a 6-in. Vigreux column at atmospheric pressure. Distillation of the residue at reduced pressure through a 24-in. spinning-band column gave a forerun of 15.7 g (46.9%) of recovered starting diene **1**, bp 57–60° (2.70 mm), and 8.20 g (41.6%) of *anti*-7-*t*-butoxybenznorbornadiene (**14**), mp 45–48°, bp 78–80° (0.20–0.25 mm). Recrystallization from hexane gave pure **14** as white prisms, mp 48–49°.[27]

Anal. Calcd for $C_{15}H_{18}O$; C, 84.07; H, 8.47. Found: C, 83.89; H, 8.62.

The infrared spectrum of **14** showed absorption at 3.26 (w), 3.36 (m), 6.88 (m), 7.19 (m), 7.32 (s), 9.08 (s), 12.55 (m), 13.08 (m), 13.43 (s), and 14.20 (s) μ; the nmr spectrum is listed in Table I.

***anti*-7-*t*-Butoxybenznorbornene (15).**—A solution of 0.374 g (1.75 mmoles) of *anti*-7-*t*-butoxybenznorbornadiene (**14**), mp 48–49°, in 50.0 ml of ethyl acetate, containing 0.050 g of 10% Pd-C as catalyst, was hydrogenated as previously described. One equivalent of hydrogen was absorbed after 5–10 min, and the reduction was allowed to continue for an additional 15 min. The catalyst was filtered off, the solvent was removed, and the remaining clear oil was chromatographed on standard alumina using hexane to give 0.380 g (quantitative yield) of *anti*-7-*t*-butoxybenznorbornene (**15**) as a clear liquid. Distillation at reduced pressure with a micro Hickman still, bath temperature *ca.* 125° (0.20 mm), gave the analytical sample, $n^{20}{}_D$ 1.5190.

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.12; H, 9.59.

The infrared spectrum (neat) of **15** showed absorption at 3.30 (s), 6.80 (s), 7.20 (m), 7.35 (s), 8.40 (s), 8.95 (s), 9.15 (s), 10.70 (s), 13.35 (s), and 13.90 (m) μ; the nmr spectrum is listed in Table II.

***anti*-7-Benznorbornadienol (2).**—A mixture of 0.214 g (1.0 mmole) of *anti*-7-*t*-butoxybenznorbornadiene (**14**), mp 47–49°, in 2.0 ml of tetrahydrofuran and 1.0 ml (0.92 g, 9.4 mmoles) of 50% aqueous sulfuric acid was stirred at room temperature for 46 hr at the end of which time, water was added and the ether phase separated. The aqueous phase was extracted with ether and the combined ether layers were dried over anhydrous magnesium sulfate. Removal of ether gave a solid residue, mp 102–105°, which was washed with small portions of hexane to give 0.145 g (92%) of *anti*-7-benznorbornadienol (**2**), mp 104–106°, identical in all respects to an authentic[2,3] sample. Similar treatment of **14** with 25% aqueous sulfuric acid gave no detectable reaction.

An alternate procedure employed for the preparation of alcohol **2** was that reported by Tanida and Tsuji.[3] This method involves the reaction of *anti*-7-benzoyloxybenznorbornadiene (**5**) with methylmagnesium iodide in ether solution. Using this procedure, *anti*-7-benznorbornadienol (**2**), mp 105–107°, was obtained in 60–65% yield. The infrared spectrum of **2** was identical to that previously reported.[2] (See Table I for the nmr spectrum of **2**.)

Reaction of Phenylmagnesium Bromide with *anti*-7-*t*-Butoxybenznorbornadiene (14).—To a refluxing benzene solution (*ca.* 10–15 ml) of phenylmagnesium bromide, prepared in the conventional manner from 0.2 g (8.0 mg-atoms) of magnesium turnings and 1.26 g (8.0 mmole) of bromobenzene, there was added a solution of 0.85 g (3.96 mmoles) of *anti*-7-*t*-butoxybenznorbornadiene (**14**) in 10 ml of benzene over a period of 10 min. The solution was refluxed under an argon atmosphere for 3 days and cooled to room temperature, and the excess Grignard reagent was destroyed by addition of water. The benzene layer was separated, washed with saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. Removal of benzene afforded a fluorescent green oil, consisting of a number of components, which could not be adequately separated by distillation, crystallization, or column chromatography on standard alumina. Distillation did afford a small quantity of an impure aliphatic alcohol (by infrared and nmr spectra) whose structure was not determined. From the chromatography there was also isolated a majority of the starting *t*-butyl ether **14**, although it was also contaminated with unidentified green material. In addition, there was isolated 5–10% of a solid, mp 140–145°, subsequently identified as *o*-dibenzoylbenzene (**16**) by comparison of its infrared spectrum with that of an authentic sample. Since **16**, mp 149–150°, is reported to result from the air oxidation of 2,5-diphenyliso-

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(27) In a separate experiment in which the crude distillate of **14** was chromatographed on alumina, two crystalline fractions were obtained (from hexane), mp 61–63° and 47–49°; however, the infrared and nmr spectra of the two solid materials were identical. From this we conclude that **14** can be isolated in two different crystalline forms from hexane, although the lower melting form is more frequently obtained.

benzofuran (**17**),[19] a bluish green fluorescening compound, **17** is thought to be the precursor of **16** in the above reaction.

Reaction of Anhydrous HCl with *anti*-7-*t*-Butoxybenznorbornadiene (14).—Using the previously reported procedure of Story and Saunders,[17] a solution of 1.45 g (6.7 mmoles) of *anti*-7-*t*-butoxybenznorbornadiene (**14**) in 15 ml of acetyl chloride was treated in an inert atmosphere with dry hydrogen chloride gas for 10 min. The reaction mixture was then heated to boiling and refluxed for 1 hr. During reflux, dry hydrogen chloride gas was bubbled through the solution for two 5-min periods. After cooling to room temperature, the excess acetyl chloride was removed under partial vacuum and the remaining residue was chromatographed on standard alumina. Elution with hexane gave a liquid which after distillation through a micro Hickman still, bath temperature *ca.* 130° (0.20 mm), afforded 0.39 g (29%) of *anti*-7-benznorbornadienyl acetate (**18**),[2] $n^{21}D$ 1.5494.

Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.09; H, 6.14.

The infrared spectrum (neat) of **18** showed absorption at 5.78 (s), 6.41 (w), 6.92 (s), 7.30 (m), 8.10 (m), 13.40 (s), and 14.34 (s) μ; the nmr spectrum is listed in Table I.

Further elution with anhydrous ether gave 0.345 g (32.5%) of *anti*-7-benznorbornadienol (**2**), mp 102–105°, identical in all respects with an authentic sample.

In a similar reaction, a solution of 0.650 g (3.0 mmoles) of **14** in 10 ml of glacial acetic acid was treated with dry hydrogen chloride for a period of 10 min. The solution was then allowed to stir at room temperature for 23 hr, at which time ice and water was added and the whole was extracted several times with ether. The ether extracts were washed with 10% aqueous sodium carbonate solution and water, and then dried over anhydrous magnesium sulfate. Removal of the ether gave a crude yellow oil which was chromatographed on standard alumina using hexane to give 0.300 g (50%) of *anti*-7-benznorbornadienyl acetate (**18**). Elution with anhydrous ether gave 0.050 g (10%) of *anti*-7-benznorbornadienol (**2**).

None of the starting *t*-butyl ether **14** was recovered from either reaction, and in the reaction employing acetyl chloride as solvent, no *anti*-7-chlorobenznorbornadiene (**12**) was detected.

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Free-Radical Hydrogen Atom Abstractions from Substituted Cumenes

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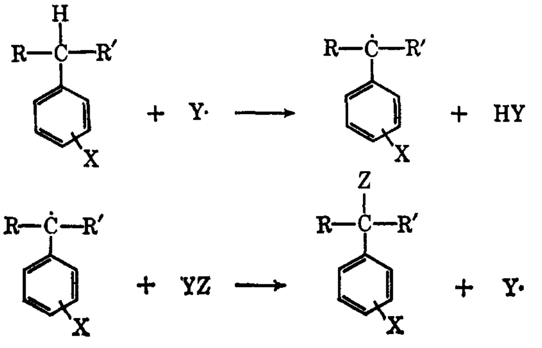
Making use of the Hammett equation, a study of the substituent effects operative in α-hydrogen abstraction from cumenes by bromine atoms and trichloromethyl radicals has been carried out. The study was conducted at 70.0°. It is felt that the ρ value of -0.38 obtained for the abstraction utilizing bromine atom represents a "normal" substituent effect. The corresponding value utilizing the trichloromethyl radical, -0.67, shows unexpected selectivity. Possible explanations for this in terms of the steric requirements of the system are offered.

The effects of ring substitution on reactions involving free-radical hydrogen abstraction from toluenes have been evaluated for several systems. Among the more common radicals which have been employed are chlorine atoms,[1,2] bromine atoms,[3-5] and the trichloromethyl radical.[6] It should be of at least equal interest to examine the relative magnitudes of these same effects in other hydrocarbon systems which also contain readily abstractable hydrogen atoms. Some studies along these lines have already appeared in the literature. All of the hydrocarbons involved may be said to undergo the reaction sequence given by eq 1 and 2. The following represent some specific examples of hydrocarbon systems other than toluenes. Martin and Gleicher have examined the abstraction by both bromine atoms and trichloromethyl radicals of the very labile hydrogen atoms in allylbenzenes.[7] Russell and Williamson have studied the oxidation of substituted cumenes by peroxy radicals.[2] More recently Huang and Lee have carried out the free-radical α-bromination of substituted ethylbenzenes.[8]



(1)

(2)

This present investigation was prompted by the appearance of the last item mentioned above. It was expected that a corresponding study on the bromination of substituted cumenes would produce a ρ value which was less than that encountered for the ethylbenzenes which, in turn, was less than that found for the toluenes.

Experimental Section

Materials.—Bromotrichloromethane (Matheson Coleman and Bell) was distilled three times and collected over the range 103.0–103.2°. Gas–liquid partition chromatography showed the presence of a single impurity comprising no more than 0.3% of the mixture. The impurity had the same retention time as carbon tetrachloride. Chlorobenzene (Matheson Coleman and Bell) was washed with dilute sulfuric acid and water and then dried over magnesium sulfate. The material was then dis-

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