Unconjugated Arylcyclopropanes. Acid-Catalyzed Addition of Acetic Acid to Highly Hindered Arylcyclopropanes

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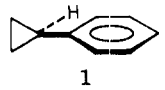
The adduct of 1-naphthylcarbene and norbornene, *endo*-3-(1-naphthyl)-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**9**) has been prepared. ^{1}H and ^{13}C NMR spectra of this system indicate that the unconjugated arylcyclopropane conformation is favored. Rotation about the naphthyl–cyclopropane bond is restricted. The temperature-dependent NMR indicates a 16.9 kcal/mol barrier to attainment of the conjugated conformation. Acetic acid adds readily under acid catalysis to the phenyl analogue *exo*-3-phenyl-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**3**) and more slowly to the more strained *endo*-3-phenyl-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**4**). Kinitic data suggest the involvement of a cationic intermediate with little transition-state charge development at the benzylic carbon. The rates of addition to substituted analogues of **3** and **4** correlate with Hammett σ values, giving ρ values of 2.53 and 2.35, respectively. Product-analysis data support the involvement of a benzylic cation, **23**. The slower rate of reaction of the more strained endo isomers has been interpreted in terms of a barrier to attainment of the conjugated conformation which appears to be the favorable conformation for protonation of arylcyclopropanes. This suggestion is supported by the observation that the unconjugated systems, *exo*- and *endo*-3-(2,6-dimethylphenyl)-*exo*-tricyclo-[3.2.1.$0^{2,4}$]octanes (**27** and **28**), add acetic acid 480 and 6.2 × 10^4 times, respectively, more slowly than **3**.

Arylcyclopropanes exist in the preferred conformation **1** in which the aromatic ring is "conjugated" with the bent



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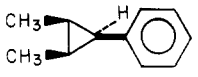

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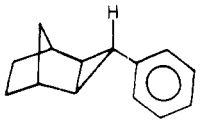
bonds of the cyclopropane ring, in the absence of large steric effects.[1-3] Estimates of the stabilization due to this conjugation range from 1.6[2] to 2.0[3] kcal/mol.[3] On the other hand, Closs and Moss[1] have shown that introduction of methyl groups cis to the phenyl ring forces the cyclopropane to adopt conformation **2** as the minimum-energy conformation. Recently we have prepared the 3-phenyltricyclo[3.2.1.$0^{2,4}$]octane systems **3** and **4**.[4] The NMR



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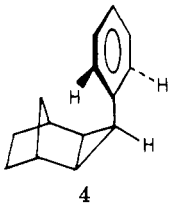

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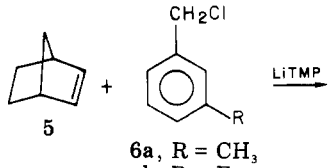
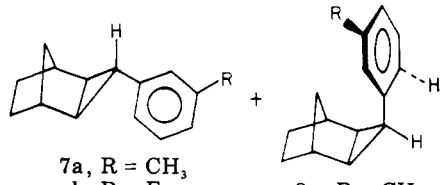
spectrum of the *exo*-phenyl epimer, **3**, was consistent with the expected conjugated conformation shown. However, the NMR of **4** showed a large upfield shift (shielding) of the syn C-8 proton, indicative of a phenyl ring in a nonconjugated conformation as shown for **4**. Examination of molecular models indicated a potentially large barrier to attainment of the conjugated conformation due to a steric interaction between the syn C-8 hydrogen and the *o*-hydrogen on the aromatic ring. The system appears to be "locked" in the unconjugated conformation. We therefore wanted to determine the barrier to attainment of the conjugated conformation, i.e., the rotational barrier in **4**. We have also observed that **4** can be deprotonated by *n*-butyllithium–TMEDA, while **3** is inert under the same conditions.[4] In view of these differences under basic conditions, we also wanted to see if reactivity differences could be observed under acidic conditions. Reported here are the results of these studies.

Scheme I



5 **6a**, R = CH_3; **b**, R = F; **c**, R = *i*-Pr



7a, R = CH_3; **b**, R = F; **c**, R = *i*-Pr

8a, R = CH_3; **b**, R = F; **c**, R = *i*-Pr

Results and Discussion

Rotational Barriers. The initial approach to the study of the rotational barrier in **4** involved the introduction of a meta substituent in order to render the C-1,C-5 pair, the C-2,C-4 pair, and the C-6,C-7 pair of atoms diastereotopic in the absence of rapid rotation. Rapid rotation about the aryl–cyclopropane bond on the NMR time scale should render these positions equivalent. The meta substituent should have no great effect on the rotational rate since the major interaction preventing the attainment of the conjugated conformation is that of the *o*-hydrogen with the syn C-8 hydrogen.

Addition of arylcarbenoids[5] to norbornene (Scheme I) gave adducts **7** and **8** as separable mixtures. Unfortunately the ^{13}C NMR spectra of **8** showed only five signals in the aliphatic region (even at low temperature), indicating fortuitous equivalence of the formally diastereotopic sets of carbons of the norbornyl ring. Even the diastereotopic methyl groups of the isopropyl substituent in **8c** are fortuitously equivalent by ^{1}H and ^{13}C NMR.

Addition of 1-naphthylcarbene to norbornene also gave a separable mixture of *endo*- and *exo*-aryl adducts. The ^{13}C NMR spectrum of the endo adduct, **9**, showed eight signals in the aliphatic region as well as ten aromatic

(1) Closs, G. L.; Moss, R. A. *J. Am. Chem. Soc.* **1964**, *86*, 4042-53.
(2) Closs, G. L.; Klinger, H. B. *J. Am. Chem. Soc.* **1965**, *87*, 3265-6.
(3) Parr, W. J. E.; Schaefer, T. *J. Am. Chem. Soc.* **1977**, *99*, 1033-5.
(4) Creary, X.; Keller, M.; Dinnocenzo, J. P. *J. Org. Chem.* **1978**, *43*, 3874-8.
(5) Olofson, R. A.; Dougherty, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 581-2.

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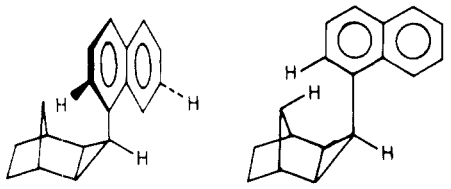
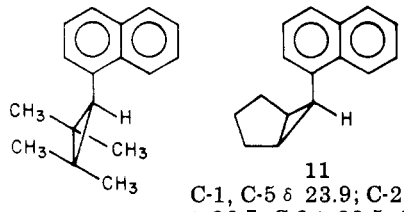


9 9a

carbons at room temperature.[6] This is indicative of slow rotation of the naphthyl group on the NMR time scale. Even the ^1H NMR spectrum shows well-separated bridgehead protons, H-1 and H-5. Figure 1 shows the temperature-dependent ^1H NMR spectrum of the bridgehead protons of **9**. The coalescence temperature is 54 ± 2 °C which corresponds to a free energy of activation of 16.9 kcal/mol. This should be a measure of the smaller rotational barrier in **9** where the *o*-hydrogen at C-2 of the naphthyl ring passes the syn C-8 hydrogen of the norbornyl system (rather than the fused phenyl ring passing the C-8 hydrogen) as shown in **9a**. This should also be a close approximation of the rotational barrier in **4** and **8** since similar processes are involved.

This rotational barrier (16.9 kcal/mol) represents an extremely large barrier[7] to attainment of the conjugated cyclopropane–aryl conformation and is probably due to the rigid and sterically conjested nature of these systems. In contrast, the ^{13}C NMR spectrum of **10** does not even show



10 11

C-1, C-5 δ 23.9; C-2, C-4 δ 26.7; C-3 δ 23.5; C-6 δ 22.0

broadening of the signals due to the potentially diastereotopic carbons at −50 °C (where **10** begins to crystallize out of solution). The behavior of **11** is similar. One observes only four aliphatic ^{13}C signals even at −80 °C. Only at this temperature does the signal at δ 23.9, due to the ring fused carbons (C-1 and C-5), begin to broaden slightly. This is indicative of a much smaller rotational barrier in the less conjested systems **10** and **11**.

Acid-Catalyzed Additions to 3 and 4. Attention was next focused on the chemical reactivities of **3** and **4**. We attribute the lack of reaction of **3** with *n*-butyllithium–TMEDA to the hindered nature of the endo C-3 proton which is protected from approach by the base. We therefore wondered about differing reactivity of **3** and **4** under acidic conditions, especially in view of the more conjested (and consequently more strained) nature of **4**.

In acetic acid (containing 0.1 M toluenesulfonic acid) both **3** and **4** add acetic acid across the external cyclopropane bond, giving acetates **12** as the major product (Scheme II). A diastereomeric mixture of **12** consisting of a 1.6:1 ratio of isomers is initially produced from **3** as evidenced by two doublets due to the benzylic proton of **12** at δ 5.33 (major isomer) and δ 5.39 (minor isomer). This

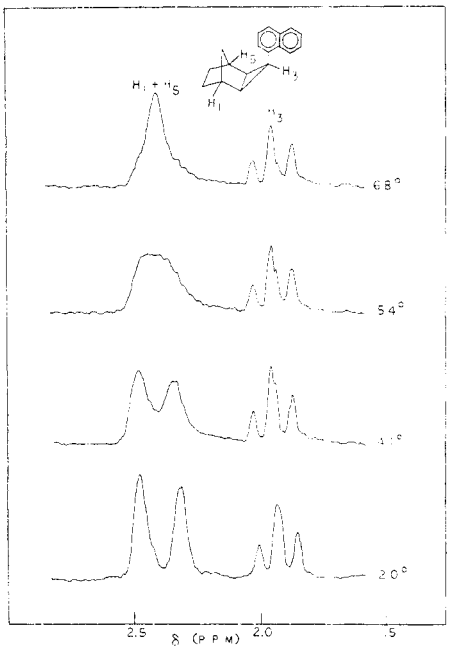
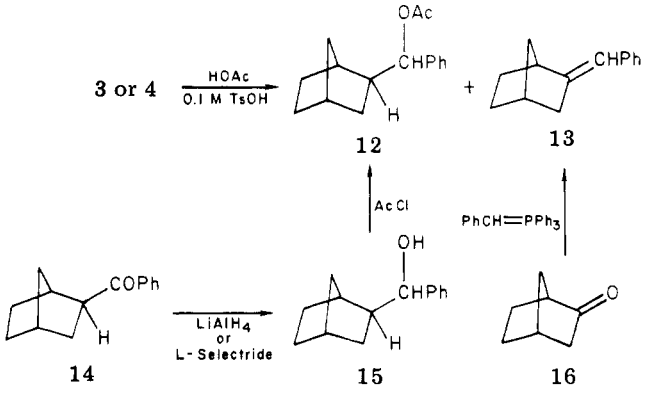


Figure 1. Temperature-dependent NMR spectrum of **9** in C_6D_6.

Scheme II



mixture slowly converts under the reaction conditions to a 1.3:1 mixture on being allowed to stand for prolonged periods. However, the minor acetate (doublet at δ 5.39) is a *primary product*. As can be shown, rearrangement of the major acetate is too slow to account for the amount of the minor acetate initially produced. Traces of alkenes **13** are also produced from **4** (and from **3** after prolonged times). The amount of **13** increases with time, and **13** can be shown to arise from elimination of acetic acid from **12** under the reaction conditions. The structures of **12** and **13** were proven by independent syntheses. Hydride reduction of *exo*-norbornyl phenyl ketone followed by acetylation gave a mixture of acetates **12**.[8] The stereochem-

(6) At above room temperature, the ^{13}C signals at δ 30.0 and 30.4 coalesce as do the signals at δ 36.3 and 37.1. The signals at δ 20.3 and 24.8 broaden while the signals at δ 20.7 and 30.7 do not change.

(7) Large barriers to aryl rotation can be seen when bulky groups are substituted in the ortho position in certain systems. For a discussion and leading references, see: (a) Westheimer, F. H. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; pp 523–55; (b) Meyer, W. L.; Meyer, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2170–1.

(8) Lithium aluminum hydride reduction–acetylation of **14** gave a 2.1:1 ratio of acetates while L-Selectride reduction–acetylation gave a 4.1:1 ratio of acetates. Tentative assignment of stereochemistry of these two acetates can be made by using Cram's rule. Cram's rule predicts **12a** as the major product and **12b** as the minor. If this rule holds for the hydride reduction of **14**, then **12a** is also the major acetate produced in the addition of acetic acid to **3** and shows the benzylic doublet at δ 5.33. For a discussion of Cram's rule, see: (a) Cram, D. J.; Elhafez, F. A. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828–35. (b) Cram, D. J.; Kopecky, K. R. *Ibid.* **1959**, *81*, 2748–55.

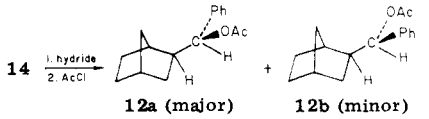


Table I. Rates[a] of Reaction in Acetic Acid-0.1 M Toluenesulfonic-1% Acetic Anhydride

compd	temp, °C	k, s^{-1}	k_{rel} (25 °C)
	25.0	8.31×10^{-5}	1.00
3	45.0	5.23×10^{-4}	
17	25.0	2.21×10^{-4}	2.66
18	25.0	5.73×10^{-5}	0.69
7b	25.0	1.15×10^{-5}	0.14
4	100.0	1.10×10^{-3}	
	80.0	2.50×10^{-4}	
	25.0[b]	1.58×10^{-6}	1.90×10^{-2}
19	80.0	5.25×10^{-4}	
	60.0	1.03×10^{-4}	
	25.0[b]	3.53×10^{-6}	4.25×10^{-2}
20	60.0	1.90×10^{-4}	
	40.0	3.18×10^{-5}	
	25.0[b]	7.14×10^{-6}	8.59×10^{-2}
8b	100.0	2.15×10^{-4}	
	80.0	4.68×10^{-5}	
	25.0[b]	2.52×10^{-7}	3.03×10^{-3}
21	100.0	6.39×10^{-4}	
	80.0	1.44×10^{-4}	
	25.0[b]	8.68×10^{-7}	1.04×10^{-2}
22	100.0	2.12×10^{-4}	3.46×10^{-3} [c]
27	100.0	1.93×10^{-4}	
	80.0	3.95×10^{-5}	
	25.0[b]	1.73×10^{-7}	2.08×10^{-3}
28	140.0	2.23×10^{-5}	1.61×10^{-5} [d]

[a] Maximum standard deviation of 0.06 s^{-1}. [b] Extrapolated value. [c] Comparison made at 100 °C. [d] Comparison made at 140 °C.

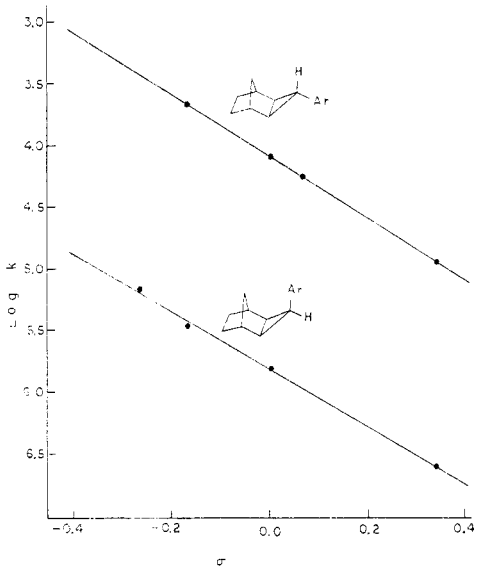
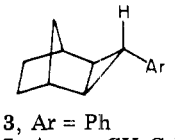


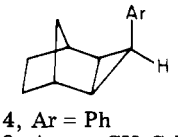
Figure 2. Plot of log k vs. σ for the reaction of 3-aryl-*exo*-tricyclo[3.2.1.$0^{2,4}$]octanes in acetic acid–0.1 M toluenesulfonic acid.

istry of the major acetate produced by this reduction–acetylation procedure was the same as that of the major acetate produced in the addition of acetic acid to **3**. Wittig reaction of norcamphor with benzylidenetriphenylphosphorane gave a mixture of alkenes **13**.

Table I gives rate data for the acid-catalyzed addition of acetic acid to **3** and **4** as well as related substrates.

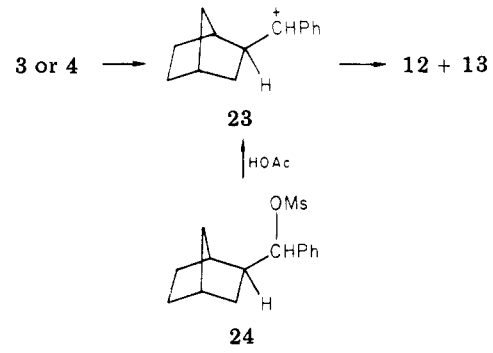


3, Ar = Ph
17, Ar = *p*-$CH_3C_6H_4$
18, Ar = *p*-FC_6H_4
7b, Ar = *m*-FC_6H_4

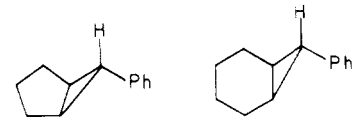


4, Ar = Ph
19, Ar = *p*-$CH_3C_6H_4$
20, Ar = *p*-$CH_3OC_6H_4$
8b, Ar = *m*-FC_6H_4

Scheme III



Surprisingly addition to **3** is more than 50 times *faster* than to **4** despite the fact that **4** is the more strained isomer.[9] A substituent effect study (Figure 2) shows that rates of reaction correlate (r = 0.9999 and 0.999, respectively) with Hammett σ values rather than Brown's σ^+ values. The ρ values are −2.53 and −2.35, respectively, for **3** and **4** and substituted analogues. The *exo*-3-phenyltricyclo[3.2.1.$0^{2,4}$]octane system (**3**) also undergoes reaction 96 times faster than the less strained analogue *exo*-6-phenylbicyclo[3.1.0]hexane (**21**) and 289 times faster than *exo*-7-phenylbicyclo[4.1.0]heptane (**22**).



21 **22**

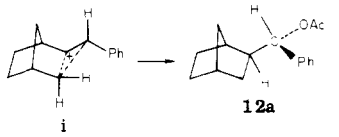
Mechanistic Considerations. Acid-catalyzed additions to cyclopropanes have been investigated in some detail. Previous data have been interpreted in terms of protonation of the cyclopropane bent bond, giving cationic intermediates.[10,11] Previous authors have suggested corner-protonated cyclopropanes[10a,c,11e] and edge-protonated cyclopropanes[11c] in acid-catalyzed reactions on the basis of stereochemical and rate data. In contrast, the addition of acetic acid to **3** is felt to involve capture of the benzylic cation **23** (Scheme III) and not capture of corner- or edge-protonated cyclopropanes. The same mixture of acetates **12** is obtained in the solvolysis of mesylates **24** as in addition of acetic acid to **3**. This argues in favor of a common intermediate, **23**. The low magnitude of the ρ values (−2.53 and −2.35) and the correlation with σ rather than with σ^+ indicate a transition state with a relatively small charge development at the benzylic carbon.[13] These

(9) Treatment of **4** with K-*t*-BuO in dimethyl sulfoxide at 100 °C converts **4** to **3** (>99.8% by GC). For a related epimerization, see ref 1.

(10) (a) DePuy, C. H.; Klein, R. A.; Clark, J. P. *J. Org. Chem.* **1974**, *39*, 483–6. (b) Depuy, C. H.; Breitbeil; F. W.; DeBruin, K. R. *J. Am. Chem. Soc.* **1966**, *88*, 3347–54. (c) DePuy, C. H.; Andrist, A. H.; Fünfschilling, P. C. *Ibid.* **1974**, *96*, 948–50.

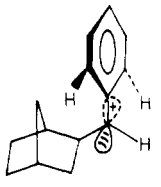
(11) (a) Nickon, A.; Lambert, J. L.; Williams, S. J. O.; Werstiuk, N. H. *J. Am. Chem. Soc.* **1966**, *88*, 3354–8. (b) Peterson, P. E.; Thompson, G. *J. Org. Chem.* **1968**, *33*, 968–72. (c) Hendrickson, J. B.; Boeckman, R. K., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 3269–73. (d) McKinney, M. A.; So, E. C. *J. Org. Chem.* **1972**, *37*, 2818–22. (e) McKinney, M. A.; Smith, S. H. *Tetrahedron Lett.* **1971**, 3657–60.

(12) Capture of an analogous corner-protonated (or edge-protonated) intermediate such as i should give *only* **12a**. In fact, a mixture of **12a** and **12b** is obtained. This argues against capture of an intermediate such as i.

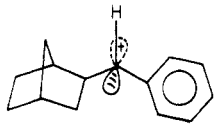


ρ values are significantly smaller (in absolute magnitude) than the value of −3.42 (σ^+ correlation) seen in the acid-catalyzed hydration of styrenes.[14] They are also consistent with expectations based on the Hammond postulate.[15] The protonation of a strained cyclopropane should be less endothermic than protonation of a double bond. Consequently an earlier transition state and resultant smaller ρ values should be seen in protonation of the strained cyclopropanes **3** and **4**.

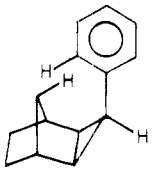
The similarity of the ρ values for additions to **3** and **4** indicates a similar degree of transition-state charge development and conjugation. Why then, do the more strained *endo*-aryl isomers add acetic acid less rapidly? One possibility is that the protonation of **4** gives an unconjugated benzylic cation, **23a** (or at least a transition



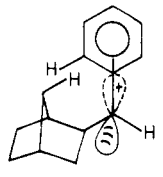
23a



23b



4a



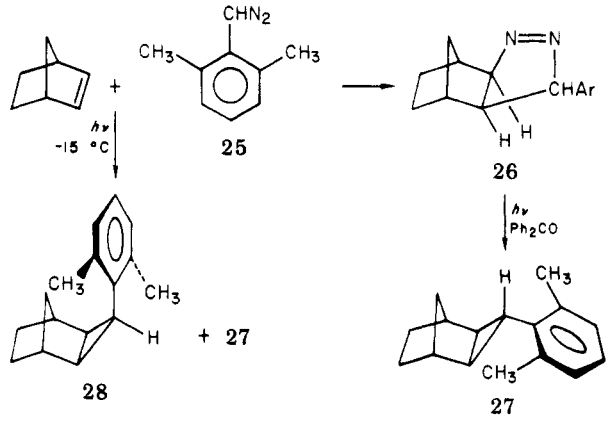
23c

state resembling **23a**), in which conjugation is reduced because of steric factors. Protonation of **3** would give a benzylic cation in conformation **23b** in which there is no barrier to delocalization and would account for the faster rate of **3**. However, this rationale does not account for the similar ρ values for reaction of **3** and **4**, which suggest a similar degree of transition-state conjugation.

Further consideration of conformational factors suggests an alternative explanation. It is suggested that protonation of **4** ($\Delta G^{\ddagger}$ = 27 kcal/mol) occurs from the less stable conformation **4a** which lies approximately 17 kcal/mol higher in energy than the ground-state conformation of **4**. The transition state leading to the initially produced cation should have some of the characteristics of **23c**. Although there is no barrier to charge delocalization in **23c**, the transition state should still reflect some of the steric strain in **4a**. Consequently, this transition state should be higher in energy than the transition state for reaction of **3** which leads to the unstrained **23b**. The net result is a slower rate of addition to **4**.

In order to gain support for this suggestion, we prepared the ortho-dimethylated system **27** as shown in Scheme IV. Room-temperature reaction of norbornene with (2,6-dimethylphenyl)diazomethane (**25**) gave pyrazoline **26**. It was hoped that a triplet-sensitized nitrogen extrusion would generate a triplet biradical intermediate from **26**. It was further anticipated that closure of such a biradical would give the thermodynamic arylcyclopropane with the aryl group having exo stereochemistry. This hope was realized. Benzophenone-sensitized photolysis of **26** gave **27** as the major product with only a trace of the endo

Scheme IV



isomer **28**. Such a sequence appears general for the preparation of pure *exo*-3-aryltricyclo[3.2.1.$0^{2,4}$]octyl systems. Pure arylcyclopropanes **3** and **18** could also be prepared in this fashion. In contrast, the direct irradiation of (2,6-dimethylphenyl)diazomethane in a norbornene–pentane mixture at −15 °C (where pyrazoline formation is slow) gave a significant amount of the *endo*-aryl isomer **28**.

Brown[16] has obtained evidence that *o*-dimethyl substitution also forces an aryl group to adopt an unconjugated conformation with respect to a cyclopropane ring. Arylcyclopropane **27** should have such an unconjugated ground-state conformation. Consequently, acetic acid addition to **27** is predicted to be slower than to **3**. This is what is observed. Arylcyclopropane **27** reacts 480 times more slowly than **3**. The endo isomer **28** reacts 6.2×10^4 more slowly than **3**.[17] These greatly reduced rates support the contention that aryl conjugation in the transition state leading to the cationic intermediate is necessary for acid-catalyzed addition to occur. In the case of **28**, where steric factors should overwhelmingly disfavor the conjugated conformation, perhaps addition can begin to occur before the attainment of the completely conjugated conformation.

Experimental Section

NMR spectra were recorded on a Varian A-60 A or Varian XL-100 spectrometer. Data are reported in δ units (parts per million relative to Me_4Si). Low-temperature spectra were recorded in CD_2Cl_2. Mass spectra were recorded on an AEI Scientific Apparatus MS 902 spectrometer or on a Du Pont DP 1 GC/MS system. Infrared spectra were recorded on a Perkin-Elmer 727B spectrometer. Elemental analyses were performed by Midwest Microlab, Ltd. Gas chromatographic analyses were carried out by using a Hewlett-Packard 5750 chromatograph equipped with a flame-ionization detector and using a 5-ft, 5% SE-30 on Chromosorb G column. A Varian 920 chromatograph with a similar column was used for sample isolation.

Preparation of 3-Phenyltricyclo[3.2.1.$0^{2,4}$]octanes 3 and 4. The preparation of mixtures of **3** and **4** from benzyl chloride, lithium tetramethylpiperidide, and norbornene has previously been described.[4] Hydrocarbon **3**, uncontaminated with **4**, could also be prepared as follows. Phenyldiazomethane[1,18] (1.33 g) in a mixture of 9.5 g of norbornene and 2 mL of pentane was held at room temperature for 4 h. The mixture was now light yellow. The norbornene was removed at reduced pressure, and the residue was dissolved in 90 mL of cyclohexane. Benzophenone (8.7 g) was added. The mixture was irradiated with Pyrex-filtered light from a Hanovia 450-W source until nitrogen evolution ceased (4

(13) DePuy has also observed a σ correlation in acid-catalyzed reactions of 1-arylcyclopropanols (see ref 10a).
(14) Schubert, W. M.; Lamm, B.; Keeffe, J. R. *J. Am. Chem. Soc.* **1964**, *86*, 4727–9.
(15) (a) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–8. (b) Fărcasiu, D. *J. Chem. Educ.* **1975**, *52*, 76–9.
(16) Brown, H. C.; Cleveland, J. D. *J. Org. Chem.* **1976**, *41*, 1792–9.
(17) This number was estimated by multiplying the rate difference between **3** and **27** at 25 °C (480) by the rate difference between **27** and **28** at 140 °C (130).
(18) Creary, X. *J. Am. Chem. Soc.* **1980**, *102*, 1611–8.

h). Gas chromatographic analysis of the crude mixture showed less than 0.5% for **4**. The entire mixture was chromatographed on 90% of silica gel and eluted with Skelly F to remove the benzophenone. A total of 1.52 g (73%) of **3** was obtained. The NMR and IR spectra of this product were identical with those of **3** prepared as previously described.

Reaction of Lithium Tetramethylpiperidide with Substituted Benzyl Halides and Alkenes. General Procedure. The arylcyclopropanes were generally prepared by addition of the appropriate arylcarbenoid to the appropriate alkene.[5] A mixture of alkene (8–10 equiv) and benzyl halide (0.8 equiv) was stirred at room temperature (with a small amount of ether when the alkene was norbornene) as a solution of LiTMP (1 equiv prepared from tetramethylpiperidine and methyllithium) in ether was added dropwise. After 20 min, water was added, and the organic phase was separated, washed with dilute HCl, and dried over Na_2SO_4. The solvents were removed by rotary evaporator, and the residue was either distilled or chromatographed on silica gel. Reactions 4, 6, and 8 (Table II) were chromatographed while the others were initially purified by distillation. The isomeric arylcyclopropanes were finally separated by preparative gas chromatography except in the case of reactions 4 and 6 where separation was achieved via column chromatography. The *endo*-aryl isomers all had shorter retention times. Table II gives details of the experimental procedures. The ratios of products given were determined by gas chromatography on the crude reaction products. The yields given represent isolated yields.

Preparation of *exo*-(4-Fluorophenyl)-*exo*-tricyclo-[3.2.1.$0^{2,4}$]octane (18). (*p*-Fluorophenyl)diazomethane[18] (650 mg) was added to 5.1 g of norbornene containing 1 mL of pentane. After 3 h at room temperature, the excess norbornene was removed at reduced pressure. The crude pyrazoline was dissolved in 70 mL of cyclohexane, and 5 g of benzophenone was added. The solution was irradiated with Pyrex-filtered light from a Hanovia 450-W source for 3.5 h. Gas chromatographic analysis showed less than 0.5% of the *endo*-aryl isomer. The crude cyclohexane solution was chromatographed on 50 g of silica gel with Skelly F elution, which completely removed the benzophenone. After the product, **18**, eluted, the solvent was removed by distillation through a Vigreux column. Distillation of the residue gave 626 mg (65%) of **18**: bp 83 °C (0.07 mm); NMR (CCl_4) δ 7.2–6.7 (4 H, m), 2.44 (2 H, m), 1.77 (1 H, t, J = 2.8 Hz), 1.6–0.5 (8 H, m). Anal. Calcd for $C_{14}H_{15}F$: C, 83.13; H, 7.48. Found: C, 83.01; H, 7.67.

Reaction of 3 with 0.1 M Toluenesulfonic Acid in Acetic Acid. A 303-mg sample of **3** was dissolved in 25 mL of a 0.1 M toluenesulfonic acid solution in acetic acid containing 1% acetic anhydride. After 24 h at 25 °C, a standard aqueous workup was carried out. After the extract was dried over $MgSO_4$, the solvent was removed by rotary evaporator, leaving 391 mg (97%) of crude acetates **12**. The major acetate showed a benzylic doublet (J = 10.5 Hz) at δ 5.33. The minor acetate showed a benzylic doublet (J = 10.0 Hz) at δ 5.39: NMR ($CDCl_3$) δ 7.4–7.0 (5 H, br s), 5.39 (0.43 H, d, J = 10 Hz), 5.33 (0.57 H, d, J = 10.5 Hz), 2.11 (2 H, m), 2.00 and 1.98 (3 H, two incompletely resolved singlets), 1.9–0.8 (9 H, m). The acetate ratio was 1.3:1 as determined by NMR. The spectrum of the mixture (acetates **12**) was identical with an equilibrated mixture prepared independently. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.45; H, 8.29.

In a separate run, reaction for 60 min at 25 °C (25% reaction) gave an acetate ratio of 1.6:1. Reaction for 138 min at 25 °C (50% reaction) gave approximately the same acetate ratio.

Reaction of 4 with 0.1 M Toluenesulfonic Acid in Acetic Acid. A solution of 223 mg of **4** in 20 mL of 0.1 M toluenesulfonic acid in acetic acid–1% acetic anhydride was heated at 60 °C for 20 h (5 half-lives). After a standard aqueous workup, 240 mg of crude products was obtained. Gas chromatographic analysis showed alkenes **13** (E/Z ratio of 5) as the major product along with acetates **12**. Samples of alkenes **13** were isolated by preparative gas chromatography and identified by NMR spectral comparison with authentic samples prepared as described below. In a separate run, reaction of **4** for 4 h and 50 min at 60 °C gave acetates **12** as the major product with only about 10% of alkenes **13**. In a control experiment, heating a sample of acetates **12** in 0.1 M toluenesulfonic acid in acetic acid at 60 °C for 20 h produced alkenes **13**.

Reaction of Norcamphor with Benzylidenetriphenylphosphorane. A mixture of 21 mL of a 0.65 M solution of sodium ethoxide in ethanol and 4 g of benzyltriphenylphosphonium chloride was stirred at room temperature for 10 min. Norcamphor (1.13 g) was added, and the mixture was refluxed for 15 h. The mixture was diluted with 20 mL of Skelly F and filtered. Water was added, and the triphenylphosphine oxide which crystallized was filtered off. After the mixture was dried over $MgSO_4$, the solvent was removed by rotary evaporator. The residue was chromatographed on 16 g of silica gel and eluted with 5% ether in Skelly F. Alkenes **13** eluted rapidly, and the solvent was removed by rotary evaporator. Distillation gave 1.59 g (84%) of a mixture of alkenes **13**, bp 77–84 (0.07 mm). The E/Z ratio was 0.9:1. Samples of each alkene were isolated by preparative gas chromatography: NMR of **13** (E isomer, $CDCl_3$) δ 7.4–7.0 (5 H, m), 6.26 (1 H, t, J = 2.5 Hz), 2.80 (1 H, m), 2.6–2.0 (3 H, m), 1.9–1.0 (6 H, m); NMR of **13** (Z isomer, $CDCl_3$) δ 7.4–6.9 (5 H, m), 6.08 (1 H, br s), 3.23 (1 H, m), 2.6–2.0 (3 H, m), 2.0–1.1 (6 H, m). Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.03; H, 8.90.

Preparation of Acetates 12 from *exo*-Norbornyl Phenyl Ketone (14). (A) Lithium Aluminum Hydride Reduction. A solution of 460 mg of *exo*-norbornyl phenyl ketone[19] in 5 mL of ether was added dropwise to 150 mg of lithium aluminum hydride in 8 mL of ether. Sodium hydroxide in water was then added. The ether phase was then dried over $MgSO_4$, and the solvent was removed by rotary evaporator, leaving 502 mg of crude alcohol **15**. A 70-mg sample of crude **15** in 0.5 mL of pyridine was added to a mixture of 200 mg of acetyl chloride in 2 mL of pyridine. After the mixture was warmed to 60 °C for 15 min, a standard aqueous workup followed. The ether extract was dried over Na_2SO_4, and the solvent was removed by rotary evaporator. Distillation gave 78 mg (93%) of acetates **12**, bp 97 °C (0.06 mm). The major acetate showed a benzylic doublet (J = 10.5 Hz) at δ 5.33. The minor acetate showed a benzylic doublet (J = 10.0 Hz) at δ 5.39. The ratio of the major acetate to the minor acetate was 2.1 as determined by the ratio of the signals at δ 5.33 and 5.39.

(B) L-Selectride Reduction. A 4-mL sample of a 1.0 M solution of lithium tri-*sec*-butylborohydride in THF was cooled to −78 °C, and a solution of 0.76 g of ketone **14** in 4 mL of ether was added dropwise. The mixture was slowly warmed to room temperature, and excess hydrogen peroxide and NaOH in water was carefully added. A standard aqueous workup followed. After the extract was dried over Na_2SO_4, the solvents were removed by rotary evaporator. The crude mixture of alcohols **15** weighed 0.75 g. A 115-mg sample of the crude alcohols in 0.5 mL of pyridine was added to a slurry of 240 mg of acetyl chloride in 2 mL of pyridine. After the mixture was warmed for 20 min at 60 °C, a standard aqueous workup followed. Distillation gave 130 mg (96%) of acetates **12**, bp 97 °C (0.06 mm). The major acetate showed a doublet at δ 5.33 while the minor acetate showed a doublet at δ 5.39. The ratio of the major to minor acetate was 4.1 as determined by the ratio of the signals at δ 5.33 (major) and 5.39 (minor).

Product Stability Studies on Acetates 12. A solution of 68 mg of acetates **12** (from the $LiAlH_4$ reduction–acetylation procedure; major acetate to minor acetate ratio of 2.1) in 4 mL of 0.1 M toluenesulfonic acid was heated at 45 °C for 3.5 h. After a standard aqueous workup, 62 mg of acetates was isolated. Gas chromatographic analysis showed the presence of about 5% of alkenes **13**. The ratio of the major acetate (doublet at δ 5.33) to the minor acetate (doublet at δ 5.39) was now 1.3. The NMR spectrum was identical with that of the products obtained from reaction of **3** with 0.1 M toluenesulfonic acid in acetic acid for 24 h at 25 °C.

In a similar fashion, treatment of a sample of acetates **12** (from the L-Selectride reduction–acetylation procedure; major acetate to minor acetate ratio of 4.1) in 0.1 M toluenesulfonic acid in acetic acid at 25 °C for 141 min changed the major to the minor acetate ratio to 2.9.

Acetolysis of Mesylate 24. A solution of 134 mg of alcohols **15** (from $LiAlH_4$ reduction of **14**) and 91 mg of triethylamine in 3 mL of methylene chloride was cooled to −40 °C, and 87 mg of

(19) Lewis, F. D.; Johnson, R. W.; Ruden, R. A. *J. Am. Chem. Soc.* **1972**, *94*, 4292–7.

Table II. Reaction of Lithium Tetramethylpiperidide with Benzyl Halides and Alkenes

reaction	benzyl halide	alkene	products (% yield)	NMR (solvent), δ
1	*m*-$CH_3C_6H_4CH_2Br$ (6a)	norbornene	7a (16)	^{1}H NMR (CCl_4) 7.3–6.8 (4 H, m), 2.45 (2 H, m), 2.30 (3 H, s), 1.73 (1 H, t, J = 3 Hz), 1.4 (4 H, m), 1.2–0.6 (4 H, m)
			8a (33)	^{1}H NMR ($CDCl_3$) 7.2–6.8 (4 H, m), 2.42 (2 H, m), 2.32 (3 H, s), 1.80 (1 H, t, J = 8 Hz), 1.37 (4 H, m), 1.12 (2 H, d, J = 8 Hz), 0.42 (2 H, m); ^{13}C NMR 21.4, 21.8, 23.0, 30.2, 30.6, 36.2, 125.8, 126.0, 128.0, 129.5, 137.6, 140.4
2	*m*-$FC_6H_4CH_2Cl$ (6b)	norbornene	7b (11)	^{1}H NMR ($CDCl_3$) 7.3–6.5 (4 H, m), 2.39 (2 H, m), 1.79 (1 H, t, J = 2.5 Hz), 1.7–1.1 (5 H, m), 1.01 (2 H, d, J = 2.5 Hz), 0.74 (1 H, br d, J = 11 Hz)
			8b (14)	^{1}H NMR ($CDCl_3$) 7.3–6.5 (4 H, m), 2.39 (2 H, m), 1.76 (1 H, t, J = 7.5 Hz), 1.6–1.2 (4 H, m), 1.13 (2 H, d, J = 7.5 Hz), 0.39 (2 H, m); ^{13}C NMR 22.0, 22.9, 29.9, 30.1, 36.0, plus 12 aromatic signals
3	*m*-(*i*-Pr)$C_6H_4CH_2Cl$ (6c)	norbornene	7c (16)	^{1}H NMR ($CDCl_3$) 7.3–6.8 (4 H, m), 2.86 (1 H, heptet, J = 7 Hz), 2.42 (2 H, m), 1.82 (1 H, t, J = 2.5 Hz), 1.5–0.5 (8 H, m), 1.23 (6 H, d, J = 7 Hz)
			8c (28)	^{1}H NMR ($CDCl_3$) 7.3–6.8 (4 H, m), 2.87 (1 H, heptet, J = 7 Hz), 2.42 (2 H, m), 1.82 (1 H, t, J = 7.8 Hz), 1.5–1.0 (6 H, m), 1.23 (6 H, d, J = 7 Hz), 0.39 (2 H, m); ^{13}C NMR 21.9, 23.2, 24.0, 30.3, 30.5, 34.0, 36.2, 123.3, 126.2, 126.9, 128.1, 140.4, 148.7
4	1-(chloromethyl)-naphthalene	norbornene	9 (24)	^{1}H NMR ($CDCl_3$) 8.6–8.3 (1 H, m), 7.9–7.1 (6 H, m), 2.46 (1 H, m), 2.40 (1 H, m), 1.95 (1 H, t, J = 8 Hz), 1.7–1.0 (6 H, m), 0.30 (2 H, m); ^{13}C NMR 20.3, 20.7, 24.8, 30.0, 30.4, 30.7, 36.3, 37.1, 124.8, 125.2, 125.3, 125.5, 125.8, 126.2, 128.0, 132.7, 133.6, 136.9
			exo-3-(1-naphthyl)-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (19)	^{1}H NMR ($CDCl_3$) 8.4–8.2 (1 H, m), 7.9–7.1 (6 H, m), 2.54 (2 H, m), 2.26 (1 H, t, J = (1 H, t, J = 3 Hz), 1.7–1.3 (5 H, m), 1.17 (2 H, d, J = 3 Hz), 0.88 (1 H, br d, J = 11 Hz)
5	*p*-$CH_3C_6H_5CH_2Cl$	norbornene	17 (27)	^{1}H NMR (CCl_4) 7.2–6.8 (4 H, m), 2.42 (2 H, m), 2.27 (3 H, s), 1.73 (1 H, t, J = 3 Hz), 1.5–1.0 (8 H, m)
			19 (29)	^{1}H NMR (CCl_4) 7.2–6.8 (4 H, m), 2.38 (2 H, m), 2.30 (3 H, s), 1.74 (1 H, t, J = 7.5 Hz), 1.37 (4 H, m), 1.07 (2 H, d, J = 7.5 Hz), 0.40 (2 H, m)
6	*p*-$CH_3OC_6H_4CH_2Cl$	norbornene	20 (16)	^{1}H NMR ($CDCl_3$) 7.3–6.7 (4 H, AA′BB′ q), 3.80 (3 H, s), 2.38 (2 H, m), 1.74 (1 H, t, J = 7.5 Hz), 1.35 (4 H, m), 1.08 (2 H, d, J = 7.5 Hz), 0.40 (2 H, m)
			exo-3-(4-methoxyphenyl)-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (29)[a]	^{1}H NMR ($CDCl_3$) 7.1–6.7 (4 H, AA′BB′ q), 3.78 (3 H, s), 2.40 (2 H, m), 1.78 (1 H, t, J = 2.5 Hz), 1.6–0.6 (8 H, m)
7	1-(chloromethyl)-naphthalene	tetramethyl-ethylene	10[b] (45)	^{1}H NMR (CD_2Cl_2) 8.2–7.2 (7 H, m), 1.73 (1 H, s), 1.40 (6 H, s), 0.93 (6 H, s); ^{13}C NMR 19.3, 23.4, 23.8, 36.5, 125.3, 125.4, 125.5, 126.3, 128.0, 128.4, 134.0, 134.6, 136.5
8	1-(chloromethyl)-naphthalene	cyclopen-tene	11 (52)	^{1}H NMR ($CDCl_3$) 8.6–8.3 (1 H, m), 8.0–7.2 (6 H, m), 2.26 (1 H, t, J = 8 Hz), 2.1–1.6 (6 H, m), 1.5–1.0 (1 H, m), 0.3 to −0.3 (1 H, m); ^{13}C NMR 22.0, 23.5, 23.9, 26.7, 125.3, 125.5, 125.6, 126.4, 126.5, 128.3, 133.4, 135.5
			exo-6-(1-naphthyl)bicyclo-[3.1.0]hexane (10)	^{1}H NMR ($CDCl_3$) 8.4–8.1 (1 H, m), 7.9–7.1 (6 H, m), 2.2–1.4 (9 H, m)

[a] Mp 62–63 °C. [b] Mp 70–71 °C.

methanesulfonyl chloride in 0.4 mL of methylene chloride was added dropwise. The mixture was warmed to −10 °C, and a standard aqueous workup followed. All solutions were kept cold during the workup. After the extract was dried over $MgSO_4$, the solvents were removed at less than 0 °C on a rotary evaporator. The crude mesylate was immediately dissolved in 20 mL of acetic acid which was 0.1 M in sodium acetate and contained 1% acetic anhydride. After 4.5 h at 22 °C a standard aqueous workup was carried out. After the extract was dried over $MgSO_4$, the solvents were removed by rotary evaporator, leaving 148 mg (92%) of acetates **12**. The major acetate showed a benzylic doublet at δ 5.33 while the minor acetate showed a benzylic doublet at δ 5.39. The ratio of these acetates was 1.6 as determined by NMR.

In a similar fashion, 180 mg of alcohols **15** (from L-Selectride reduction of **14**), 124 mg of triethylamine, and 116 mg of methanesulfonyl chloride gave crude mesylate **24**. The mesylate, after 5.5 h in 30 mL of acetic acid–0.1 M sodium acetate, gave 210 mg (99%) of acetates **12**. As before, the major acetate showed a doublet at δ 5.33, and the minor acetate showed a doublet at δ 5.39. The acetate ratio was 1.6 as determined by NMR.

Preparation of *exo*-6-Phenylbicyclo[3.1.0]hexane (21). A solution of 0.88 g of phenyldiazomethane[18] in 20 mL of cyclopentene was held at room temperature for 10 days. Excess cyclopentene was removed under vacuum. The crude pyrazoline was dissolved in 65 mL of cyclohexane, and 6 g of benzophenone was added. The solution was irradiated (Hanovia 450-W source) with Pyrex filtering until nitrogen evolution ceased (4 h). Gas chromatographic analysis showed about 7% of *endo*-6-phenylbicyclo[3.1.0]hexane along with **21** as the major product. The entire mixture was chromatographed on 65 g of silica gel with Skelly F elution. The first fractions were enriched in the endo isomer. The later fractions were almost pure (99.5%) exo isomer **21**. After solvent removal by distillation, the residue was distilled, giving 0.70 g (59%) of **21**: NMR ($CDCl_3$) δ 7.3–6.8 (5 H, m), 2.0–1.0 (9 H, m). Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.82; H, 8.68.

Preparation of *exo*-7-Phenylbicyclo[4.1.0]heptane (22). A solution of 540 mg of phenyldiazomethane in 50 mL of cyclohexene was irradiated for 9 h with Pyrex filtered light (Hanovia 450-W source). The excess cyclohexene was removed by distillation. The residue was distilled at 1.1 mm to give 715 mg (90%) of a product mixture consisting of 3-(3-cyclohexenyl)cyclohexene,[20] 3-benzylcyclohexene,[21a] *endo*-7-phenylbicyclo[4.1.0]heptane,[5,21] *exo*-7-phenylbicyclo[4.1.0]heptane (**22**),[5,21] 1,2-diphenylethane, and 1,2-diphenylethylene in a 0.15:0.79:1.0:0.91:0.05:0.03 ratio as determined by gas chromatography. Samples of each product were isolated by preparative gas chromatography and were identified by NMR and gas chromatography–mass spectrometry. A sample of **22** for kinetic studies was isolated by preparative gas chromatography. Previously reported **22** had the following NMR spectrum ($CDCl_3$): δ 7.3–6.8 (5 H, m), 2.2–1.7 (4 H, m), 1.56 (1 H, t, J = 2.5 Hz), 1.4–1.1 (6 H, m).

Preparation of (2,6-Dimethylphenyl)diazomethane (25). 2,6-Dimethylbenzaldehyde (1.00 g) was added to 1.48 g of *p*-toluenesulfonylhydrazine in 5 mL of methanol. The mixture was cooled to about 0 °C, and 1.95 g (86%) of solid tosylhydrazone (mp 145–147 °C) was collected. The tosylhydrazone (1.95 g) was dissolved in 13.5 mL of a 0.50 M sodium methoxide in methanol solution. The methanol was removed by rotary evaporator, and the solid salt was evacuated at 0.1 mm for 1 h. The dry salt was then pyrolyzed (safety shield) at 0.1 mm in an oil bath. The red-orange diazo compound **25** began to collect in a receiver cooled to −78 °C at an oil bath temperature of 90 °C. The oil bath was slowly raised to 170 °C. The red-orange **25** which had collected in the cooled receiver was redistilled (shield): 0.70 g (74%); bp 43–44 °C (0.07 mm). The product contained about 7% of 2,6-dimethylbenzonitrile ($\nu_{C\equiv N}$ = 4.49 μm) which was identified by IR, NMR, and mass spectral data on a sample isolated by preparative gas chromatography. Samples of **25** were unstable for prolonged periods at room temperature: NMR (CCl_4) δ 6.93 (3 H, br s), 4.73 (1 H, s), 2.28 (6 H, s).

Preparation of *exo*-3-(2,6-Dimethylphenyl)-*exo*-tricyclo[3.2.1.0^{2,4}]octane (27). A solution of 650 mg of (2,6-dimethylphenyl)diazomethane (**25**) in 7 g of norbornene and 2 mL of pentane was kept at room temperature for 7.5 h. Excess norbornene was removed under reduced pressure, and the crude pyrazoline **26** was dissolved in 60 mL of cyclohexane. Five grams of benzophenone was added, and the solution was irradiated with Pyrex-filtered light (Hanovia 450-W source) for 2 h and 20 min. Gas chromatographic analysis showed about 4% of the endo isomer **28** along with **27** as the major product. The entire solution was chromatographed on 50 g of silica gel and eluted with 3% ether in Skelly F. Initial fractions were enriched in the endo isomer, **28**. Later fractions were greater than 99% **27**. After the solvent was removed by rotary evaporator, the residue was distilled, giving 668 mg (71%) of **27**: bp 94–96 °C (0.08 mm); NMR ($CDCl_3$) δ 6.94 (3 H, br s), 2.5–2.3 (9 H, m with singlet at 2.37), 1.7–1.0 (5 H, m), 0.91 (2 H, d, J = 3 Hz), 0.77 (1 H, br d, J = 11 Hz). Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.55; H, 9.72.

Photolysis of (2,6-Dimethylphenyl)diazomethane in Norbornene at −15 °C. (2,6-Dimethylphenyl)diazomethane (**25**, 40 mg) was added to 3.75 g of norbornene and 4.05 g of pentane at −78 °C. The mixture was sealed in a Pyrex tube and cooled in an ice–ethanol mixture to −15 °C. The solution was irradiated for 40 min at −15 °C. Gas chromatographic analysis showed **27** and **28** in a 1.67:1 ratio along with about 15% of 2- and 3-(2,6-dimethylbenzyl)pentanes and an unidentified product. The solvents were removed at reduced pressure, and the residue was distilled, giving 38 mg (65%) of a product mixture containing **27** and **28**. Samples of each were isolated by preparative gas chromatography: NMR of **28** ($CDCl_3$) δ 6.93 (3 H, s), 2.42 (6 H, s), 2.38 (2 H, m), 1.51 (1 H, t, J = 7 Hz), 1.35 (4 H, m), 1.23 (2 H, d, J = 7 Hz), 0.36 (2 H, m).

***p*-Toluenesulfonic Acid Catalyzed Addition of Acetic Acid to Arylcyclopropanes. Kinetics Procedure.** Approximately 60 mg of the appropriate arylcyclopropane and biphenyl (internal standard) were dissolved in 4 mL of 0.1 M toluenesulfonic acid in acetic acid containing 1% acetic anhydride. In the case of **21**, *n*-butylbenzene was the internal standard. The solution was divided into eight portions and sealed in tubes. The tubes were immersed in a constant-temperature bath at the appropriate temperature for a given amount of time. The contents of each tube were then diluted with 2 mL of ether, extracted with two 3-mL portions of water and 2 mL of a 1 M K_2CO_3 solution, and dried over Na_2SO_4. The ether extracts were then analyzed for unreacted arylcyclopropane by gas chromatography. Rate constants were calculated by standard procedures. Correlation coefficients were in all cases greater than 0.999.

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Registry No. **3**, 66966-40-3; **4**, 67010-34-8; **5**, 498-66-8; **6a**, 620-19-9; **6b**, 456-42-8; **6c**, 74705-35-4; **7a**, 74998-74-6; **7b**, 74998-75-7; **7c**, 74998-76-8; **8a**, 75044-13-2; **8b**, 75044-14-3; **8c**, 75044-15-4; **9**, 74998-77-9; **10**, 74998-78-0; **11**, 75010-78-5; **12a**, 74998-80-4; **12b**, 74998-81-5; (*E*)-**13**, 67683-48-1; (*Z*)-**13**, 67683-47-0; **14**, 948-15-2; **15** (isomer 1), 74998-82-6; **15** (isomer 2), 74998-83-7; **16**, 497-38-1; **17**, 74998-84-8; **18**, 74998-85-9; **19**, 75044-17-6; **20**, 74998-86-0; *endo*-**21**, 58647-78-2; *exo*-**21**, 58647-76-0; *endo*-**22**, 10503-37-4; *exo*-**22**, 10503-36-3; **24** (isomer 1), 74998-87-1; **24** (isomer 2), 74998-88-2; **25**, 74998-89-3; **26** (R = 2,6-$CH_3C_6H_3$), 74998-90-6; **26** (R = *p*-FC_6H_4), 74998-91-7; **27**, 74998-92-8; **28**, 75044-18-7; phenyldiazomethane, 766-91-6; *exo*-**11**, 74998-79-1; *exo*-**9**, 75044-16-5; acetic acid, 64-19-7; (*p*-fluorophenyl)diazomethane, 73900-13-7; benzyltriphenylphosphonium chloride, 1100-88-5; cyclopentene, 142-29-0; 3,3a,4,5,6,6a-hexahydro-3-phenylcyclopentapyrazole, 74998-93-9; cyclohexene, 110-83-8; 3-(3-cyclohexenyl)cyclohexene, 41585-33-5; 3-benzylcyclohexene, 4714-10-7; 1,2-diphenylethane, 103-29-7; 1,2-diphenylethylene, 588-59-0; 2,6-dimethylbenzaldehyde, 1123-56-4; *p*-toluenesulfonylhydrazine, 1576-35-8; 4-methylbenzenesulfonic acid (phenylmethylene)hydrazide, 1666-17-7; 2-(2,6-dimethylbenzyl)pentane, 74998-94-0; 3-(2,6-dimethylbenzyl)pentane, 74998-95-1; 1-(chloromethyl)naphthalene, 86-52-2; *p*-methylbenzyl chloride, 104-82-5; *p*-methoxybenzyl chloride, 824-94-2; tetramethylethylene, 563-79-1; *exo*-**20**, 75044-19-8.

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