Acetolysis of Dibenzonorbornadienyl-1-carbinyl Trifluoromethanesulfonate and Comparison with the Norbornyl-1-carbinyl System and Its Unsaturated Analogues

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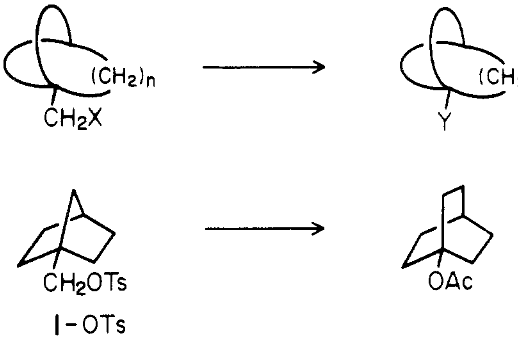
Received January 17, 1978

The preparation of dibenzonorbornadienyl-1-carbinyl derivatives (**5**) is described. The acetolysis of the trifluoromethanesulfonic acid ester (triflate, **5**-OTf) gives the acetate with retention of configuration and the internally returned dibenzobicyclo[2.2.2]octadien-1-yl triflate (**13**). The acetolysis of the benzonorbornadienyl-1-carbinyl system (**4**) previously reported is reinvestigated using the triflate and shown to proceed by a similar pathway. The acetolysis of dibenzobicyclo[2.2.2]octadienyl-1-carbinyl triflate (**6**-OTf) gives only the ring-enlarged dibenzobicyclo[3.2.2]nonadien-1-yl acetate (**14**). These rates and products are compared with those reported in acetolyses of norbornyl-1-carbinyl (**1**), norbornenyl-1-carbinyl (**2**), and benzonorbornenyl-1-carbinyl (**3**) arenesulfonates. The absence of the unsaturated bridge-migrated products is established. The dissociation constants of the corresponding bridgehead acids are determined in 50% aqueous ethanol. A linear relation is found between the logarithms of the acetolysis rates and the dissociation constants. Therefore, evidence for anchimeric assistance by the unsaturated linkage in these systems is not found; rather the inductive effect of these bonds accounts for the results observed.

Solvolysis of bicyclic bridgehead neopentyl systems proceeds with ready rearrangements forming bridgehead substituted products.[1] A representative example is the acetolysis of norbornyl-1-carbinyl tosylate (**1**-OTs) which produced bicyclo[2.2.2]octyl-1-yl acetate in 85% yield.[2] Effects of unsaturation in the [2.2.1] system have been investigated by Wilt, Bly, and their co-workers with norbornenyl-1-carbinyl tosylate (**2**)[3,4] and benzonorbornenyl-1-carbinyl tosylate (**3**).[5] Of particular interest are the absence of etheno (or benzo) bridge-migrated products and the formation of considerable amounts of unrearranged products. Introduction of additional unsaturation has been investigated by Chenire et al.[6] with benzonorbornadienyl-1-carbinyl tosylate (**4**). A major path of this acetolysis proceeds without accompanying rearrangement. Interest in the changes of the rearrangement manner with unsaturation led us to undertake a study of the dibenzonorbornadienyl-1-carbinyl system (**5**) and, in addition, the dibenzobicyclo[2.2.2]octadienyl-1-carbinyl system (**6**). With these present results the solvolytic behavior of bicyclo[2.2.1] bridgehead neopentyl systems will be complete.

Scheme I



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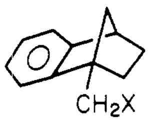

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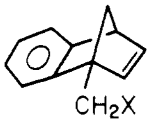

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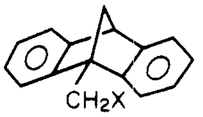

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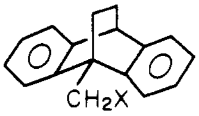

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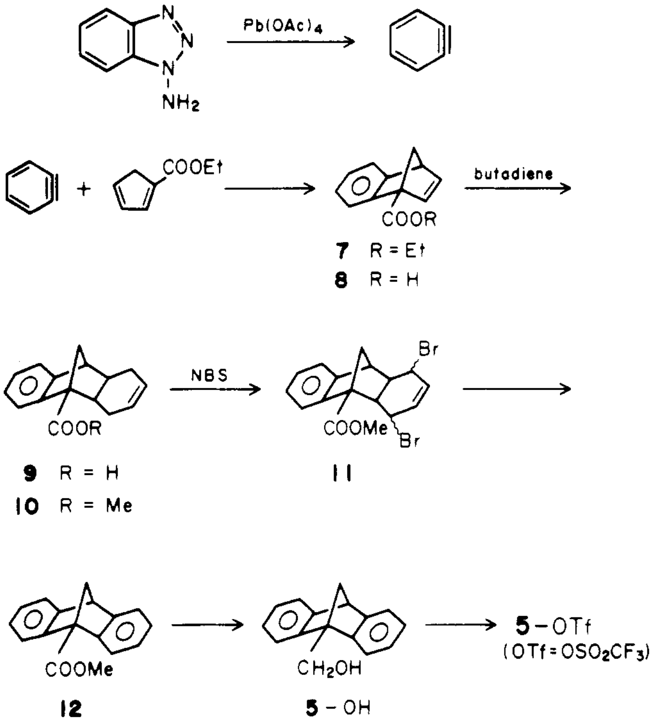
Scheme II



Results

Preparation. 1-Bromobenzonorbornadiene was previously prepared by Wilt and Chenier[7,8] starting from benzonorbornadiene via a relatively long reaction sequence. Benzyne, generated by thermal decomposition of 1,2,3-benzothiadiazole 1,1-dioxide, was added to methyl cyclopentadienyl-1-carboxylate affording methyl benzonorbornadienyl-1-carboxylate (**7**, R = Me) in a yield of 30% (based on *o*-nitrobenzenesulfinic acid the benzyne precursor was prepared from).[9] Since dimerization of cyclopentadienyl-1-carboxylate is very facile at 10 °C–room temperature which is necessary for the thermal decomposition,[10] we considered that a benzyne generation at a much lower temperature might give a better result and, in this respect, adapted treatment of 1-aminobenzotriazole with lead tetraacetate.[11] The benzyne thus generated

0022-3263/78/1943-3274$01.00/0

Table I. Acetolysis Rates of Bridgehead Carbinyl Triflates

triflate system	registry no.	temp, °C	k_1, s^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, cal/deg	rel rate at 100 °C
benzonorbornadienyl **4**	66687-87-4	75.0	1.05×10^{-4}	20.3	−18.8	
		100.0	8.01×10^{-4}			6.4
dibenzonorbonadienyl **5**	66687-88-5	100.0	1.25×10^{-4}	25.8	−7.6	1
		125.0	11.9×10^{-4}			
neopentyl[a]	66687-89-6	50.0	1.05×10^{-4}	25.0	0.58	
		75.0	18.6×10^{-4}			
		25.0[b]	3.68×10^{-6}			
		100.0[b]	2.25×10^{-2}			180
dibenzobicyclo[2.2.2]octadienyl **6**	66687-90-9	75.0	0.452×10^{-4}	27.7	0.9	
		100.0	7.10×10^{-4}			5.7
norbornyl **1**[c]	66687-91-0	100.0	1.59×10^{-1}			1272
norbonenyl **2**[d]	66687-92-1	100.0	4.21×10^{-2}			337
benzonorbornenyl **3**[e]	66687-93-2	100.0	4.34×10^{-3}			35

[a] For the tosylate, the literature data[12] determined at uniform and comparable concentration (0.0796 M of tosylate) are 8.32×10^{-8} s^{-1} at 74.71 °C and 1.60×10^{-6} s^{-1} at 99.58 °C. Calculation by a FACOM computer gives the rates 5.25×10^{11} s^{-1} at 25.0 °C and 1.68×10^{-6} s^{-1} at 100.0 °C. [b] The rates of triflate at 25.0 and 100.0 °C are calculated from those observed at 50 and 75 °C. Comparison between the rates of triflate and tosylate gives the OTf/OTs rate ratios as 7.01×10^4 at 25 °C and 1.34×10^4 at 100 °C. [c] For the tosylate, the literature data[5] are 1.13×10^{-5} s^{-1} at 99.5 °C and 2.70×10^{-4} s^{-1} at 133.0 °C. Calculation gives 1.19×10^{-5} s^{-1} at 100.0 °C. The OTf/OTs ratio at 100 °C (footnote *b*) gives the listed rate. [d] A rate of the brosylate was reported as 9.98×10^{-7} s^{-1} at 80 °C.[4b] A rate of the tosylate was reported as 7.3×10^{-5} s^{-1} at 132.5 °C (ref 6). With the OBs/OTs rate ratio of 3, a rate of the tosylate at 100 °C is calculated as 3.14×10^{-6} s^{-1}. [e] For the tosylate, the literature[5] indicates 1.02×10^{-6} s^{-1} at 110.0 °C, 5.53×10^{-6} s^{-1} at 131.0 °C, and 55.7×10^{-6} s^{-1} at 154.0 °C. Calculation gives 3.24×10^{-7} s^{-1} at 100 °C and the listed rate is obtained from the OTf/OTs ratio in footnote *b*.

at −60 °C in methylene dichloride was successfully added to ethyl cyclopentadienyl-1-carboxylate giving **7** in about 85% yield. This ester was hydrolyzed by aqueous sodium hydroxide to the acid **8**, which was heated with a benzene solution of 1,3-butadiene in a Diels–Alder reaction. The adduct (**9**) was transformed into a methyl ester (**10**) by warming it in methanol containing a trace of sulfuric acid. Treatment with *N*-bromosuccinimide in the presence of a catalytic amount of azobis(isobutyronitrile) gave dibromide **11**, which was refluxed in *o*-dichlorobenzene in the presence of sodium carbonate to eliminate HBr. The yield from **10** to **12** was 42–48%. Reduction of **12** with lithium aluminum hydride gave carbinol **5**-OH, which was esterified to trifluoro methanesulfonate (triflate) **5**-OTf.

As reference compounds, neopentyl triflate and dibenzobicyclo[2.2.2]octadienyl-1-carbinyl triflate (**6**-OTf) were prepared from the corresponding carbinols.

Acetolysis. The acetolyses of **5**-OTf, neopentyl triflate, and **6**-OTf were performed in glacial acetic acid with 0.02 M triflate, 0.022 M sodium acetate buffer, and 1% acetic anhydride. The acetolysis of **4**-OTf was also carried out for comparison with the data reported on the corresponding tosylate.[6] The rate data are listed in Table I and the reactivities are compared at 100 °C. The acetolysis rates of neopentyl tosylate reported[12] were extrapolated to 25 and 100 °C. Comparison of rates of the triflate gave the triflate/tosylate rate ratios as 7.01×10^4 at 25 °C and 1.34×10^4 at 100 °C. The remarkably constant ratios which are in a range of $10^{4.3}$–$10^{5.3}$ at 25 °C have been found in a variety of systems.[13] The present ratio is not exceptional. Reported rates of the related systems **1**–**3**, which were determined using tosylates or brosylates,[3–5] were thus converted into rates of the triflates and compared.

Products from the acetolysis of **5**-OTf were the acetate (**5**-OAc) of retained configuration, dibenzobicyclo[2.2.2]octadien-1-yl triflate (**13**) via internal return, and no other detectable compound. For the product **13**, the possibility of a dibenzobicyclo[3.2.1]octadien-2-yl structure was excluded by ^{1}H and ^{13}C NMR spectra. The products composition varied with the reaction temperature and the added sodium acetate buffer. The varying yields of **5**-OAc and **13** were determined by VPC and are shown in Table II as normalized values.

The acetolysis of **6**-OTf gave the ring-enlarged dibenzobicyclo[3.2.2]nonadien-1-yl acetate (**14**) in a nearly quantitative yield. Acetolysis of system **4** was reinvestigated at 100 °C using the triflate. The retained acetate (**4**-OAc) was obtained in 80% yield and benzobicyclo[2.2.2]octadien-1-yl triflate by internal return in 20% yield. Therefore, the occurrence of a similar type of rearrangement in both systems (**4** and **5**) was confirmed.

Table II. Dependence of Yield of 5-OAc[b] and 13[c] upon Reaction Temperature and Added Sodium Acetate[a]

temp, °C	[CH_3COONa], M	**5**-OAc, %	**13**, %
100	0	54.3	45.7
	0.02	55.4	44.6
	0.04	58.6	41.4
	0.20	67.2	32.8
125	0	39.5	60.5
	0.02	40.4	59.6
	0.20	58.1	41.9

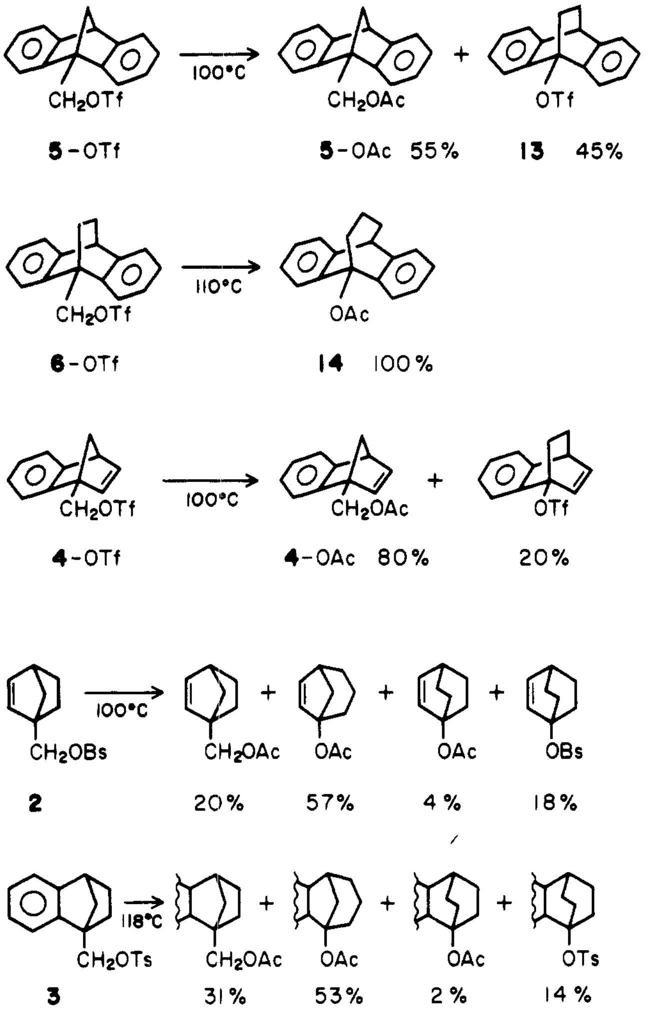
[a] The acetolyses were performed with a 0.02 M solution of **5**-OTs in glacial acetic acid containing 1% acetic anhydride. Yields were determined by VPC, normalized, and based on theory. [b] Registry no. 66687-94-3. [s] Registry no. 66687-95-4.

Acidity Constants. In order to obtain information on the inductive effects of the aromatic rings and the double bonds in the present systems, the pK_a of the bridgehead carboxylic acids and benzoic acid were determined in 50% ethanol–water. The results are listed in Table III, which shows the similar effects of the homoallylically positioned vinyl and aromatic functionalities, ca. a 0.4–0.5 pK_a unit decrease compared to the saturated model, norbornane-1-carboxylic acid. Also, the effects are nearly additive.

Discussion

The acetolysis rates vary in the range of $10^{3.1}$ in the norbornyl and norbornenyl systems (**1**–**5**). Presence of the double bond and/or the benzene ring does not result in any rate enhancement, but rate retardation. Products from **5**-OTf and **4**-OTf do not involve any unsaturated bridge migration. In the acetolyses of the **2** and **3** systems, the literature[4,5] shows the absence of such a migration. Therefore, the rates and products do not give any indication of π participation by the unsaturation. This seems reasonable, because the rigid bicyclic

Scheme III



structure of the 2–5 systems prevents the achievement of the necessary perpendicular spira geometry in a phenonium ionlike transition state. Whereas in the acetolyses of the monoenes (2 and 3) the ethano bridge migration affords the [3.2.1] derivatives as the most important products, the rearrangements observed in the acetolyses of the dienes (4 and 5) were only due to the methano bridge.

Correlation between logarithms of the rate constants (Table I) and the pK_a of the corresponding bridgehead acids (Table III) was calculated by regression analysis. The correlation coefficient was 0.9417 [degree of freedom, $f = n - 2$ ($n = 6$)]. The regression line, as shown in Figure 1, had a slope of 3.1622 and an intercept of −20.7834. The fair linearity obtained suggests that the inductive factor is a significant effect.[14]

Of note are the effects of reaction temperatures and the added sodium acetate on the product composition from **5**-OTf (Table II). Increasing temperature favors formation of the product by internal return, **13**, and increasing amounts of sodium acetate favor the acetate of retained configuration, **5**-OAc. The latter result indicates that some of **5**-OAc is formed via an S_N2 reaction. The reactions under the kinetic conditions are dissected into the internal return path, k_{int}, and the formation of 5-OAc, k_s. Arrehenius plots of k_{int} (5.58×10^{-5} s^{-1} at 100 °C and 7.09×10^{-4} s^{-1} at 125 °C) give 29.3 kcal mol^{-1} for $\Delta H^{\ddagger}$ and −0.044 eu for $\Delta S^{\ddagger}$. The same plots of k_s (6.93×10^{-5} s^{-1} at 100 °C and 4.81×10^{-4} s^{-1} at 125 °C) give 22.1 kcal mol^{-1} for $\Delta H^{\ddagger}$ and −18.7 eu for $\Delta S^{\ddagger}$.

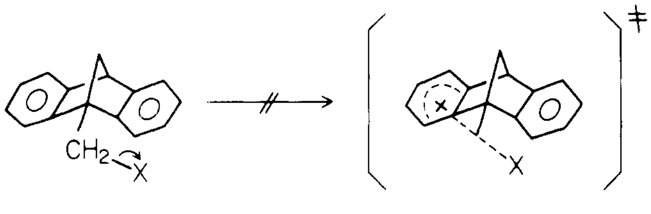


Table III. Acidity Constants of Bridgehead Carboxylic Acids

1-carboxylic acid	registry no.	pK_a in 50% EtOH–H_2O (v/v)
norbornane		6.37[a]
norbornene		5.98[a]
benzonorbornene		5.88[a]
benzonorbornadiene	5890-15-3	5.45[c], 5.46[b]
dibenzonorbornadiene	60070-69-1	5.50[c]
dibenzobicyclo[2.2.2]octadiene	20202-05-5	5.61[c]
benzoic acid		5.55[c], 5.50[a]

[a] Cited from ref 5. Data at 25 °C. [b] Cited from ref 6. Data at 24.6 °C. [c] Present work. Determined at 23 °C.

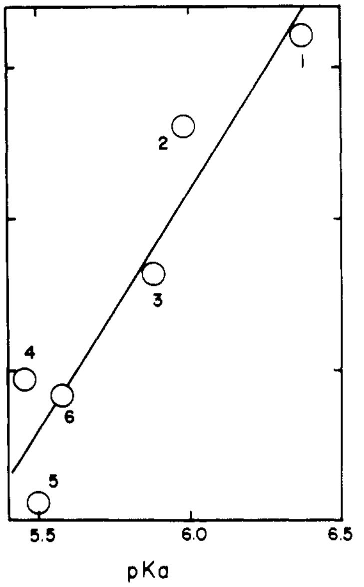


Figure 1. Correlation of log k_1 for carbinyl triflates against pK_a for bridgehead carboxylic acids: k_1 at 100 °C in acetolysis, pK_a at 23–25 °C in 50% ethanol-water, and correlation coefficient = 0.9417.

Experimental Section

Melting points were taken by capillary and are corrected. Infrared spectra were determined with a 215 Hitachi grating infrared spectrophotometer and ^{1}H NMR spectra with a Varian T-60A.

Cycloaddition of Benzyne to Ethyl Cyclopentadienyl-1-carboxylate. The dimer of cyclopentadiene-1-carboxylic acid was prepared by treatment of cyclopentadienyl anion (obtained from the diene and sodium dispersion in toluene) with carbon dioxide according to the literature.[15] The dimer was converted into the ethyl ester by being warmed in ethanol containing a catalytic amount of sulfuric acid. The dimer ester was thermally decomposed into the monomer ester and immediately used for cycloaddition.

To a stirred methylene dichloride suspension of 421 mmol of the ester and 337 mmol of lead tetraacetate was dropwise added a solution of 281 mmol of 1-aminobenzotriazole in methylene dichloride at −60 °C. An exothermic reaction was observed during the addition. After stirring for 2–3 h, the precipitate was filtered and the filtrate was washed with water, dried, and evaporated. The residue was distilled under reduced pressure giving ethyl benzonorbornadienyl-1-carboxylate (7) in 88% yield (based on the triazol): bp 92 °C (3 mm); IR (film) 1735 cm^{-1} (C=O); NMR (CCl_4) δ 1.3 (t, 3 H, CH_3), 2.5 (s, 2 H, methylene bridge), 3.82 (s, 1 H, bridgehead), 4.3 (q, 2 H, $COOCH_2CH_3$, 6.6–7.4 (m, 6 H, vinyl and aromatic).

Diels-Alder Cycloaddition of 1,3-Butadiene to Benzonorbornadiene-1-carboxylic Acid (8). The ester 7 was hydrolyzed by 5% aqueous sodium hydroxide to 8, which had the physical constants as reported.[6] In an ampule a mixture of 505 mg of 8 and a trace of hydroquinone was added to a chilled solution of 20 molar equiv of butadiene in 7 mL of benzene. The ampule was sealed and heated at 150 °C for 3 days. The butadiene polymer was eliminated by distillation under reduced pressure and the residue was added to *n*-hexane. Thus, 378 mg (58.1%) of the adduct **9** was crystallized, mp 179–181 °C (from CCl_4). Treatment of the mother liquor with silica gel chromatography gave a second crop, 111 mg (17.1%): NMR (CCl_4) δ 1.7–2.8 (m, 8 H, cyclohexene ring and methylene bridge), 3.0 (s, 1 H, bridgehead), 5.8–6.1 (m, 2 H= VINYL(= 6/9–7/7 (m, 4 H, aromatic), 11.9 (s, 1 H, COOH); IR (CCl_4) 1710 cm^{-1} (C=O). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.15; H, 6.69.

Methyl Dibenzonorbornadienyl-1-carboxylate (12). The adduct **9** was esterified by being warmed in methanol in the presence of catalytic amounts of sulfuric acid. A stirred mixture of 396 mg (1.56 mmol) of the ester **10**, 578 mg (3.12 mmol) of *N*-bromosuccinimide, and a trace of azobis(isobutyronitrile) in 40 mL of carbon tetrachloride was refluxed under nitrogen for 2.5 h and then filtered. The filtrate was concentrated under reduced pressure and the residue was extracted to get the dibromide **11** in 95.4% yield. A solution of **11** in *o*-dichlorobenzene was added dropwise to a boiling solution of *o*-dichlorobenzene containing a molar equivalent of sodium carbonate. After being refluxed for an additional hour, the mixture was concentrated under reduced pressure. The residue was dissolved into ether and the ether solution was washed with water, dried, and evaporated affording 168 mg of **12** (43% yield): mp 123–125 °C (from methanol); NMR (CCl_4) δ 2.7 (d, 2 H, methylene bridge), 3.9 (s, 3 H, $COOCH_3$), 4.2 (s, 1 H, bridgehead), 6.8–7.5 (m, 8 H, aromatic); IR (CCl_4) 1741 cm^{-1} (C=O). Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.79; H, 5.62.

The carboxylic acid, mp 197–200 °C, was obtained by alkaline hydrolysis.

Dibenzonorbornadienyl-1-carbinol (5-OH). Reduction of **12** with lithium aluminum hydride gave **5**-OH, mp 167–168 °C. Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.56; H, 6.45.

The triflate was prepared by treatment of a solution of **5**-OH in pyridine and ether with trifluoromethanesulfonic acid anhydride under ice cooling: mp 102–103 °C (from *n*-hexane); NMR ($CDCl_3$) δ 2.60 (d, 2 H, methylene bridge), 4.35 (1 H, bridgehead), 5.45 (s, 2 H, CH_2OSO_2), 6.9–7.5 (8 H, aromatic). Anal. Calcd for $C_{17}H_{13}O_3SF_3$: C, 57.62; H, 3.70; S, 9.05. Found: C, 57.80; H, 3.93; S, 9.40.

Dibenzobicyclo[2.2.2]octadienyl-1-carbinol (6-OH). Treatment of dibenzobicyclo[2.2.2]octadiene-1-carboxylic acid (obtained by Diels–Alder addition of ethylene to anthracene-9-carboxylic acid)[16] with lithium aluminum hydride in tetrahydrofuran followed by the usual workup afforded **6**-OH: mp 137.5–138 °C (from methylene dichloride and *n*-hexane); NMR ($CDCl_3$) δ 1.2–1.9 (m, 4 H, ethylene bridge), 2.9 (s, 1 H, OH), 4.22 (broad s, 1 H, bridgehead), 4.4 (s, 2 H, CH_2OH), 7.0–7.5 (m, 8 H, aromatic). Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.41; H, 6.71.

The triflate: mp 105–106 °C; NMR ($CDCl_3$) δ 1.6 (broad s, 4 H, ethylene bridge), 4.2 (broad s, 1 H, bridgehead), 5.6 (s, 2 H, CH_2OSO_2), 7.0–7.4 (m, 8 H, aromatic). Anal. Calcd for $C_{18}H_{15}O_3SF_3$: C, 58.69; H, 4.10; S, 8.70. Found: C, 58.76; H, 4.27; S, 8.93.

Kinetic Studies. Standard procedures were followed for the acetolyses. Standardized 0.022 M sodium acetate in redistilled glacial acetic acid containing 1% acetic anhydride was the solvent, with a triflate concentration of 0.02 M. Aliquots were sealed in ampules and heated at the reaction temperature. The excess sodium acetate was back-titrated in the ampule with standard 0.004 M perchloric acid in acetic acid using bromophenol blue indicator. The first-order plots of triflates were linear. The rates and activation parameters were calculated using a FACOM computer.

Studies of Acetolysis Products. A 0.02 M solution of the triflate (**5**-OTf) in 30 mL of acetic acid containing a molar equivalent of sodium acetate and 1% acetic anhydride was sealed into an ampule and heated for about 10 half-lives at 125 °C. The reaction mixture was evaporated under reduced pressure and the residue was extracted with ether. The ether solution was washed with aqueous sodium carbonate and water, dried, and evaporated. The oil obtained was analyzed by VPC and the two products were isolated by preparative thin-layer chromatography using benzene solvent. The major and less polar product was identified as **dibenzobicyclo[2.2.2]octadien-1-yl triflate (13)**: mp 93–94 °C; NMR ($CDCl_3$) δ 1.65–2.7 (m, 4 H, ethylene bridge), 4.25 (t, 1 H, bridgehead), 7.0–7.7 (m, 8 H, aromatic). Anal. Calcd for $C_{17}H_{13}O_3SF_3$: C, 57.62; H, 3.70; S, 9.05. Found: C, 57.74; H, 3.66; S, 9.26. The minor more polar product was identified as **5**-OAc: mp 99–100 °C; NMR ($CDCl_3$) δ 2.1 (s, 3 H, CH_3CO), 2.59 (d, 2 H, methylene bridge), 4.3 (s, 1 H, bridgehead), 5.1 (s, 2 H, CH_2OCO), 6.8–7.4 (m, 8 H, aromatic); IR ($CDCl_3$) 1740 cm^{-1} ($OCOCH_3$). The product composition and effects of reaction temperature and added sodium acetate on it were investigated as described in Table II.

The reaction of **4**-OTf was similarly carried out at 100 °C. The previously reported **4**-OAc[6] was obtained in 80% yield and the internally returned benzobicyclo[2.2.2]octadien-1-yl triflate in 20% yield as an oil. For this triflate, NMR ($CDCl_3$) δ 1.5–2.5 (m, 4 H, ethano bridge), 3.9 (m, 1 H, bridgehead), 7.1–7.5 (m, 4 H, aromatic). When the bridgehead proton is irradiated, the C_2 vinyl proton appears at δ 6.8 as the A part of the AB quartet and the C_3 vinyl proton at 6.5 as the B part.

Dibenzobicyclo[3.2.1]nonadien-1-yl Acetate (14). The acetolysis of **6**-OTf at 110 °C afforded **14** in a nearly quantitative yield: mp 122.5–123 °C (from *n*-hexane–methylene dichloride). NMR ($CDCl_3$) δ 1.1–2.2 (m, 6 H, bridge protons), 2.31 (s, 3 H, $OCCH_3$), 4.05 (t, 1 H, bridgehead), 7.2 (8 H, aromatic); IR ($CHCl_3$) 1740 cm^{-1} ($OCOCH_3$). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 82.08; H, 6.52.

Acknowledgment. We thank Mr. Tsunetoshi Honma and Hiroshi Hashizume for their technical assistance.

Registry No.—**5**-OH, 60070-70-4; **6**-OH, 66687-96-5; **7**, 66687-97-6; **9**, 66687-98-7; **10**, 66687-99-8; **11**, 66719-19-5; **12**, 66688-00-4; **14**, 66688-01-5; benzyne, 462-80-6; ethyl cyclopentadienyl-1-carboxylate, 16179-27-4; benzobicyclo[2.2.2]octadien-1-yl triflate, 66688-02-6.

References and Notes

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(7) We thank Professors J. W. Wilt of Loyola University of Chicago and P. J. Chenier of the University of Wisconsin—Eau Claire for helpful correspondence in 1974 and 1975 on the synthesis of the dibenzonorbornadien-1-carbinyl systems.

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