Addition Reactions of *syn*- and *anti*-7-*tert*-Butylnorbornenes[1]

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Cyclic and noncyclic additions to *syn*- and *anti*-7-*tert*-butylnorbornenes have been studied. Reactions of *anti*-7-*tert*-butylnorbornene generally occurred exo,cis independent of the cyclic or noncyclic nature of the transition state. An exception was catalytic hydrogenation which involved 25% endo,cis reduction, a reflection of structural strain in the exocyclic catalyst–olefin complex. Strain factors and nonbonded interactions impacted on all exo additions to the anti olefin as evidenced by retarded rates relative to norbornene. Cyclic additions to *syn*-7-*tert*-butylnorbornene either failed to occur or proceeded slowly to endo product. Noncyclic, or two-stage, additions of thiophenol and mercury(II) to the syn olefin did not occur, a reflection of the steric inhibition presented by the *syn*-7-*tert*-butyl radical.

anti- (**1**) and *syn*-7-*tert*-butylnorbornenes (**2**) have recently been synthesized from 7-*tert*-butylnorbornadiene.[2] The availability of these olefins has permitted the study of their reactions with reagents which add to olefins through both cyclic and noncyclic transition states. Comparable additions to *syn*- and *anti*-7-acetoxynorbornenes[3–7] occurred in an exo manner with the syn isomer exhibiting a faster rate due to the stabilization of the transition state through chelation. An exception was catalytic hydrogenation where steric inhibition slowed the reduction of the syn ester relative to the anti and also forced the syn acetate to experience 40% endo hydrogenation.

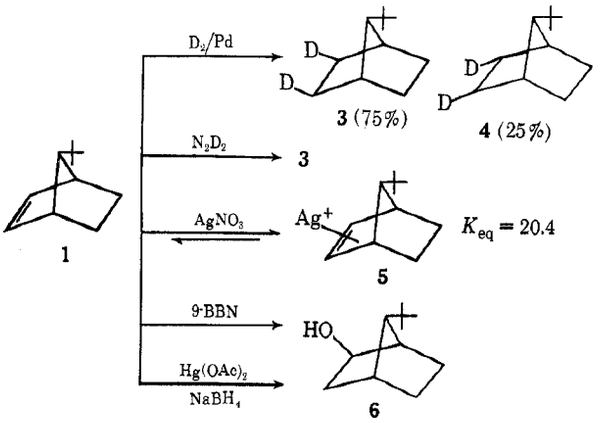
The latter reaction may be viewed as being representative of the types of reactions observed by Brown and coworkers during a study of cyclic and noncyclic additions to 7,7-dimethylnorbornene.[8–14] Brown has found that, in general, reactions involving cyclic transition states, *e.g.*, catalytic hydrogenation, either failed in the presence of the *syn*-7-methyl group or gave endo products. On the other hand, two-stage, or noncyclic additions, were considerably less sensitive to the presence of the 7-methyl group and yielded exo product, albeit the rates were depressed relative to norbornene.[14] It was the purpose of the present study to contrast the behavior of norbornenes bearing a nonpolar, bulky 7 substituent with these previous findings.

Results and Discussion

The reactions of *anti*-7-*tert*-butylnorbornene (**1**) with various reagents are shown in Scheme I. While the dominance of exo addition indicated that the chemistry of **1** was comparable to that of norbornene and *anti*-7-acetoxynorbornene,[3–7] detailed study of these reactions revealed a sensitivity to the 7-*tert*-butyl group that was not apparent from casual inspection of the structure of this olefin. The influence of this 7 substituent became apparent on the basis of three distinct observations: low reaction rates for *anti*-7-*tert*-butylnorbornene relative to norbornene; endo addition during catalytic hydrogenation of **1**; a smaller K_{eq} for silver ion complexation compared to K_{eq} for norbornene.

SCHEME I

ADDITION REACTIONS OF *anti*-7-*tert*-BUTYLNORBORNENE



That reactions of *anti*-7-*tert*-butylnorbornene were slow relative to those of norbornene is illustrated by Table I. Rate retardation was observed independent of the cyclic or noncyclic nature of the reaction. Complexation of the two olefins with silver ion was measured utilizing the gas chromatographic method of Muhs and Weiss.[15] Norbornene gave a K_{eq} of 49.5 while K_{eq} for the silver(I)–*anti*-7-*tert*-butylnorbornene complex was 20.8, representing a reduction in complex stability by a factor of 2.4.[16]

TABLE I

RELATIVE RATES OF REACTION OF NORBORNENE AND *anti*-7-*tert*-BUTYLNORBORNENE

Reagent	$k_{norbornene}/k_{ant}$
N_2H_2	1.55
H_2	3.77
9-BBN	3.73
$Hg(OAc)_2$	5.49
m-$ClC_6H_4CO_3H$	5.16

(1) Presented in part at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, PETR 103.

(2) W. C. Baird, Jr., and J. H. Surridge, *J. Org. Chem.*, **37**, 304 (1972).

(3) W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *J. Amer. Chem. Soc.*, **89**, 410 (1967).

(4) B. Franzus, W. C. Baird, Jr., E. I. Snyder, and J. H. Surridge, *J. Org. Chem.*, **32**, 2845 (1967).

(5) W. C. Baird, Jr., and M. Buza, *ibid.*, **33**, 4105 (1968).

(6) B. Franzus, W. C. Baird, Jr., and J. H. Surridge, *ibid.*, **33**, 1288 (1968).

(7) W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *ibid.*, **34**, 2944 (1969).

(8) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).

(9) H. C. Brown, M.-H. Rei, and K.-T. Liu, *ibid.*, **92**, 1760 (1970).

(10) H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 1990 (1970).

(11) H. C. Brown and J. H. Kawakami, *ibid.*, **92**, 3817 (1970).

(12) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **92**, 6914 (1970).

(13) H. C. Brown and K.-T. Liu, *ibid.*, **92**, 3502 (1970).

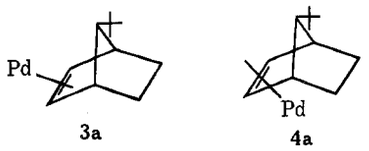
(14) H. C. Brown and K.-T. Liu, *ibid.*, **93**, 7335 (1971).

(15) M. A. Muhs and F. T. Weiss, *ibid.*, **84**, 4697 (1962).

(16) No silver(I)-*anti*-7-*tert*-butylnorbornene complexation was detected with aqueous silver nitrate.[17] This failure has been attributed to the insolubility of the C_{11} olefin in aqueous silver(I) nitrate. Control experiments have confirmed the sensitivity of the aqueous silver nitrate procedure to olefin size and have indicated that C_7–C_8 olefins represent the upper limit for the study of silver(I) complexes in water.

(17) (a) J. G. Traynham and M. F. Sehnert, *J. Amer. Chem. Soc.*, **78**, 4024 (1956); (b) J. G. Traynham and J. R. Olechowski, *ibid.*, **81**, 571 (1959).

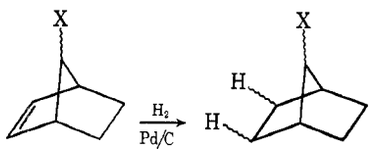
Catalytic hydrogenation of *anti*-7-*tert*-butylnorbornene using deuterium as the reducing gas gave 75% exo,cis and 25% endo,cis addition (Scheme I). Comparable endo,cis addition has not been observed with norbornene[18] or the *anti*-7-acetoxy derivative.[7] The formation of the endo,cis dideuterated norbornene (**4**) has indicated that the reduction has involved endocyclic olefin–catalyst coordination (**4a**) as well as the anticipated exocyclic complex (**3a**).



3a **4a**

The 7-*tert*-butyl group also produced an unusual effect on the relative rates of hydrogenation of the isomeric 7-*tert*-butylnorbornenes. In Table II are

TABLE II
RELATIVE RATES OF REDUCTION OF 7-SUBSTITUTED NORBORNENES



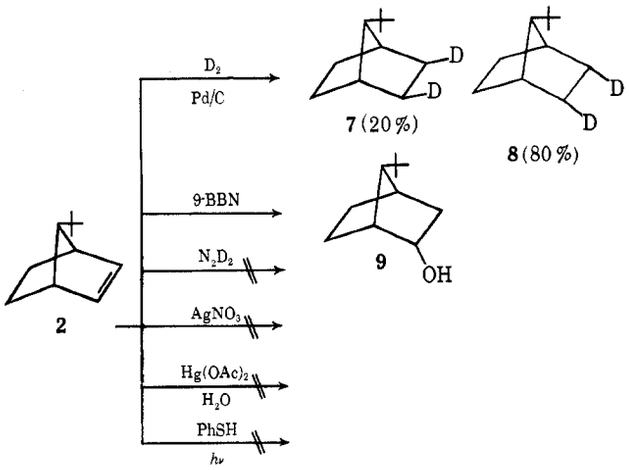
X (anti)	X (syn)	% exo,cis addition	k_{anti}/k_{syn}	Ref
OH		100	0.9	9
	OH	100		
CH_3			2	22
	CH_3			
$OOCCH_3$		100	16.8	9
	$OOCCH_3$	60		
$(CH_3)_3C$		75	9.6	This work
	$(CH_3)_3C$	20		

presented the relative rates of reduction of various syn–anti pairs as a function of the 7 substituent. While small radicals had little or no effect on the relative rates, large groups slowed the reduction of the syn isomer by blocking exo attack.[23] In this sense the data of Table II were inconsistent, for the acetoxy group appeared to exert greater steric influence than the more bulky *tert*-butyl group while simultaneously permitting a higher level of exo reduction of the syn olefin.

The conclusion derived from the consideration of these facts was that the 7-*tert*-butyl group was diminishing the reactivity of the anti double bond even though no direct steric or electronic relationship was evident. Since all the reactions described involved the conversion of the norbornene skeleton to that of norbornane, a common factor that rationalized the behavior of the anti double bond was the development of repulsive interaction between the anti-7-*tert*-butyl group and the exo,cis 5,6 hydrogens in the transition state. Such nonbonded interactions would retard exo electrophilic additions and would encourage endo attack where feasible.[24] The fact that diimide reduction provided the smallest rate differential was a reflection of minimal steric crowding by the cyclic six-membered transition state.[25]

In Scheme II are summarized the reactions of *syn*-7-*tert*-butylnorbornene (**2**) with various reagents. The

SCHEME II
ADDITION REACTIONS OF *syn*-7-*tert*-BUTYLNORBORNENE



results were in accord with those anticipated on the basis of the steric bulk presented by the 7-*tert*-butyl group to reactions of the syn double bond. Reactions that proceeded through cyclic intermediates failed to occur [diimide reduction, silver(I) complexation] or gave endo products (hydrogenation, hydroboration). In these cases the influence of the *tert*-butyl group was comparable to Brown's results with 7,7-dimethylnorbornene.[6-14] The 80% endo,cis hydrogenation of **2** *vs.* 90% for the 7,7-dimethyl compound is ascribed to the different catalysts employed.[18] Both norbornenes failed to complex silver(I); the 7,7-dimethyl derivative, however, experienced 100% exo reduction by diimide, a reagent to which the 7-*tert*-butyl compound was passive. This distinction is attributed to the ability of the diimide transition state to tolerate a *syn*-7-methyl group,[14] but not a *tert*-butyl group.

Noncyclic, or two-stage, additions to 7,7-dimethylnorbornene have been shown to be insensitive to the 7-methyl radical. These reactions have proceeded to yield exo product, presumably because the adding reagent did not approach the double bond symmetrically, but instead attacked the end of the olefinic bond. This direction of approach neutralized the steric influence of the 7-methyl, and the reaction proceeded normally with little or no rate retardation.

(18) Reduction of norbornene over a borohydride reduced platinum catalyst has been reported to give 10% endo reduction.[19] Catalytic hydrogenation in this laboratory has consistently utilized a 10% palladium-on-charcoal catalyst (Matheson Coleman and Bell) over which endo addition to norbornene has not been observed. While this difference may be due to the nature and the activity of the two catalysts, it is true the reductions over platinum are complicated by hydrogen–deuterium exchange and scrambling.[20] The latter reactions are not significant over palladium at room temperature.[6,20,21]

(19) H. M. Bell, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1964.

(20) (a) R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957); (b) H. C. Volger and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **87**, 1356 (1968).

(21) R. L. Burwell, Jr., B. K. C. Shim, and H. C. Rowlinson, *J. Amer. Chem. Soc.*, **79**, 5142 (1957).

(22) V. A. Mironov, B. D. Polkovnikov, E. P. Mikos, T. M. Fadeeva, and A. A. Akhrem, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 129 (1970).

(23) (a) T. J. Howard and B. Morley, *Chem. Ind. (London)*, 73 (1967); (b) T. J. Howard, *Recl. Trav. Chim. Pays-Bas*, **83**, 992 (1964); (c) S. Mitsui, K. Hebiguchi, and H. Saito, *Chem. Ind. (London)*, 1746 (1967).

(24) The influence of various 7 substituents on the stereochemistry of catalytic reduction of norbornenes has been previously discussed.[2]

(25) E. J. Corey, W. L. Mock, and D. J. Pasto, *J. Amer. Chem. Soc.*, **83**, 2957 (1961). The size of the diimide transition state has permitted exo reduction of 7,7-dimethylnorbornene although steric arguments would have predicted that no reaction would occur.[14]

With the 7-*tert*-butyl compound, this was not the case, and oxymercuration with aqueous mercury(II) acetate and free radical addition of thiophenol failed to occur.[26] The combined bulk of the 7 substituent and the reagents was apparently sufficient to preclude reaction independent of the mode of attack. Endo addition was naturally excluded by the endo 5,6 protons.

Experimental Section

Infrared spectra were recorded on a Beckman IR-5A spectrophotometer. Nmr spectra were measured on Jeol Minimar and Varian Associates A-60 and HA-100 spectrometers using tetramethylsilane as an internal standard. Analytical vapor phase chromatography (vpc) was performed on a Perkin-Elmer 154D fractometer and a Perkin-Elmer Model 226 capillary gas chromatograph. Preparative scale gas chromatography was performed on a Varian Aerograph Model A-700 instrument. Melting points and boiling points are not corrected. All reagents were obtained from commercial sources and were used as received.

Reactions of *anti*-7-*tert*-Butylnorbornene (1). Oxymercuration.[27]—To a suspension of 300 mg (0.95 mmol) of mercury(II) acetate in 2 ml of water and 1 ml of tetrahydrofuran was added a solution of 110 mg (0.73 mmol) of *anti*-7-*tert*-butylnorbornene in 2 ml of tetrahydrofuran. The reaction mixture gradually decolorized. After 5 min the reaction was treated with 3 *M* sodium hydroxide and 0.5 *M* sodium borohydride and worked up in the normal manner. Infrared analysis showed the crude product to be a mixture of an alcohol and an acetate ester. The ester was saponified by refluxing the crude product with 0.1 g of sodium methoxide in 5 ml of methanol. The alcohol was isolated by dilution of the saponification mixture with water and extraction with pentane. Removal of the pentane solvent gave 75 mg (62%) of *exo*-2-hydroxy-*anti*-7-*tert*-butylnorbornane (**6**), mp 84.5–85°, which was shown to be identical with an authentic sample.[2] Vpc analysis (3 ft × 0.25 in., 3% Dowfax column, 100°, 135 ml/min) showed the alcohol to be homogeneous.

Diimide Reduction.—The reduction was performed utilizing 111.9 mg (0.74 mmol) of *anti*-7-*tert*-butylnorbornene, 385.7 mg (2 mmol) of potassium azodicarboxylate in 1 ml of methanol-d_1, and 0.25 ml of acetic acid-d_1 in 0.75 ml of methanol-d_1. The reaction yielded 106 mg (94%) of 2,3-dideuterio-7-*tert*-butylnorbornane (**3**), which was homogeneous by vpc (2 m × 0.25 in. polypropylene glycol column, 175°, 80 ml/min): nmr ($CDCl_3$) δ 2.04 (m, 2, >CH), 1.54–1.85 (m, 2, exo >CHH), 1.24 (m, 1, HC-*tert*-Bu), 0.98–1.20 (m, 4, endo >CHH), 0.90 [s, 9, $(CH_3)_3C$]. Analysis of the exo,endo proton areas showed that the reduction had occurred exclusively exo,cis.

Hydrogenation.—*anti*-7-*tert*-Butylnorbornene (188.2 mg, 1.25 mmol) was reduced with deuterium over 38 mg of 10% palladium on charcoal in 5 ml of methanol in a gas buret apparatus. The product was isolated by dilution with water and extraction with pentane. Removal of the solvent gave 160 mg (85%) of 2,3-dideuterio-7-*tert*-butylnorbornane (**3**, **4**). The nmr spectrum ($CDCl_3$) was identical with that described above except for the relative areas of the exo (2.5) and the endo (3.5) protons, which corresponded to 75% exo,cis and 25% endo,cis reduction.

Silver Nitrate Complexation.—The general procedure has been described.[4] A 0.5 *M* solution of *anti*-7-*tert*-butylnorbornene in carbon tetrachloride and a saturated aqueous solution of silver nitrate were shaken together for 3 hr at room temperature. No measurable complex formation was observed during this interval.

The formation of a silver complex was also investigated by the gas chromatographic method of Muhs and Weiss.[15] Two 6 ft × 0.25 in. vpc columns were employed: 30% ethylene glycol on Chromosorb P (70%) and 30% 0.35 *M* silver nitrate in ethylene glycol in Chromosorb P (70%). The columns were operated at 40° and 480 ml/min helium flow. A control experiment with norbornene gave an equilibrium constant of 49.5 (lit. 62).[16] Under identical conditions *anti*-7-*tert*-butylnorbornene gave a silver ion complexation constant of 20.7. The ratio of the equilibrium constants, $K_{eq_{norbornene}}/K_{eq_{anti}} = 2.4$.[28]

Competitive Reactions of Norbornene and *anti*-7-*tert*-Butylnorbornene.—In the general procedure equimolar amounts of norbornene and *anti*-7-*tert*-butylnorbornene were dissolved in the appropriate reaction solvent, and *n*-decane was added as an internal standard for vpc analysis. The olefin solution was reacted with a limited amount (~50 mol %) of the various reagents. Samples of the reaction were periodically removed, quenched, and analyzed by vpc for olefin content. Relative reaction rates were calculated from the equation

$$k_{norbornene}/k_{anti} = \frac{\log[(norbornene)_0/(norbornene)]}{\log[(anti)_0/(anti)]}$$

The ratios reported represent the average of at least three separate determinations. Pertinent details are summarized in Table III.

TABLE III

Reagent (mmol)	Norbornene, mmol	Anti, mmol	$k_{norbornene}/k_{anti}$	Vpc method	Ref
$Hg(OAc)_2$ (1.01)	1.43	1.05	5.49	*a*	27
H_2 (~1.0)	1.06	1.07	3.77	*b*	7
N_2H_2 (0.42)	0.50	0.47	1.55	*b*	3
9-BBN (0.78)	0.98	0.88	3.73	*b*	29
m-$CO_3HC_6H_4Cl$ (0.36)	0.48	0.55	5.16	*b*	12

[a] 4 m × 0.25 in. 20% polypropylene glycol, 170°, 25 ml/min. [b] 300 ft × 0.01 in. DC-550 silicone, 140°, 30 psig.

Competitive Reduction of *syn*- and *anti*-7-*tert*-Butylnorbornenes.—A mixture of 0.43 mmol of *syn*-7-*tert*-butylnorbornene and 1.44 mmol of *anti*-7-*tert*-butylnorbornene was hydrogenated in a gas buret over 10% palladium on charcoal in 5 ml of methanol. Samples were periodically removed and analyzed by vpc (method b) using *n*-decane as an internal standard. The relative rate, k_{anti}/k_{syn}, was calculated as shown above; the average of eight determinations covering the range 12–80% reduction was 9.6.

Reactions of *syn*-7-*tert*-Butylnorbornene (2). Hydroboration.[29]—To 5 ml of 0.78 *M* 9-BBN in tetrahydrofuran was added 300 mg (2 mmol) of *syn*-7-*tert*-butylnorbornene in 1 ml of tetrahydrofuran. The reaction was stirred under nitrogen at room temperature for 20 hr. To the reaction were added 1 ml of 6 *M* sodium hydroxide and 1 ml of 30% hydrogen peroxide, and the reaction was refluxed for 1 hr. The aqueous phase was saturated with sodium chloride, and the tetrahydrofuran layer was separated and dried over magnesium sulfate. The ether was removed by distillation to give 350 mg of clear oil. Vpc analysis (3 ft × 0.25 in. 3% Dowfax, 100°, 135 ml/min) showed that ~25% of starting olefin remained. The product (retention time 12 min) was separated by vpc to give 136 mg (54% based on olefin consumed) of white needles, mp 85–85.5°. The acetate ester (acetyl chloride–pyridine) gave a single peak, retention time 22.0 min, on a 300 ft × 0.01 in. DC-550 silicone column, 150°, 30 psig. *Anal.* Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.12; H, 11.75. Nmr ($CDCl_3$) δ 4.57 (m, 1, J = 19 Hz, exo HCO), 2.08 (s, 1, OH), 1.93–2.32 (m, 2, >CH), 1.06–1.91 (m, 7, exo,endo $>CH_2$, HC-*tert*-Bu), 0.96 [s, 9, $(CH_3)_3C$]. The nmr spectrum was that anticipated for *endo*-2-hydroxy-*syn*-7-*tert*-butylnorbornane (**9**).

Hydrogenation.—A sample of *syn*-7-*tert*-butylnorbornene (1.87 mg, 1.25 mmol) was reduced with deuterium according to the procedure described for reduction of the anti isomer. The iso-

(26) Less bulky reagents did attack *syn*-7-*tert*-butylnorbornene. Trifluoroacetic acid reacted to give a mixture of products that was not characterized. Mercury(II) trifluoroacetate in tetrahydrofuran and in benzene mercurated the olefin; the resulting adduct was too labile to permit reliable characterization. Nmr experiments, however, suggested that the adduct was not exocyclic.

(27) H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

(28) Control experiments utilizing octene-1 and dodecene-1 as model olefins gave a ratio of constants, $K_{eq_{C_8}}/K_{eq_{C_{12}}} = 1.5$. This value has shown that the K for the *anti*-7-*tert*-butyl olefin is lower than anticipated on the basis of diminished solubility of a C_7 *vs.* C_{11} olefin.

(29) E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5200 (1968).

lated yield of pure norbornane was 132 mg (71%): nmr ($CDCl_3$) δ 2.10 (m, 2, $\geq$CH), 1.30–1.76 (m, 3.6, exo >CHH), 1.26 (m, 1, HC-*tert*-Bu), 0.98–1.18 (m, 2.4, endo >CHH), 0.92 (s, 9, $(CH_3)_3C$]. Deuterium addition had occurred 80% endo,cis.

Diimide Reduction.—The reduction of 200 mg (1.35 mmol) of *syn*-7-*tert*-butylnorbornene with diimide was attempted as described above. The olefin was exposed to a fourfold molar excess of diimide generated by two charges of potassium azodicarboxylate over a period of 3 hr. Analysis by vpc (300 ft × 0.01 in. DC-550 silicone column, 115°, 30 psig) showed that the starting olefin was recovered quantitatively.

Silver Nitrate Complexation.—*syn*-7-*tert*-Butylnorbornene failed to complex silver nitrate in aqueous solution. The olefin showed identical retention times on both silver nitrate–ethylene glycol and ethylene glycol vpc columns.

Oxymercuration.—Oxymercuration of the syn olefin was attempted with mercury(II) acetate in aqueous tetrahydrofuran.[27] The reaction was stirred at room temperature for 24 hr; no discharge of the characteristic yellow color of the mercury salt suspension occurred. The reaction was worked up according to the standard procedure to recover unreacted olefin. The absence of product was confirmed by vpc analysis.

Addition of Thiophenol.—A solution of 110 mg (1.0 mmol) of thiophenol and 150 mg (0.84 mmol) of *syn*-7-*tert*-butylnorbornene (84% syn olefin, 16% 7-*tert*-butylnorbornane) in 1 ml of *n*-hexane was stirred at 0° under nitrogen. The solution was irradiated with a Hanovia 100-W quartz ultraviolet lamp. Samples were removed periodically through a rubber septum and were analyzed by vpc for the disappearance of *syn*-7-*tert*-butylnorbornene; 7-*tert*-butylnorbornane was utilized as an internal standard. After 3.5 hr of irradiation the concentration of syn olefin was unchanged. The irradiation was interrupted, and 950 mg (1.0 mmol) of norbornene was injected into the reaction. Irradiation of the reaction mixture was resumed, and after 25 min 75% of the norbornene had reacted; after 50 min only 5% of the norbornene remained. No change in the concentration of the *syn*-7-*tert*-butyl compound was apparent.

Registry No.—**1**, 32640-84-9; **2**, 32640-83-8; **9**, 33905-54-3; **9** anti isomer, 33905-55-4.

Kinetic α-Deuterium Isotope Effects in the Reactions of Benzyl Chlorides with Cyanide Ion and in the Solvolyses of Benzyl Chlorides[1]

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α-Deuterium isotope effects have been determined for the reactions with cyanide ion and the solvolyses of *m*-chlorobenzyl chloride, benzyl chloride, and *p*-methylbenzyl chloride in 55% (by vol) aqueous Methyl Cellosolve. In almost all experiments solvolysis occurs parallel to reaction with CN^-, and it is necessary to apply eq 3 for the calculation of k_2 for the reaction with CN^-. Values of k_1 have been evaluated separately in experiments without CN^- at the same ionic strength. Only the reaction with CN^- and the solvolysis of *m*-chlorobenzyl chloride are examples of practically pure SN2 processes, and the isotope effects are nearly equal to unity. The unusually high result of k_H/k_D = 1.25–1.31 (50°) in the reaction of *p*-methylbenzyl chloride with cyanide ion supplies evidence for a reaction pathway *via* carbonium ions or ion pairs. The rate constants of the reactions of unsubstituted benzyl chloride must contain contributions of the carbonium ion pathway and, consequently, the experimental isotope effects do not refer to pure SN2 processes.

Some work has been done in this laboratory on kinetic deuterium isotope effects in reactions of methyl iodide with various nucleophiles.[3–5] The present study is concerned with α-deuterium isotope effects in SN2 reactions of a halide with a larger primary alkyl group. A suitable choice is benzyl chloride because of its relatively high reactivity. Furthermore, the presence of the aromatic ring provides the opportunity of studying the influence of remote substituents on the isotope effect. A ring substituent may affect reacting bond orders and force constants in the transition state and cause a noticeable change of the isotope effect.[6]

Previous work on deuterium isotope effects in SN2 reactions of benzyl compounds was carried out by Östman[7] and Strecker and Elias,[8] who studied the chloride ion exchange reaction of benzyl chloride. Hill and Fry[9] investigated the influence of substituents on the chlorine isotope effect in reactions of benzyl chloride with various nucleophiles. Variations in the isotope effect were mainly due to changes in the relative contributions of the SN2 and SN1 mechanisms to the overall reaction.

In this work, the α-deuterium isotope effect has been determined for the reactions of benzyl chloride, *m*-chlorobenzyl chloride, and *p*-methylbenzyl chloride with cyanide ion in 55% (by volume) aqueous Methyl Cellosolve. The investigation has been supplemented by measurements of rate constants of solvolysis of the three benzyl chlorides and their α-dideuterated variants at the same ionic strength (addition of $NaClO_4$ instead of KCN). These rate constants are needed for the treatment of the kinetic data of the reaction with cyanide ion, since solvolysis is a competing reaction. A systematic isotope effect study at a series of different temperatures has been carried out for both reactions of the mentioned three benzyl chlorides. Though further work is necessary in order to establish a noticeable substituent effect on the isotope effect of the SN2 reaction, the results are published now as the authors will not have the opportunity to continue the work in the very near future.

The following parallel reactions occur in a solution containing benzyl chloride and cyanide ion.

$$ArCH_2Cl + CN^- \longrightarrow ArCH_2CN + Cl^- \quad (k_2)$$

$$\left.\begin{aligned} ArCH_2Cl + H_2O + CN^- &\longrightarrow ArCH_2OH + Cl^- + HCN \\ ArCH_2Cl + ROH + CN^- &\longrightarrow ArCH_2OR + Cl^- + HCN \end{aligned}\right\} \quad (k_1)$$

(1) Taken in part from the thesis of Mr. Chih-kuo Ho, submitted in partial fulfillment of the requirements for the degree of Master of Science to the College of Pharmaceutical Sciences, Columbia University, 1969.

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(3) A. V. Willi and C. M. Won, *J. Amer. Chem. Soc.*, **90**, 5999 (1968).

(4) A. V. Willi and C. M. Won, *Can. J. Chem.*, **48**, 1452 (1970).

(5) C. M. Won and A. V. Willi, *J. Phys. Chem.*, **76**, 427 (1972).

(6) C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, **84**, 817 (1962); E. R. Thornton, *ibid.*, **89**, 2915 (1967).

(7) B. Östman, *ibid.*, **87**, 3163 (1965).

(8) H. Strecker and H. Elias, *Radiochim. Acta*, **7**, 22 (1967); *Chem. Ber.*, **102**, 1270 (1969).

(9) J. W. Hill and A. Fry, *J. Amer. Chem. Soc.*, **84**, 2763 (1962).