strate used. However, analyses for the products of alkaline hydrolysis were performed and several conclusions were drawn. First, it appears that little or no β elimination occurs in alkaline solution up to approximately pH 10.0. Secondly, the release of thiol as the ester hydrolyzes can, in the case of simple *N*-acetyl-*S*-acylcysteinamides, be quantitatively accounted for by the DTNB method. The picture which emerges for the dipeptides, however, is different; only modest fractions of total thiol released at infinite time can be accounted for by this method. However, the time course for production of thiol, as measured during the hydrolysis of dipeptide **6**, reveals that nearly quantitative amounts of thiol are released during the first 5 half-lives of the reaction, following which the amount of thiol diminishes. It would appear that thiol liberated is converted to some secondary product the nature of which, with the exception that oxidation to sulfenic acid is ruled out (see Experimental Section), is not known.

What are the implications of the modest rate facilitations observed in this study for the understanding of the reactivity of S-acyl-G3PD? First, the reactivity of simple *S*-acylcysteines toward hydroxide ion is about 20-fold greater than would have been expected on the basis of the valus of pK_a for the conjugate acid of the leaving group (Table III). Second, both the flanking serine and threonine residues do lead to appreciable increases in the reactivity of the adjacent thiol ester. Having both serine and threonine present in the same molecule might lead to either addition or multiplication of the catalytic effects, depending on whether the catalytic mechanisms are different or the same. At best, one might anticipate a total increase in reactivity toward hydroxide ion of some 200-fold in the presence of both serine and threonine functions. Combining this rate increase with that observed for the simple *S*-acylcysteines leads to a maximal total factor of perhaps 4000. While such a reactivity increase certainly partially bridges the gap between the reactivity of the acyl enzyme and that of simple thiol esters, it would still fall at least three orders of magnitude short of accounting for all of the difference. Hence the reactivity of the acyl enzyme must depend to a major extent on catalytic mechanisms involving residues not in the primary sequence of amino acids at the active site.

Registry No.—**2**, 36914-96-2; **3**, 16820-83-0; **6**, 36912-46-6; **7**, 36914-97-3; **8**, 36912-47-7.

Acknowledgment.—The expert technical assistance of Mr. Alan Stafford is gratefully acknowledged.

Studies on 3,3-Diaryltricyclo[3.2.1.0^{2,4}]octanes. I. Synthesis and Reactions of *exo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]oct-6-ene and Its Derivatives[1]

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The thermal reaction of diphenyldiazomethane and norbornadiene affords mono and bis adducts. These pyrazolines can be thermally transformed to polycyclic hydrocarbons with stereospecific loss of nitrogen. Comparison is made to similar reactions reported in the literature. The title hydrocarbon so obtained has been characterized by its nmr spectrum, most notably by the singlet resonance of its endo H-2,4 protons. Reactions in this system that have been studied include the reaction of the hydrocarbon with bromine and the solvolysis of the exo- and endo-6 tosylates. Both processes proceed *via* the same rearrangement solely to nortricyclyl derivatives, presumably because the phenyl groups present stabilize overwhelmingly the cation precursor to these derivatives. An exo/endo rate difference of over 4000 in aqueous dioxane implies that anchimeric assistance is well developed in the exo isomer. Possible mechanistic pathways are discussed. Other transformations of the title hydrocarbon to unrearranged dibromides and to its exo epoxide are also mentioned.

Although the unsubstituted tricyclo[3.2.1.0^{2,4}]-ocyl system has had its chemistry explored in a variety of processes,[3] much less is known about the 3,3-disubstituted cases. Two of the interesting results from our early studies on the exo-3,3-diphenyl-substituted system were the solvolytic rearrangements undergone by the *syn*- and *anti*-8-tosylates.[4] To understand more of the chemistry associated with the tricycle, the investigation of the title compound itself, as well as its 6 derivatives, was undertaken.

Discussion

Synthesis and Characterization of *exo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]oct-6-ene.—Addition of diphenyldiazomethane to norbornadiene afforded pyrazoline **1** which in turn was converted thermally into the title

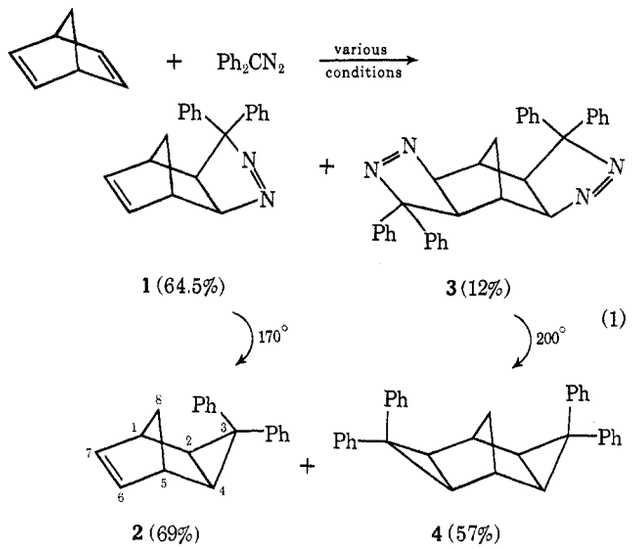
(1) Taken from portions of the dissertation of T. P. M., Loyola University of Chicago, 1970; Abstracts, 5th Great Lakes Regional Meeting of the American Chemical Society, Bradley University, Peoria, Ill., June 1971, Paper 55.

(2) National Science Foundation Trainee, 1969–1970.

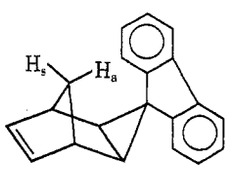
(3) Of the many studies extant, the following are of special interest to the present article. (a) Synthesis of exo tricyclic 6-ene: H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Amer. Chem. Soc.*, **86**, 1347 (1964). This preparation leads to 18% bicyclo[3.2.1]octadiene as well: T. J. Katz and S. A. Cerefice, *ibid.*, **93**, 1049 (1971). This fact must be considered when one peruses earlier studies in this area. (b) Synthesis of endo tricyclic 6-ene: K. B. Wiberg and W. Bartley, *ibid.*, **82**, 6375 (1960). (c) Solvolysis of arenesulfonates of exo and endo tricyclic 8-alcohols: H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); J. S. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969). (d) Solvolysis of arenesulfonates of endo and exo tricyclic 6-alcohols: K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965). (e) Hydrogenation of endo and exo tricyclic 6-enes: P. K. Freeman and K. B. Desai, *ibid.*, **36**, 1554 (1971). (f) Photochemical isomerization of endo and exo tricyclic 6-enes: H. Prinzbach and W. Eberbach, *Chem. Ber.*, **101**, 4083 (1968). (g) Reduction of endo and exo 6-oxides: B. C. Henshaw, D. W. Rome, and B. L. Johnson, *Tetrahedron*, **27**, 2255 (1971); D. W. Rome and B. L. Johnson, *ibid.*, **27**, 2271 (1971).

(4) J. W. Wilt and T. P. Malloy, *J. Amer. Chem. Soc.*, **92**, 4747 (1970).

compound **2**. Minor amounts of the bis adduct **3**[5] and its thermal product **4** were also obtainable in this reaction sequence (eq 1).



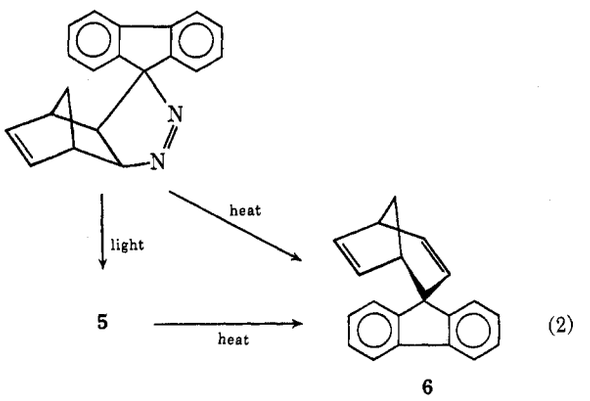
Similar reactions have been reported.[5,6] Most importantly, Filipescu and DeMember[6a] have prepared the fluorenylidene analogs of **1** and **2** and have characterized these compounds spectrally. The nmr spectra of **1** and **2** correspond to those reported for their products with the important exception in **2** that the anti 8-hydrogen (syn to the diphenylcyclopropyl moiety) is shielded (δ 0.63, doublet) relative to its syn 8-hydrogen neighbor (δ 0.93, doublet). In **5**, one of Filipescu and DeMember's compounds, this situation is reversed. In **5**, the anti 8-H (syn to the

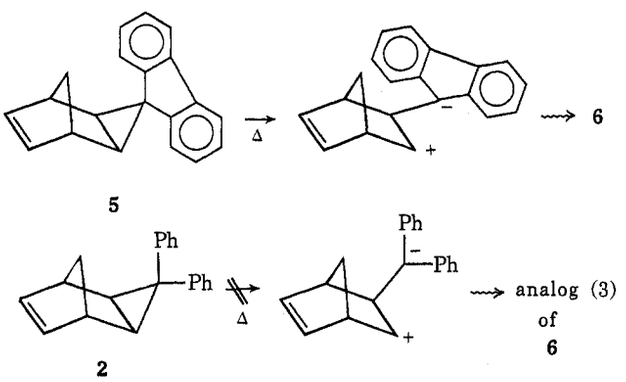


5

fluorenylidene) is reported[6a] at δ 2.58 (doublet) while its syn neighbor is at δ 1.39 (doublet). Clearly this difference results from the different environment of the anti 8-H's in **2** and **5**. In the latter, as mentioned by Filipescu and DeMember,[6a] this hydrogen butts the 1'-fluorenylidene hydrogen and lies in the aromatic σ plane, resulting in deshielding In **2**, however, framework molecular models indicate that the anti 8-H lies in the π-electron region of the proximate phenyl group, resulting in shielding. The exo nature of the cyclopropyl ring in **2** was apparent from the sharp singlet resonance at δ 1.72 arising from the H-2,H-4 pair of endo hydrogens. An unfavorable geometry precludes coupling of these hydrogens with the bridgeheads 1 and 5. Apparently the long-range "W coupling" anticipated with the syn 8-H is so small that its existence is implicated only by the nonringing nature of this singlet. Exactly the same thing was noted for **5**.[6a] The bis,exo nature of **4** was likewise shown by the singlet nature of the resonance due to the endo cyclopropyl hydrogens at δ 1.78.

One of the more interesting differences between the earlier[6a] and present work is the mode of formation of **2** compared to **5**. When the pyrazoline precursor to **5** was *photolyzed*, **5** was produced. Upon *thermolysis*, however, the pyrazoline yielded **6**, not **5**. Indeed, thermolysis of **5** also gave **6** (eq 2), and it seems possible that **5**, not **6**, forms first under both sets of conditions from the pyrazoline. The spectral data given above show that no such thermal rearrangement of **2** (or its pyrazoline precursor **1**) to an analogously rearranged bicyclo[3.2.1]octadiene occurred in this work. We prefer not to comment extensively on this striking difference, largely because we feel the mechanism proposed[6a] for the formation of **6** is untested. If, however, the transformation of **5** is begun as Filipescu and DeMember suggested (eq 3), then





the difference with **2** may lie in the decreased stability of benzhydryl *vs.* 9-fluorenyl anion. The pK_A of fluorene is 22.8 whereas that of diphenylmethane is 33.1.[7] While the quantitative significance of these acidity values should maybe not be overemphasized,[8] nonetheless, a difference of 11 pK_A units is not minor. Obviously the difference indicates that the purported conversion of **5** *via* heterolysis into a zwitterion *could* be easier with it than with **2**. The isolation of only exo products (**2** and **4**) from the pyrazoline adducts indicates that these adducts were also exo in configuration. To our knowledge, nitrogen loss from

(5) The bis adduct was reported earlier by R. Fleischmann, Dissertation, University of Munich, 1957. *Cf.* R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963). The stereochemistry of the bis adduct was illustrated as shown above in the text but no proof was offered. On the basis of the nmr evidence we concur in this assignment of a racemic structure rather than the alternative meso structure (see Experimental Section).

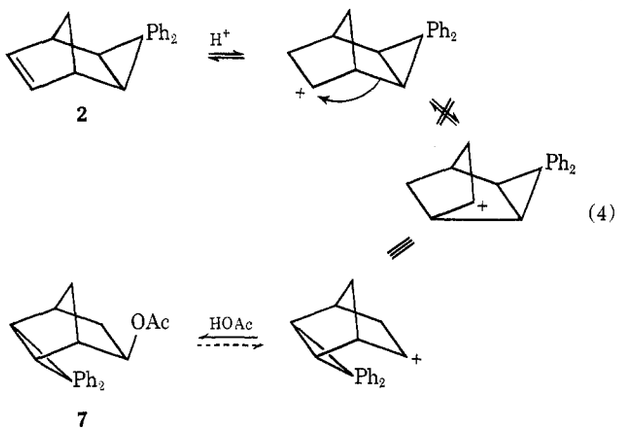
(6) (a) N. Filipescu and J. R. DeMember, *Tetrahedron*, **24**, 5181 (1969); (b) J. R. DeMember and N. Filipescu, *J. Amer. Chem. Soc.*, **90**, 6425 (1968); (c) A. A. Lamola, *ibid.*, **91**, 4786 (1969).

(7) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 27.

(8) Different pK_A values result in different solvent media; see ref 7.

thermolysis of pyrazolines *in such systems* is always stereospecific. Endo pyrazolines[9] yield endo cyclopropanes; exo pyrazolines yield exo cyclopropanes,[6a] though rearrangement may occur here subsequent to cyclopropane formation. On occasion, however, nitrogen loss does not even occur.[10]

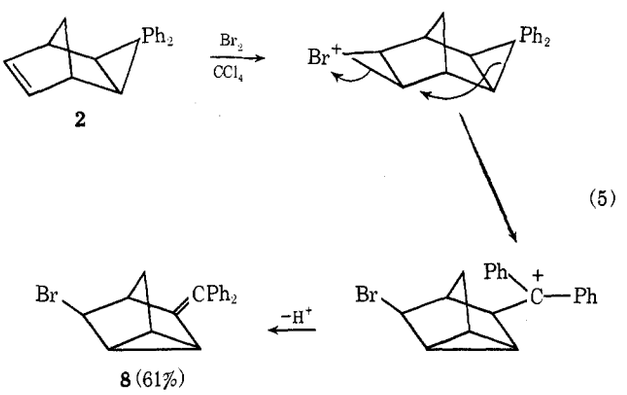
Functionalizations of 2.—Attempts to reverse the orientation of the cyclopropyl moiety in **2** from exo to endo as shown (eq 4) were unrewarding.[13] A complex



(4)

mix of apparently polymeric hydrocarbons was obtained. A possible reason for this disappointing result is that the ions shown in eq 4 (depicted as classical species for convenience) do not interrelate as shown. Rather, conversion into *benzhydryl* cationic species may occur, followed by polymerization. Such a view is supported by solvolysis studies (*vide infra*). The endo series, represented by **7** and other derivatives, is available by another route, however.[9,14]

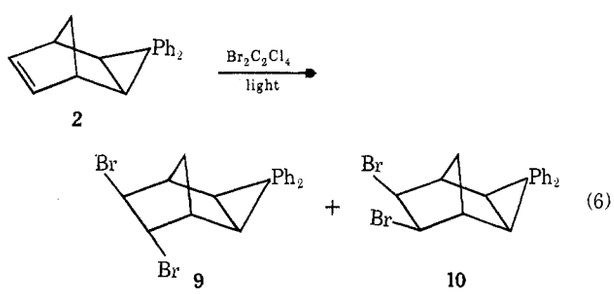
Nonetheless, a clean rearrangement could be manifested with **2**. Reaction with bromine led to monobromide **8** as the only isolated product in 61% yield (eq 5). The pathway and structure assigned to **8**



(5)

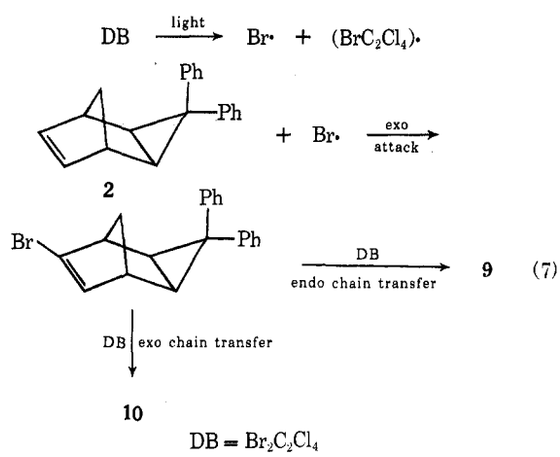
seemed reasonable on several grounds. First, the gross skeletal change shown in eq 5 is the same as that obtained in solvolysis studies (*vide infra*). Second, the loss of the exo cyclopropyl moiety of **2** was clear from the absence of the endo H-2,H-4 singlet resonance in the nmr spectrum of the bromide. And lastly, the presence of a single bromine (from combustion analysis) with its attendant -CHBr- resonance at δ 4.33 and the close similarity of the upfield portion of the nmr spectrum of the product to that of olefin **16** (*vide infra*) also suggested structure **8**. Nonetheless, it should be pointed out that the configuration of the bromine is supposed on the basis of the pathway only. We have no definitive evidence otherwise against the epimeric configuration.

An ionic pathway rather than a radical one in eq 5 was seemingly demanded by the fact that radical addition of bromine to **2** using dibromotetrachloroethane[15] led to *di*bromo adducts with *retained* structure (eq 6). The trans isomer (81%, **9**) possesses



(6)

triplet -CHBr resonances at δ 4.37 and 3.95, ($J \simeq$ 3 Hz) that indicated an endo and exo bromine, respectively. The cis isomer (19%, **10**) possessed a doublet ($J \simeq 2$ Hz) integrating to two hydrogens (both-CHBr's) at δ 4.10. The identity of the two hydrogens and the evidence of "W coupling" to the 8 position clearly showed the two bromines to be exo. Mechanistically, the addition probably followed the path shown (eq 7),



(7)

a path analogous to that reported earlier[15b] for another case.

Solvolysis of the 6-Alcohols.—A major goal in the study of **2** and its derivatives was the solvolysis of the tosylates of the 6-alcohols **11** and **12**. These alcohols

(9) J. W. Wilt and D. R. Sullivan, Abstracts, 6th Great Lakes Regional Meeting of the American Chemical Society, Michigan Technological University, Houghton, Mich., June 1972, p 64. The endo cyclopropanes so produced are easily differentiated from their exo isomers by nmr analysis. The H-2,H-4 pair of exo hydrogens in the endo analogs show triplet resonances downfield from the singlet observed with the exo compounds.

(10) The pyrazoline adducts of norbornene[11] and 5-norbornenone[12] fail to undergo the process.

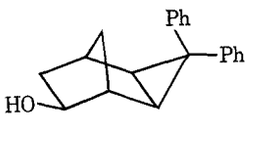
(11) N. S. Zefirov, P. Kadziauskas, and Yu. K. Yuriev, *Zh. Obshch. Khim.*, **36**, 23 (1966).

(12) R. S. Bly, F. B. Culp, Jr., and R. K. Bly, *J. Org. Chem.*, **35**, 2235 (1970).

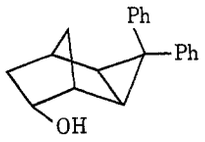
(13) For a discussion of the interrelationship between cations from *exo*- and *endo*-tricyclo[3.2.1.0^{2,4}]octyl systems, see J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *J. Amer. Chem. Soc.*, **91**, 5601 (1969).

(14) J. W. Wilt and D. R. Sullivan, to be published. The route involved addition of diphenyldiazomethane to 7-*tert*-butoxynorbornadiene, separation of the endo adducts, conversion into the endo cyclopropanes, and lastly modification or replacement of the functional groups.

(15) (a) E. S. Huyser and D. N. DeMott, *Chem. Ind. (London)*, 1954 (1963); (b) J. W. Wilt and P. J. Chenier, *J. Org. Chem.*, **35**, 1562 (1970).

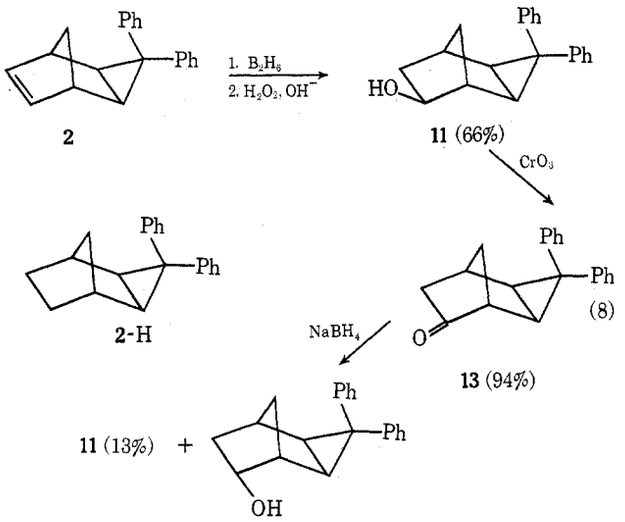


11



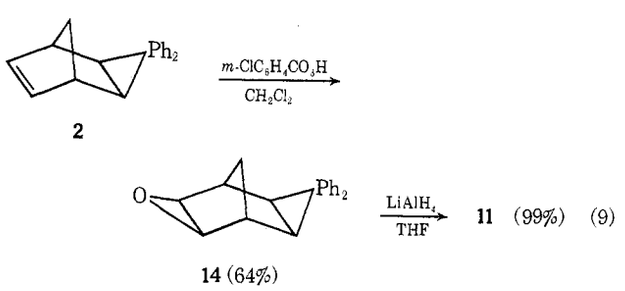
12

were readily prepared by the sequence outlined (eq 8),



a sequence modeled after that used by Wiberg and Wenzinger[3d] for the nonphenyl analogs. The oxidative hydroboration of **2** produced essentially pure exo 6-alcohol **11** (–CHOH δ 3.88), as would be expected. However, some protolysis product **2**-H was also detected in small amount (4%). The absence of vinyl absorption and the sharp singlet at δ 1.52 (endo H-2,-H-4) support the structure assigned, as does its formation under these conditions.[16]

Oxidation of **11** to ketone **13** was accomplished by Sarett's method. Reduction of **13** with sodium borohydride led to a 86:14 mixture of 6-alcohols with **12** predominating (–CHOH– δ 4.25). Exo alcohol **11** also was obtained from epoxidation of **2** to the exo oxirane **14** followed by treatment with lithium aluminum hydride (eq 9). The exo nature of **14** was indicated by the



sharp singlet resonance of the oxiranyl endo hydrogen pair. No reductive rearrangement of epoxide **14** to isomers of **11**, as has been reported for several other norbornene oxides, was observed.[3g,17] Tosylates of **11** and **12** were then readily prepared in the usual manner.[19]

Solvolysis of the tosylates **11**-OTs and **12**-OTs in 80% aqueous dioxane proceeded *via* first-order kinetics. Theoretical infinity titers were obtained after 10 half-lives. The kinetic and activation parameter data are gathered in Table I.

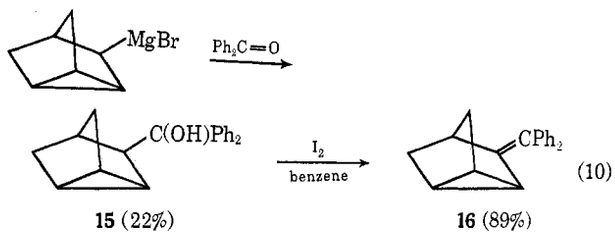
TABLE I

SOLVOLYSIS[a] OF 3,3-DIPHENYLTRICYCLO[3.2.1.0^{2,4}]OCT-6-YL TOSYLATES, **11**-OTs AND **12**-OTs

Tosylate	Temp,[b] °C	10^5k, sec^{-1} [c]	ΔH^*, kcal mol^{-1}	ΔS^*, eu
11-OTs	55.5	3.11 ± 0.05		
	64.0	7.82 ± 0.13		
	76.2	29.2 ± 0.10		
	25.0[d]	6.02 ± 0.90 × 10^{-7} [e]	23.7 ± 1.2	−7.44 ± 2.9
12-OTs	111.0	1.65 ± 0.01		
	121.0	4.41 ± 0.03		
	131.0	12.4 ± 0.20		
	25.0[d]	1.44 ± 0.50 × 10^{-10} [e]	30.2 ± 3.2	−2.47 ± 3.2

[a] In dioxane–H_2O, (80:20 v/v) containing 2,6-lutidine (0.044 *M*). [b] Below 100° the temperatures are ±0.2°; above 100°, ±0.3°. [c] Computer calculated. The error limits are standard deviations. [d] All data at 25° are extrapolated from data at higher temperatures. [e] This value is *k*, not 10^5k.

Both **11**-OTs and **12**-OTs underwent identical solvolytic rearrangements in quantitative yield to nortricyclyl derivatives, *viz.*, alcohol **15** from **11**-OTs and hydrocarbon **16** from **12**-OTs. The formation of but one product in these cases contrasts markedly with earlier studies on simple cases.[3d,13] The spectra of these products were in accord with the structures assigned. Confirmatory evidence was obtained, nevertheless, by treatment of benzophenone with nortricyclylmagnesium bromide (eq 10). Alcohol **15** so



formed was then conveniently dehydrated with iodine in hot benzene to **16**. The samples of **15** and **16** prepared in this way were identified with the solvolysis products. The formation of **15** from **11**-OTs and **16** from **12**-OTs is presumably a consequence of the different temperatures[20] used for the preparative solvolyses (65 *vs.* 134°). Alcohol **15** does *not* dehydrate to **16** under solvolysis conditions; so the precursor to **16** is

(16) In the analog of 2-H where the phenyl groups are replaced by a fluorenylidene group, the endo hydrogen pair resonate at δ 1.83 and again are a singlet.[6a]

(17) The lack of rearrangement with **14** (99% yield of **11**) is curious. Both the endo and exo 6-oxides in the parent (nonphenyl) system rearrange upon reduction with lithium aluminum hydride, as do norbornene *exo*-oxide and benzonorbornadiene *exo*-oxide.[3g] The mechanisms suggested for these rearrangements[3g,18] would seemingly apply to **14** also and its structural fidelity in this reduction appears anomalous.

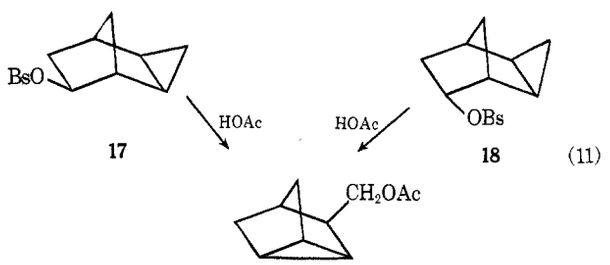
(18) G. D. Sargent, M. J. Harrison, and G. Khoury, *J. Amer. Chem. Soc.*, **91**, 4937 (1969).

(19) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(20) Higher temperatures are known to maximize elimination/substitution ratios. *Cf.* E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 489.

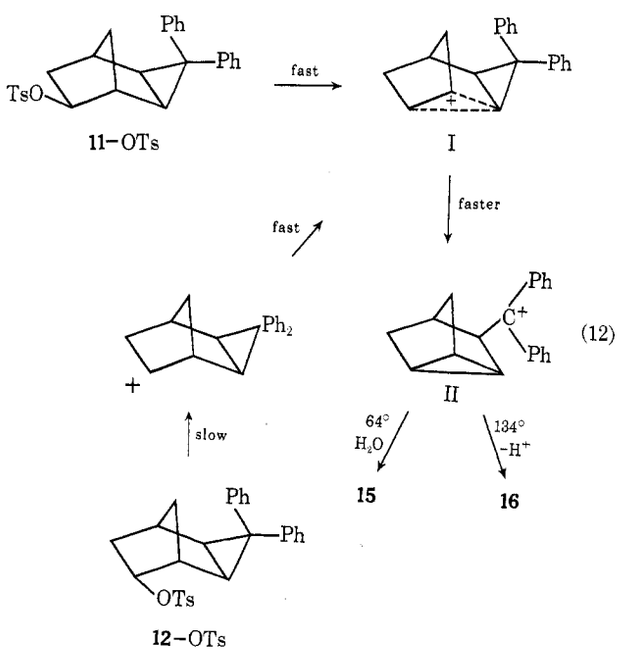
not **15**. Rather, some ion (*vide infra*) is precursor to both of them or the different products result from different mechanisms.

The obvious precedents to the present solvolysis are the earlier studies of principally Wiberg and Wenzinger[3d] and partly Berson, *et al.*,[13] on the parent tricyclo[3.2.1.0^{2,4}]octyl analogs of **11**-OTs and **12**-OTs. These earlier (and complicated) acetolytic studies uncovered much information on this type of system. The interested reader is directed to them. The present study in aqueous dioxane was, however, simpler than these in several respects. Ion-pair return was apparently obviated by the more polar medium, so rather free (essentially dissociated) ions may be invoked, and the complex kinetic schemes needed to rationalize the earlier studies do not seem necessary here. Among the products Wiberg and Wenzinger observed from both **17** and **18** was the nortricyclene **19** (eq 11). Whereas **19** was a minor product in the



(11)

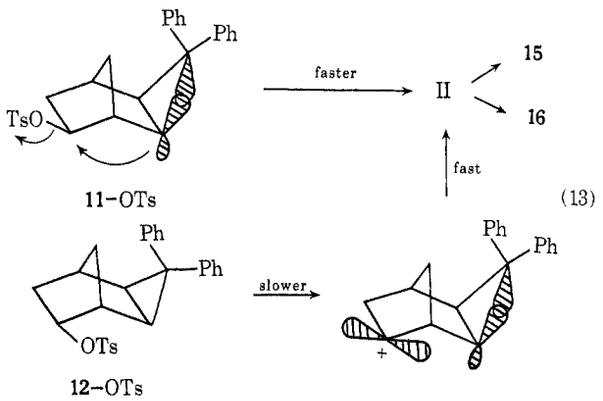
earlier studies (8.6%), in the present case the analogous product (**15** or **16**) was the sole product. If ion I be formed from both **11**-OTs and **12**-OTs (though undoubtedly with different rates), its isomerization to II would be rapid and probably irreversible because II is a benzhydryl cation (eq 12). Such an ionic



(12)

intermediate as well stabilized as is II would then swamp out any other potential product-forming ions. The net result would be to simplify both the kinetics (no internal return to kinetically slower isomers) and the products (one product instead of many).

That **11**-OTs and **12**-OTs do indeed differ in the rate-determining step is apparent from their rate ratio of 4180 at 25° (k_{17}/k_{18} = 1250 at 25° in HOAc[3d]). It is in fact conceivable that ion I is completely bypassed as no products from it were observed. Rather, II might form directly utilizing cyclopropyl participation from **11**-OTs and indirectly from **12**-OTs as shown (eq 13).[21] No clear-cut choice between the schemes given in eq 12 and 13 is made from the present



(13)

work. Other studies in progress in the system will, however, produce further data[22] and, hopefully, allow such a decision.

Experimental Section

Melting points were taken on a calibrated Fisher-Johns block. Boiling points are uncorrected. Infrared spectra (λ) were determined on 1% KBr disks using a Beckman IR-5A instrument. Only prominent or structurally significant absorptions are usually given (in microns).[23] Nuclear magnetic resonance spectra (nmr) were taken in deuteriochloroform on a Varian A-60A spectrometer. Values are given in parts per million (δ) downfield from internal TMS. The usual splitting abbreviations are used. Integration of signals agreed with the structural assignments. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Addition of Diphenyldiazomethane to Norbornadiene.—Diphenyldiazomethane[24] (6.67 g, 34.3 mmol), norbornadiene (freshly distilled material from Frinton Laboratories, S. Vineland, N. J., 9.09 g, 98.6 mmol), and dimethylformamide (5 ml) containing a few milligrams of anhydrous copper sulfate were slowly warmed to 60° until the reaction became self-sustaining. Heating was discontinued as the solution was stirred at 60° for 2 hr (the red solution became light orange). The cooled solution was reduced in volume by rotary evaporation. Acetone (15 ml) was then added and the material was thoroughly chilled. The pale yellow precipitate so formed was collected and recrystallized several times from methanol to give the white monoadduct **1**: yield 6.34 g (64.5%); mp 147.5–149.5 dec; λ 6.47 μ (N=N); nmr δ 7.25–7.67 (m, Ar–H), 6.30 (t, vinyl H's), 5.30 (d, –CHN=N–), 3.61 and 2.23 (broad singlets, bridgehead H's), 2.87 (broad doublet, –CHCPh$_2$–), 1.10 and 0.75 (d, CH$_2$[25]).

Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34. Found: C, 84.15; H, 6.33.

The mother liquor from the acetone solution was concentrated to produce a sticky solid which was recrystallized several times from 95% ethanol. The bis adduct **3** so obtained was a white crystalline solid: yield 1.01 g (12%); mp 227–230° dec; λ 6.42 μ (N=N); nmr δ 7.25–7.52 (m, Ar–H, 5.10 (d, –CHN=N–), 2.92

(21) A similar path has been suggested in the tetracyclo[4.3.0.0^{2,4}.0^{3,7}]-nonane ("deltacyclane") system by P. K. Freeman, D. M. Balls, and J. N. Blazevich, *J. Amer. Chem. Soc.*, **92**, 2051 (1970).

(22) In particular, eq 12 and 13 may be differentiable by a $\rho\sigma^+$ study in that benzhydryl cationic stability should *directly* influence the latter but not the former.

(23) Complete details are available in the dissertation of T. P. M.

(24) J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).

(25) No assignment is made as to which resonance is due to the anti and which to the syn protons.

(broad doublet, -CHCPh$_2$-), 2.47 (broad singlet, bridgehead H's), 0.10 (broad s, CH_2). The doublet J value was *ca.* 7 Hz.

Anal. Calcd for $C_{33}H_{28}N_4$: C, 82.47; H, 5.87. Found: C, 82.69; H, 5.92.

The structure assigned to **3** is supported by the identity of the bridgehead H's. Had the additions of diphenyldiazomethane been identical in orientation, a meso product with a difference in the bridgehead H's should have resulted. The strong upfield shift of the bridge methylene H's is surprisingly dramatic, being even farther upfield than the bridge H's in **4** (*vide infra*). Presumably the shift resulted from powerful shielding caused by the proximate aromatic *and* azo functions.

The addition above was carried out under other conditions as well. Reactions with neat norbornadiene, or in dioxane solvent, some with no copper salt, some at 25° and others at intermediate temperatures all gave **1** and **3**, though monoaddition was clearly favored by use of neat norbornadiene. Dioxane, curiously, has been found to be deleterious in other reactions of this type.[26] Higher temperatures disfavored a clean reaction. The described procedure was the most economical in time and chemicals, however.

***exo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]oct-6-ene (2).**—Adduct **1** (2.28 g, 7.95 mmol) was heated as a neat melt in a wax bath at 170° for 30 min. Nitrogen (92%) was evolved. The cooled product was chromatographed on alumina (70 g). Elution with hexane gave white crystalline **2** which was then recrystallized several times from methanol: yield 1.42 g (68.6%); mp 82–83.5°; λ 3.33–3.36, 6.25, 6.66, 6.90, 7.92, 9.34, 9.96, 10.99, 11.44, 12.00, 13.01, 13.36, 13.96–14.36, 14.86, 15.82 μ; nmr δ 7.03–7.50 (m, Ar–H), 6.57 (t, vinyl H's $J \simeq 2$ Hz), 3.07 (m, bridgehead H's), 1.72 (sharp s, endo H-2,4), 0.93 (d, syn 8-H), 0.63 (d, anti 8-H, $J_{syn,anti} \sim 10$ Hz); λ_{max}^{EtOH} 227 nm (ε 18,000), 262, 267, 273.

Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.97; H, 7.05.

***exo,exo*-3,3,7,7-Tetraphenyltetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane (4).**—As described for **1**, adduct **3** (1.50 g, 3.54 mmol) was heated at 200° for 30 min. Isolation was *via* chromatography on alumina (25 g) by elution with carbon tetrachloride. White crystalline **4** was then purified by several recrystallizations from methanol: yield 1.02 g (57%); mp 205–207°; λ (quite featureless) 3.32, 3.42, 6.27, 6.71, 6.92, 13.10, 13.41, 14.25–14.41, 15.52 μ; nmr δ 6.70–7.28 (m, Ar–H), 2.85 (m, bridgehead H's), 1.78 (sharp s, endo H-2,4,6,8), 0.18 (m, CH_2).

Anal. Calcd for $C_{33}H_{28}$: C, 93.35; H, 6.65. Found: C, 93.09; H, 6.77.

Attempted Exo to Endo Isomerization of 2.—Reaction of **2** (2.94 g, 11.4 mmol) with glacial acetic acid (7.3 g) and sulfuric acid (50%, 0.4 g) on a steam bath for 4 hr resulted in a black solution. The cooled solution was neutralized with potassium hydroxide and extracted with ether. The ether extracts yielded a black tar. Saponification of the tar afforded a red sludge which was chromatographed on alumina (150 g). Various products eluted. The first fraction, eluted with carbon tetrachloride, was colorless, weighed 0.2 g and melted at 100–110°. Various characterizations indicated it to be a hydrocarbon, but no definite structure seemed assignable to it. Further elution with a variety of solvents gave colored materials of higher and higher mp, up to 210°. Presumably these substances were polymeric in nature, but no further studies were performed.

***exo*-5-Bromo-3-benzhydrylidenenortricyclene (8).**[27]—To hydrocarbon **2** (2.58 g, 10 mmol) in carbon tetrachloride (10 ml) at 0° was added bromine (1.76 g, 11 mmol) in carbon tetrachloride (15 ml) dropwise over a 1-hr period. The solution was then stirred at 25° for 1 hr as hydrogen bromide evolved. The material was then evaporated to yield a yellow oil. Trituration of this oil with 95% ethanol afforded a flocculent white solid which was purified by several recrystallizations from methanol: yield 2.05 g (61%); mp 107.5–108.5°; λ (strong absorptions only) 6.92, 8.30, 12.06, 12.34, 12.96, 13.20, 13.46, 14.18 μ; nmr δ 7.20–7.67 (m Ar–H), 4.33 (broad s, -CHBr), 2.88 (broad s, H-4 bridgehead), 2.53–1.70 (complex m, H-1,2,6 and CH_2).

Anal. Calcd for $C_{20}H_{17}Br$: C, 71.23; H, 5.08. Found: C, 71.22; H, 5.14.

The appearance of the complex multiplet mentioned (δ 2.53–1.70) resembled that observed in olefin **16** (*vide infra*).

***trans*- and *exo,cis*-6,7-Dibromo-*exo*-3,3-diphenyltricyclo-[3.2.1.0^{2,4}]octanes (9 and 10, Respectively).**—A solution of hydrocarbon **2** (1.30 g, 5 mmol) and 1,2-dibromotetrachloroethane[28] (1.63 g, 5 mmol) in carbon tetrachloride (20 ml) was irradiated with a 275-W sun lamp under a reflux condenser. The deep yellow solution turned red. After 1 hr the solvent and tetrachloroethylene produced in the reaction were evaporated. The red oily residue, which later solidified, amounted to 1.5 g (71% yield). No combustion analysis was attempted. Analysis by nmr spectroscopy indicated the trans dibromide **9** comprised 81% of the crude product: nmr 7.00–7.50 (m, Ar–H), 4.37 (t, exo H-6), 3.95 (t, endo H-7), 2.77 (m, bridgehead H's), 1.77–0.62 (complex m, endo H-2,4 and CH_2). Also present (19%) was the exo,cis-dibromide **10**: nmr δ 7.00–7.50 (m, Ar–H), 4.10 (d, endo H-6,7), 3.05 (broad s, bridgehead H's), 1.77–0.62 (complex m, endo H-2,4 and CH_2). The coupling constants observed for **9** follow (J in Hz): exo-6,endo-7 = endo-7,anti-8 ("W" coupling) = exo-6,bridgehead = 3 Hz. That for **10** was endo-6,7,anti-8 ("W" coupling) = 2 Hz.

***exo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]octan-*exo*-6-ol (11).**—Reaction of diborane with hydrocarbon **2** (25.8 g, 0.10 mol) was achieved as described for the parent case.[3d] The product obtained upon removal of the solvent was chromatographed on silica gel (400 g). Elution with 1:4 hexane–benzene yielded *exo*-3,3-diphenyltricyclo[3.2.1.0^{2,4}]octane (**2**-H): wt 1.10 g (4.2%); mp 79.5–81.5° (after recrystallization from methanol); λ (strong absorptions only) 3.41, 6.71, 6.91, 11.06, 11.36, 12.86, 13.14, 13.31, 14.16, 14.36 μ; nmr δ 7.56–7.20 (m, Ar–H), 2.57 (broad s, bridgehead H's), 1.52 (s, endo H-2,4), 1.42 (broad s, 6,7-CH_2's), 0.62 (distorted d, 8-H anti to phenyls), 0.52 (distorted d, 8-H syn to phenyls).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 91.99; H, 7.74.

Further elution using 1:1 ether–chloroform produced alcohol **11** as a sticky solid that afforded white crystals upon recrystallization from hexane: yield 18.3 g (66.3%); mp 133.5–135°; λ 3.05, 9.50 μ (C–OH); nmr δ 7.58–7.00 (m, Ar–H), 3.88 (broad d, endo H-6), 2.50 (m, bridgehead H's), 2.27 (s, OH), 2.13–1.00 (complex m, 7-CH_2, endo H-2,4), 0.87 (d, 8-H anti to phenyls), 0.47 (d, 8-H syn to phenyls, $J_{syn,anti} \simeq 11.5$ Hz). No evidence for the endo isomer **12** was found.

Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 87.32; H, 7.41.

***exo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]oct-*exo*-6-yl Tosylate (11-OTs).**—Alcohol **11** was treated with *p*-toluenesulfonyl chloride in pyridine in the customary fashion[19] to produce **11**-OTs: 99% yield; mp 120–123° dec upon several recrystallizations from benzene and petroleum ether (bp 30–60°).

Anal. Calcd for $C_{27}H_{26}O_3S$: C, 75.32; H, 6.09. Found: C, 75.14; H, 6.25.

***exo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]octan-6-one (13).**—Oxidation of alcohol **11** (10.0 g, 36.2 mmol) with chromium trioxide in pyridine[29] was performed as described for the parent case.[3d] Ketone **13** was recrystallized from hexane. The white crystalline solid weighed 9.32 g (94%); mp 117.5–119.5°; λ 5.74 μ (C=O); nmr δ 7.62–7.17 (m, Ar–H), 2.88 (m, bridgehead H's), 2.12 (m, 7-CH_2), 1.78 (q, $J \simeq 7$ Hz, AX pattern of endo H-2,4), 0.85 (broad s, 8-CH_2).

Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.37; H, 6.67.

***exo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]octan-*endo*-6-ol (12).**—To ketone **13** (4.0 g, 14.6 mmol) dissolved in absolute ethanol (50 ml) was added at 25° sodium borohydride (1.1 g, 29 mmol) in small quantities over a 15-min period. The reaction was completed on a hot plate for 2 hr. The mixture was then cooled and diluted with water. The flocculent precipitate was collected and dried, wt 3.67 g (91%). Analysis by nmr spectroscopy indicated the presence of 14% alcohol **11** and 86% alcohol **12**. The latter was obtained pure upon four recrystallizations from hexane as a white solid: mp 152.5–153.5°; λ 3.07, 9.50 μ (C–OH); nmr δ 7.57–6.95 (m, Ar–H), 4.25 (doublet of triplets, exo H-6, $J_{exo\text{-}6,exo} = 9.5$ Hz, $J_{exo\text{-}6,H\text{-}5} = J_{exo\text{-}6,endo\text{-}7} = 3.5$ Hz), 2.53 (m, bridgehead H's), 2.28 (s, OH), 2.13–1.53 (complex array, endo H-2,4,

(26) J. W. Wilt and P. K. Mookerjee, to be published.

(27) The prefix exo is arbitrary here. Structure **8** has the bromine exo in the sense that it is on the same side as the original methano bridge of **2**. The bromine is actually endo to the newly created methano bridge bearing the benzhydrylidene moiety.

(28) The material results from reaction of tetrachloroethylene and bromine (275-W sun lamp, white solid, dec. ~100°).

(29) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, **75**, 422 (1963).

exo H-7), 0.93 (broad doublet with further splitting, endo H-7), 0.45 (narrow m, 8-CH_2). The AB H-7 pair possessed a $J \simeq 12$ Hz.

Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 87.20; H, 7.42.

***exo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]oct-*endo*-6-yl Tosylate (12-OTs).**—Alcohol **12** yielded tosylate **12**-OTs upon treatment with *p*-toluenesulfonyl chloride in the usual way.[19] Upon recrystallization from absolute ethanol the product was a white solid, 68% yield, mp 155–157°.

Anal. Calcd for $C_{27}H_{28}O_3S$: C, 75.32; H, 6.09. Found: C, 75.54; H, 6.18.

***exo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]oct-6-ene *exo*-Oxide (14).**—*m*-Chloroperbenzoic acid (85% material, 2.23 g, 11 mmol of peracid) in methylene chloride (21 ml) was added dropwise over a 15-min period to a solution of hydrocarbon **2** (2.58 g, 10 mmol) in methylene chloride (10 ml). The temperature was maintained below 25° during the addition and at 25° for 1.5 hr afterward. The excess peracid was destroyed with 10% sodium bisulfite solution (10 ml). The solution was then extracted with aqueous potassium bicarbonate, aqueous sodium hydroxide, and then water alone. The methylene chloride solution was dried ($MgSO_4$) and evaporated. The residual oxide **14** so obtained was recrystallized from methanol: yield 1.76 g (64%); mp 150–152°; λ (prominent absorptions only) 3.35, 6.70, 9.96, 11.80, 12.05, 13.30, 14.20–14.35 μ; nmr δ 7.55–7.07 (m, Ar–H), 3.35 (s, endo H-6,7), 2.76 (broad s, bridgehead H's), 1.67 (s, endo H-2,4), 0.77 (d, 8-H anti to phenyls), 0.33 (d, 8-H syn to phenyls, $J_{anti,syn}$ = 12 Hz).

Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.82; H, 6.72.

Reduction of Oxide 14 with Lithium Aluminum Hydride.—Oxide **14** (1.62 g, 5.9 mmol) was reduced with lithium aluminum hydride (0.24 g, 5.9 mmol) in tetrahydrofuran solvent (25 ml) at 25° for 3 days. After processing, the reaction yielded only alcohol **11**, wt 1.62 g (99%), mp, mmp, and spectra identical with those given above (*vide supra*). The tosylates were also identical.

(3-Nortricyclyl)diphenylcarbinol (15).—3-Nortricyclylmagnesium bromide was prepared under nitrogen from the bromide (Frinton Laboratories, S. Vineland, N. J., 5.0 g, 28.9 mmol) and magnesium (0.72 g, 30 g-atoms) in anhydrous ether (15 ml). The reaction was initiated with some methyl iodide. Benzophenone (4.55 g, 50 mmol) in ether (15 ml) was then added, and the deep red solution was stirred for 30 min. Saturated ammonium chloride solution (10 ml) was added next, and the yellow organic layer that resulted was separated, washed, and dried ($MgSO_4$). Upon removal of the ether a yellow oil was obtained. Chromatography on alumina (500 g) separated this oil into benzophenone (with hexane elution), 1.24 g (24% recovery); alcohol **15** (with 1:4 benzene–CCl_4), crude weight 1.50 g (22%), mp 50–60°; unidentified oils (with chloroform), 1.3 g; and benzopinacol (with chloroform), 2.55 g (28%). The last product presumably resulted from bimolecular reduction of benzophenone with unreacted magnesium in the Grignard solution. Alcohol **15** was purified by recrystallization from pentane at −78° and from aqueous methanol: mp 75–77°; λ 2.86, 8.42–8.45 μ (*t*-C–OH); nmr δ 8.03–7.35 (m, Ar–H), 2.73 (s, OH), 2.40 (s, bridgehead H-4), 2.22 (d, exo H-5 $J_{exo\text{-}5,endo\text{-}5}$ = 12 Hz), 1.53 (broad s, bridgehead H-1), 1.35–0.87 (complex m, all remaining H's).

Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.62; H, 7.26.

3-Benzhydrylidenenortricyclene (16).—A mixture of alcohol **15** (0.60 g, 2.19 mmol), one small crystal of iodine, and benzene (50 ml) were refluxed under a water separator overnight. The solution was then washed with 10% aqueous sodium thiosulfate and water. The benzene solution was dried ($MgSO_4$) and evaporated. The brown viscous residue was then chromatographed on alumina (50 g). Elution with hexane produced olefin **16** as a white solid: yield 0.52 g (89%); mp 66.5–68° (after recrystallization from methanol containing a little water); λ (prominent absorptions only) 6.02, 6.92, 11.20, 12.07, 12.42, 12.67, 12.97, 13.97, 14.32 μ; nmr δ 7.12 (narrow m, Ar–H), 2.53 (broad s, bridgehead H-4), 1.82–1.30 (complex m, all remaining H's).

Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 93.01; H, 7.06.

The olefin could also be prepared by dehydration of alcohol **15** with 20% sulfuric acid–80% acetic acid,[30] but the yield was only 28%.

Solvolysis of Tosylates.—Dioxane was purified by a published procedure.[31] A solvent mixture of purified dioxane and water (80:20 v/v) containing freshly distilled 2,6-lutidine (0.044 *M*) was used in the solvolyses. Freshly recrystallized tosylates **11**-OTs and **12**-OTs were weighed into the solvent separately, each concentration being 0.03 *M*. Ampoules containing this solution were sealed under nitrogen, thermostated at given temperatures (see Table I) and periodically removed. The rate of the solvolysis was followed by titration of the unchanged lutidine with standardized hydrochloric acid to a bromphenol blue end point. The rate constants were obtained from the first-order rate expression with the aid of a least-squares computer program written in WAT IV language.[32] Activation parameters were calculated from the Eyring equation.

Preparative solvolyses were carried out analogously. Tosylate **11**-OTs (0.65 g, 1.51 mmol) in the solvent (50 ml) was heated at 65° for 24 hr in a pressure bottle under nitrogen. Evaporation of the solvent left an oil which was washed with water and taken up in hexane. The hexane solution was extracted thoroughly with 10% hydrochloric acid and water, dried ($MgSO_4$), and evaporated. The residual oil solidified slowly (2 months) to a solid, wt 0.41 g (99%), with spectra identical with those of alcohol **15**. One recrystallization from aqueous methanol gave white crystalline material, mp and mmp with authentic **15** 74.5–77°. Tosylate **12**-OTs (0.45 g, 1.04 mmol) in the solvent (45 ml) was heated at 134° for 17.5 hr in a pressure bottle under nitrogen. The processing described above gave a sticky solid, wt 0.29 g (100%), with spectra identical with those of **16**. Chromatographic purification on alumina with hexane eluent gave the product as a white solid, mp and mmp with authentic **16** 66–68°.

Registry No.—**1**, 35497-23-5; **2**, 35495-68-2; **3**, 35497-25-7; **4**, 35497-27-9; **8**, 36976-50-8; **9**, 36976-51-9; **10**, 36976-52-0; **11**, 36994-54-4; **11**-OTs, 36976-53-1; **12**, 36976-54-2; **12**-OTs, 36976-55-3; **13**, 36994-55-5; **14**, 36976-56-4; **15**, 36976-57-5; **16**, 36976-58-6.

(30) E. W. Garbisch, *J. Org. Chem.*, **26**, 4165 (1961).

(31) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1957, p 285.

(32) We thank Professors A. K. Jameson and J. F. Reed of this department for their assistance in this regard.