mately 3 ml of the hexane solution was withdrawn with a Pasteur pipet and stored in a vial. The first few drops of the aqueous layer were discarded and the remainder of the solution was stored in a vial until analysis.

To prepare samples for the reference beam for the spectrophotometric analysis of both the hexane and the aqueous layers, an extraction was carried out exactly as described above except that 2 ml of 70% aqueous ethanol was used in place of the ester solution.

The 70% aqueous ethanol solution was prepared by weight, employing the appropriate corrections for buoyancy.[17] Reagent absolute ethanol (Pharmco) and distilled water were used without further purification. The solvent was stored in a sealed 2-l. erlenmeyer flask, equipped with a siphoning device.

Kinetic runs were carried out in 3-ml quartz uv cells (Pyrocell Manufacturing Company) which had a 1-cm path length. The cells had ground-glass stoppers, which were tightly sealed during the kinetic runs to minimize evaporation.

Beers' law plots of absorbance at 2610 Å *vs.* concentration were linear for both the exo and endo *p*-nitrobenzoate esters over the range of concentration through which the solvolysis kinetics were followed. Similar plots for *p*-nitrobenzoic acid both at 2710 Å (λ_{max} of the acid) and at 2610 Å (λ_{max} of the ester) were linear.

Rate constants were calculated from a sub-routine for plotting $\ln (A_t - A_\infty)$ *vs.* time of a computer program devised by York,[18] modified by Dr. Michael Marron and used previously by Dr. John Conkling for calculating the rates of solvolysis of deuterated norbornyl brosylates.[19] An IBM 7094 computer was used for the calculations, giving the first-order rate constant and standard deviation for each run.

Acknowledgment. We wish to thank the National Science Foundation for the financial support of this work. We are grateful to Professor Alex Nickon and Dr. Raymond Weglein for commenting on the manuscript.

Registry No.—**9a,** 22467-58-9; **9a** free alcohol, 3212-15-5; **9b,** 53432-35-2; **9b** free alcohol, 53432-36-3; **10a,** 13351-30-9; **10a** free alcohol, 3212-16-6; **10b,** 53432-37-4; **10b** free alcohol, 53466-51-6; norcamphor, 497-38-1; methyl iodide-d_3, 865-50-9; *p*-nitrobenzoyl chloride, 122-04-3; methyl iodide, 74-88-4.

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(10) For the solvolysis of 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate (**4**) cited previously,[4] Humski observed that the k_H/k_D varied somewhat with the amount of elimination products as the solvent was changed from 50 to 70% dioxane–water. It should be pointed out that different amounts of elimination into the methyl groups of the undeuterated and deuterated *p*-nitrobenzoate esters could influence the k_H/k_D for **9** and **10.**
(11) Correction to 75° does not effect these numbers significantly.
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Bicyclo[3.2.0]hept-6-en-2-yl Carbonium Ion. 2-Methyl Substituent Effects[1]

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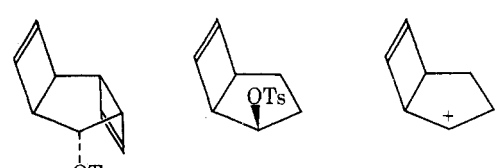
The methyl substituent effects on the rates and products of the solvolysis reactions of *exo*- and *endo*-2-methylbicyclo[3.2.0]hept-6-en-2-yl *p*-nitrobenzoates (**6**-OPNB and **5**-OPNB, respectively) were investigated by comparing those of the demethylated analogs (**7**-OTs and **2**-OTs, respectively) to elucidate the nature of the bicyclo[3.2.0]hept-6-en-2-yl carbonium ion **3.** The acetolysis rate of **7**-OTs indicates a rate enhancement of 3500 (25°) when compared to that of **2**-OTs, while **6**-OPNB undergoes solvolysis at a rate only 2.8 times as fast as **5**-OPNB at 25°. The acetolysis of **7**-OTs gives exclusively *anti*-7-norbornenyl acetate **14,** while **2**-OTs undergoes acetolysis to a 35:65 mixture of **7**-OAc and **14.** On the other hand, **5**-OPNB and **6**-OPNB yield exclusively **6**-OH through one common classical carbonium ion **15.** The above results suggest that **3** is mainly stabilized by a homoallylic interaction to lead to the initial carbonium ion **12,** which rearranges to the stable bishomocyclopropenyl carbonium ion **13.**

Although there is no straightforward demonstration of the existence of homoallylic carbonium ion intermediates, the unusual reactivities and stereospecific products of the solvolysis reactions of some rigid polycyclic ring compounds have been interpreted by homoallylic interactions between electron-deficient carbinyl carbon and electron-rich double bond.[2] In our recent study of *anti*-tricyclo[5.2.0.$0^{2,5}$]nona-3,8-dien-6-yl tosylate (**1**-OTs)[3] we observed that the rate of acetolysis of **1**-OTs is enhanced by a factor of 7.3×10^4 when compared to that of *endo*-bicyclo[3.2.0]hept-6-en-2-yl tosylate (**2**-OTs) which is in the partially similar ring system. In connection with this result, it



1-OTs **2**-OTs **3**

seems to be of some interest to further investigate the nature of the bicyclo[3.2.0]hept-6-en-2-yl carbonium ion **3.**[2-4] Thus, *exo*- and *endo*-2-methylbicyclo[3.2.0]hept-6-en-2-yl *p*-nitrobenzoates (**6**-OPNB and **5**-OPNB, respectively) and

Table I
Kinetic Data for Solvolysis of *exo*- and *endo*-2-Methylbicyclo[3.2.0]hept-6-en-2-yl *p*-Nitrobenzoates (6-OPNB and 5-OPNB), *exo*-Bicyclo[3.2.0]hept-6-en-2-yl Tosylate (7-OTs), and Related Compounds

Substrate	Temp, °C	k, sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu	k rel
6-OPNB[a]	125	$(1.71 \pm 0.02) \times 10^{-5}$ [b]	29.8 ± 0.3	−6.1 ± 0.8	
	150	$(1.68 \pm 0.02) \times 10^{-4}$ [b]			
	25	3.80×10^{-11} [c]			2.8
5-OPNB[a]	125	$(3.45 \pm 0.07) \times 10^{-6}$ [b]	28.2 ± 0.2	−13.2 ± 0.5	
	150	$(3.06 \pm 0.03) \times 10^{-5}$ [b]			
	25	1.38×10^{-11} [c]			(1.0)
7-OTs[d]	25	$(9.59 \pm 0.11) \times 10^{-6}$ [b]	23.9 ± 0.2	−1.5 ± 0.7	3.5×10^3
	50	$(2.35 \pm 0.04) \times 10^{-4}$ [b]			
2-OTs	25	2.70×10^{-3} [e]	28.1 ± 0.6[e]	−3.6 ± 1.5[e]	(1.0)
1-OTs	25	1.97×10^{-4} [e]	25.2 ± 1.4[e]	+9.0 ± 4.8[e]	7.3×10^4

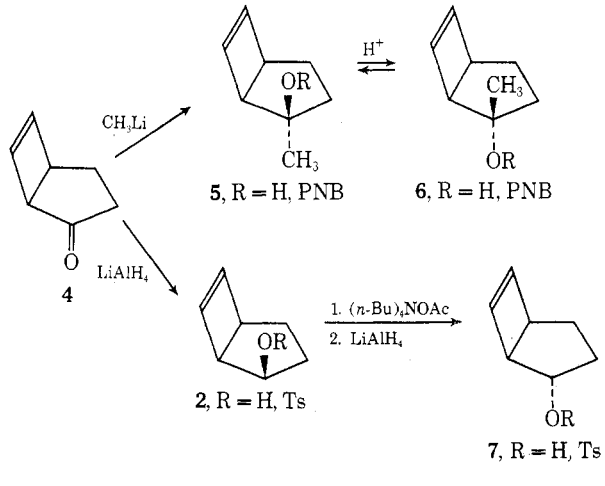
[a] *Ca.* 0.006 *M* in 50% acetone–50% water by volume. [b] The errors are deviation from the average of two runs. [c] Value extrapolated from data at higher temperature. [d] *Ca.* 0.02 *M* in acetic acid buffered with 0.045 *M* sodium acetate. [e] Reference 3.

the demethylated analogous tosylates (**7**-OTs and **2**-OTs, respectively) have been synthesized and studied to obtain a quantitative assay of the methyl substituent effects on **3** formed in the solvolysis reactions. These results would provide some evidence for the existence of the homoallylic interaction in the transition state of the solvolysis reactions.

Results and Discussion

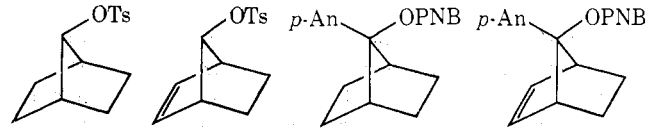
The known ketone **4**[5] was treated with freshly prepared methyllithium to produce exclusively **5**-OH in 83% yield, which was converted to **5**-OPNB in the usual fashion. The exo epimer (**6**-OH) was obtained by an acid-catalyzed isomerization of **5**-OH in low yield (17%) and converted to **6**-OPNB. The stereochemical assignments for the exo and endo epimers were based upon the methyllithium reaction of **4** and their nmr spectral data. Since attack of methyllithium on ketones would usually occur from the less hindered side of carbonyl groups, the only one product obtained here might be the endo epimer (**5**-OH). The nmr spectra of **5**-OPNB and **6**-OPNB show that the methyl group of **6**-OPNB absorbs at δ 1.20 which is shielded by 0.13 ppm more than of **5**-OPNB as expected by a result of diamagnetic anisotropic shielding effect. The exo alcohol (**4**-OH)[4b] was obtained by inversion of **2**-OTs[3] with tetra-*n*-butylammonium acetate in dry acetone[6] followed by lithium aluminum hydride reduction and was converted to **7**-OTs (23% based on **2**-OTs) (Scheme I).

Scheme I



The solvolytic reactivity of **7**-OTs was measured in buffered acetic acid by the uv absorbance method,[3] and the reactivities of **5**-OPNB and **6**-OPNB were measured in 50% aqueous acetone by the titrimetric method.[3] The kinetic data are summarized in Table I where literature values for related compounds are involved for comparison.

Generally, it has been known that the introduction of electron-releasing substituents at a cationic center leads to diminution in participation by double bonds resulting in a classical carbonium ion.[2a,7] For example, the acetolysis rate of *anti*-7-norbornenyl tosylate (**9**) is enhanced by a factor of 10^{11} over that of 7-norbornyl tosylate (**8**),[8] while 7-*p*-anisyl-*anti*-7-norbornenyl *p*-nitrobenzoate (**11**) undergoes solvolysis at a rate only 2.5 times greater than 7-*p*-anisyl-7-norbornyl *p*-nitrobenzoate (**10**).[9] Thus, a comparison of the exo/endo rate ratio for **5**-OPNB and **6**-OPNB to that for **2**-OTs and **7**-OTs will account for the natures of the initial intermediates formed on ionization of these isomeric compounds.



8 (1)[a] **9** (10^{11}) **10** (1) **11** (2.5)

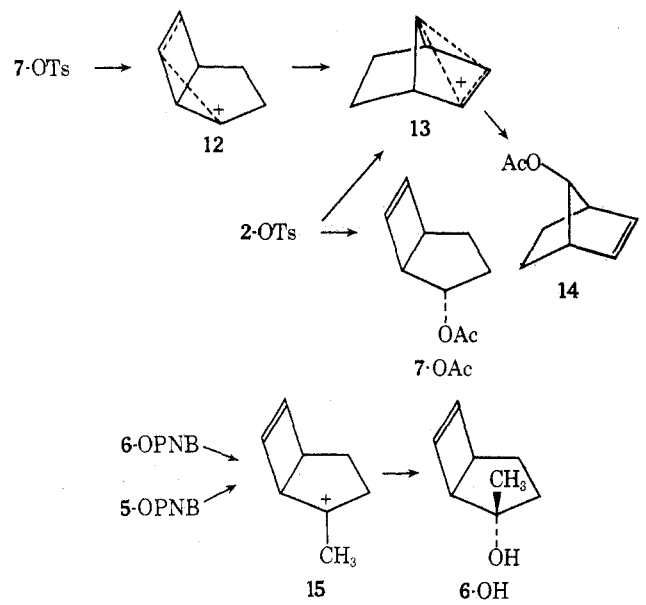
[a] k rel in parentheses.

It is clear from Table I that **7**-OTs is 3.5×10^3 times more reactive than **2**-OTs while **6**-OPNB undergoes solvolysis at a rate 2.8 times as fast as **5**-OPNB at 25°. This result suggests that the high reactivity of **7**-OTs might be mainly due to participation of the double bond in the ionization at the reaction site to produce the homoallylic carbonium ion **12**. Here, it is interesting to note that even **7**-OTs is less reactive than **1**-OTs in spite of the fact that the similar homoallylic interaction should be expected in their transition states. The difference in the reactivity of **1**-OTs and **7**-OTs (*ca.* 20) appears to result from a combination of two factors. First, an increase in reactivity of **1**-OTs probably results from a ground-state interaction[10] with the *anti*-cyclobutene ring providing relief of strain at the transition state. Second, there is likely a more favorable geometry for the homoallylic interaction by the double bond in **1**-OTs than in **7**-OTs; since the nmr spectral study of **7**-OTs suggests **7**-OTs in a "boat" conformation,[11] this conformation would provide decrease in the homoallylic interaction because of the prolonged distance between the reaction center and the double bond, compared to the rigid tricyclic tosylate (**1**-OTs).

The acetolysis of **7**-OTs gives exclusively *anti*-7-norbornenyl acetate **14**, while **2**-OTs undergoes acetolysis to a 35:

65 mixture of 7-OAc and 14 in accord with Story's result.[2a] From the kinetic data and the solvolysis studies, it is suggested that the incipient positive center of 7-OTs is stabilized first by the homoallylic interaction to produce the initial carbonium ion intermediate 12,[12] which rapidly rearranges to the bridged carbonium ion 13. On the other hand, 2-OTs leads predominantly to 13 and, at the same time, partially to 7-OAc by attack of solvent. Both epimeric *p*-nitrobenzoates, 5-OPNB and 6-OPNB, however, yield exclusively 6-OH as only the monomeric alcohol, suggesting one common classical carbonium ion intermediate 15 which is captured by solvent from the less hindered side. The observations are summarized in Scheme II.

Scheme II



The difference in the activation energies of 7-OTs (ΔH^* = 23.9 kcal/mol) and 2-OTs (ΔH^* = 28.1 kcal/mol) also suggests the significant difference in the stabilization of their transition states. The conformational studies of these bicyclic ring systems by X-ray analysis are under investigation.

Experimental Section

Melting points were taken on a Yamato MP-21 melting point apparatus and uncorrected. Infrared spectra were recorded on a Shimadzu IR-400 spectrophotometer and ultraviolet spectra were determined with a Shimadzu UV-200 spectrophotometer. Nuclear magnetic resonance spectra were recorded using a Hitachi R-24 instrument with the chemical shift (δ) given in parts per million down from TMS. Gas–liquid chromatography was performed on a Shimadzu GC-4B instrument. Mass spectra were determined with a JEOL-Q10 mass spectrometer. Microanalyses were determined in the microanalytical laboratory of Institute of Physical and Chemical Research, Wako-shi, Saitama, Japan.

***endo*-2-Methylbicyclo[3.2.0]hept-6-en-2-ol (5-OH).** To freshly prepared methyllithium in ether (*ca.* 0.05 mol) was added dropwise a solution of 4[3] (4.0 g, 0.037 mol) in 20 ml of ether at room temperature under nitrogen atmosphere. The resulting solution was stirred for 30 min. The excess methyllithium was destroyed by addition of ammonium chloride, and water was carefully added to the flask. After separation of the organic layer, the aqueous layer was extracted with ether. The ethereal solution was combined with the organic layer, and the combined solution was washed with water and dried ($MgSO_4$). After removal of ether distillation gave the endo alcohol 5-OH as a clear oil [3.8 g, 83%, bp 60–61.0° (9 mm)]: ir (film) 3350 (OH), 3050, 2930, 1290, 1150, and 1120 cm^{-1}; nmr (CCl_4) δ 6.15 and 6.03 (2 d, AB, 2 H, vinyl, J = 2.6 Hz), 3.50 (s, 1 H, –OH), 3.05 (m, 1 H, H_5), 2.75 (d, 1 H, H_1, J = 3.6 Hz), 2.20–1.70 (*m*, 1 H), 1.60–1.20 (*m*, 3 H), and 1.10 (s, 3 H, $-CH_3$); mass spectrum *m/e* 124 (M^+), 109, and 106.

***endo*-2-Methylbicyclo[3.2.0]hept-6-en-2-yl *p*-Nitrobenzoate (5-OPNB).** To a solution of 5-OH (500 mg, 4.04 mmol) in 15 ml of dry pyridine was added *p*-nitrobenzoyl chloride (760 mg, 4.10 mmol) in small portions at 0°. After completion of the addition, the resulting solution was allowed to stand in a refrigerator for 5 days and then poured into ice–water (100 g) containing 5 ml of concentrated hydrochloric acid. The product was extracted into chloroform, which was washed with dilute hydrochloric acid, water, 5% sodium bicarbonate solution, and water and dried ($MgSO_4$). Removal of the solvent gave a precipitate which was recrystallized from hexane to yield 810 mg (74%) of 5-OPNB: mp 109.5–110.5°; ir (Nujol) 1720 (C=O), 1610, 1525, 1350, 1310, 1290, 1120, 1110, and 720 cm^{-1}; nmr (CD_3COCD_3) δ 8.20 (A_2B_2, 4 H, aromatic, J = 9.0 Hz), 6.08 and 5.99 (2 d, AB, 2 H, vinyl, J = 2.6 Hz), 3.40 (d, 1 H, H_1, J = 3.2 Hz), 3.21 (m, 1 H, H_5), 2.70–1.90 (m, 3 H), 1.70–1.40 (m, 1 H), and 1.51 (s, 3 H, $-CH_3$).

Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53. Found: C, 66.05; H, 5.46.

***exo*-2-Methylbicyclo[3.2.0]hept-6-en-2-ol (6-OH).** To a solution of 5-OH (3.4 g, 0.0275 mol) in 100 ml of pentane at 0° was added a solution of 50% sulfuric acid (50 ml). The resulting mixture was allowed to stir for 10 hr at 0° and 40 hr at water-bath temperature, following the progress of the reaction by glpc (FFAP 15%, 3 m × 3 Φ column). After separation of the organic layer the aqueous layer was extracted with ether. The ethereal solution was combined with the organic layer, and the resulting solution was washed with water, 5% sodium bicarbonate solution, and water and then dried ($MgSO_4$). Evaporation of the solvent gave a mixture of 5-OH, 6-OH, and an unidentified ketone (<3%). The mixture was purified by chromatography on a silica gel column, eluting with 25% ether in benzene to give 567 mg (16.6%) of 6-OH as a clear liquid, which is crystallized on standing: mp 42–43.5°; ir (CCl_4) 3620 (free OH), 3320 (OH), 3040, 2930, 1060, and 1040 cm^{-1}; nmr (CCl_4) δ 6.00–5.70 (m, 2 H, vinyl), 3.07 (s, 1 H, H_1), 2.43 (br s, 1 H, H_5), 2.13–1.23 (m, 2 H), 1.40 (s, 1 H, –OH), 1.21–0.75 (m, 2 H), and 1.11 (s, 3 H, $-CH_3$): mass spectrum *m/e* 124 (M^+), 109, and 106.

***exo*-2-Methylbicyclo[3.2.0]hept-6-en-2-yl *p*-Nitrobenzoate (6-OPNB).** The exo alcohol 6-OH (100 mg) was converted to the *p*-nitrobenzoate (6-OPNB) as described above for 5-OH: yield 170 mg (78%); mp 78.0–79.5°; ir (Nujol) 1720 (C=O), 1610, 1530, 1350, 1270, 1110, and 720 cm^{-1}; nmr (CD_3COCD_3) δ 8.15 (A_2B_2, 4 H, aromatic, J = 10.0 Hz), 6.11–5.76 (m, 2 H, vinyl), 4.30 (s, 1 H, H_1), 2.78 (br s, 1 H, H_5), 2.10–1.59 (m, 3 H), 1.40–1.03 (m, 1 H), and 1.20 (s, 3 H, $-CH_3$).

Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53. Found: C, 65.63; H, 5.39.

Kinetic Measurements. The ratio of acetone to water was 50:50 by volume. For each run, approximately 80 mg of each 5-OPNB and 6-OPNB was weighed into a 50-ml volumetric flask and then filled with the 50% aqueous acetone. Eight tubes, containing 6 ml of the above solution, were sealed under nitrogen and heated in a constant temperature controlled oil bath (±0.3°). After the completion of the run, 5 ml of the solution was removed for titration. To the solution, 15 ml of water was added with a few drops of 0.1% Bromothymol Blue indicator in 50% ethyl alcohol. This mixture was titrated with 0.003 *M* sodium hydroxide in methanol under nitrogen.[3]

The *exo*-tosylate (7-OTs) was solvolyzed in acetic acid containing sodium acetate, and the rates were measured as previously described.[3] The kinetic data are shown in Table I.

Preparative Solvolyses of 5-OPNB and 6-OPNB. The *endo*-*p*-nitrobenzoate (5-OPNB, 200 mg) in 100 ml of 50% aqueous acetone containing 154 mg of 2,6-lutidine was sealed in six test tubes under nitrogen and heated for 47 hr at 150°. The cooled tubes were opened, and the acetone was removed by a rotary evaporation. The product mixture was isolated by ether extraction. After removal of the solvent, the product was purified by chromatography on a silica gel column, eluting with 20% ether in benzene to give 31 mg (34%) of a product which was identified as 6-OH by nmr comparison.

The *exo*-*p*-nitrobenzoate (6-OPNB) was solvolyzed as mentioned above except for being heated for 10 hr at 150°. The exo alcohol was obtained in 30% yield.

The low isolated yields of these reactions are attributed to sublimation during drying and an unidentified hydrocarbon which has a very short retention time in glpc. The absolute yields by glpc (FFAP 15%, 3 m × 3 Φ) analyses were shown to be 45% for 5-OPNB and 51% for 6-OPNB.

Preparative Acetolyses of 2-OTs and 7-OTs. The *endo*-tosylate (2-OTs, 200 mg) in 25 ml of acetic acid containing 84.5 mg of

sodium acetate was sealed in four test tubes under nitrogen and heated for 48 hr at 100°. The cooled tubes were opened, and the solution was neutralized with sodium bicarbonate and extracted with ether. The ethereal solution was washed with saturated sodium chloride solution, dried ($MgSO_4$), and concentrated. The product was purified by chromatography on silica gel column, eluting with 20% ether in petroleum ether affording 82 mg (64%) of a mixture of 14[13] (65%) and 7-OAc (35%). The *exo*-tosylate (7-OTs, 67.8 mg) was solvolyzed at 50° to give 25 mg (58%) of 14.

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Registry No.—1-OTs, 41326-96-9; 2-OTs, 41326-98-1; 4, 1072-77-1; 5-OH, 53555-56-9; 5-OPNB, 53555-57-0; 6-OH, 53585-67-4; 6-OPNB, 53585-68-5; 7-OTs, 53585-69-6; *p*-nitrobenzoyl chloride, 122-04-3.

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(10) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1854 (1964).
(11) The nmr spectra of 7-OTs and 2-OTs show that the C-2 proton in 7-OTs absorbs at δ 4.71 with a doublet (J = 2.4 Hz) and that the C-2 proton in 2-OTs does so at δ 4.72 with a quartet (J = 8.0 Hz), suggesting 7-OTs to be in a "boat" and 2-OTs in a "chair" conformation.[4a] However, the nmr studies of 7-OH and 2-OH which have similar coupling constants with those of the corresponding tosylates show that the chemical shifts and coupling constants of these alcohols are not temperature dependent between 35 to 95° in CCl_4. The author wishes to thank Dr. K. Sato and Mrs. S. Yoshida for measurement of the temperature-dependent nmr spectra of these alcohols.
(12) In our study of 1-OTs, we suggested the possible existence of an initial carbonium ion intermediate, which rearranges to the stable norbornenyl-type carbonium ion.[3] This intermediate may be similar to the carbonium ion 12, which was also reported by Cook and Story.[4b]
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Aromatic *N*-Oxides. VII. The Reaction of Diphenyl-2-pyridylmethane *N*-Oxide with Acetic Anhydride[1]

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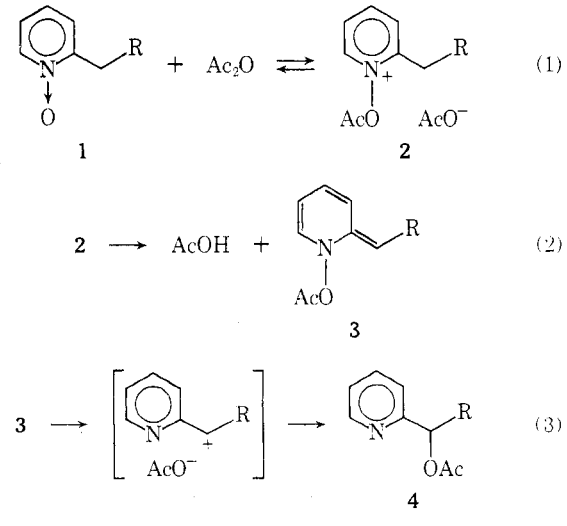
The rearrangement of diphenyl-2-pyridylmethane *N*-oxide (8) with acetic anhydride in acetonitrile was investigated. The product was identified as diphenyl-2-pyridylmethyl acetate (10). An intramolecular pathway was elucidated by a combination of oxygen-18 labeling studies and the conversion of 1-acetoxy-2-benzhydrylpyridinium perchlorate (14) to product by a base (Dabco) other than added acetate ion.

The reactions of aromatic *N*-oxides with acid anhydrides have been studied extensively since the first report in 1947 that pyridine *N*-oxide was converted to 2-pyridyl acetate when heated in acetic anhydride.[3] Twenty years ago several groups observed that alkyl substituents at C-2 of pyridine *N*-oxide altered the pathway to afford 2-pyridylmethyl acetates.[4–6] Since that time mechanistic aspects of these reactions have been thoroughly investigated and excellent reviews are available.[7,8] The generally accepted mechanism for side chain rearrangement is represented in eq 1–3, the key feature of which is the generation of an anhydrobase intermediate (3), which rearranges intramolecularly *via* an ion pair to product (4).[9]



The present work stemmed from our observation that nearly all reported examples of this rearrangement with 2-alkylpyridine *N*-oxides (1) involved structures with an α-methylene group. At the time this work was commenced we were aware of only two cases in which disubstitution at the α position of the side chain was involved; both compounds, 5[5] and 6,[10] were reported to undergo no rearrangement in acetic anhydride. Since the failure to observe the anticipated reaction with 5 and 6 could be attributed to an intramolecular interaction between the *N*-oxide moiety and the α-acetoxy group, it seemed desirable to test a simpler case of disubstitution such as 7. The choice of diphenyl-2-pyridylmethane *N*-oxide (8) was based on product considerations. Side chain rearrangement of 7 (R = alkyl) to a tertiary acetate would, upon acid hydrolysis, afford an alcohol capable of undergoing an undesirable dehydration. Subse-