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The Question of Delocalization in "Anchored" Ions with Potential Trishomoaromatic Character. 3. Ionization Studies of Tricyclo[5.3.1.0^{4,11}]undeca-2,5,8-trien-10-yl Derivatives under Short- and Long-Lived Conditions[1]

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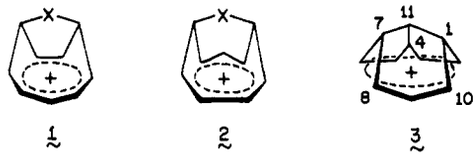
The synthesis of epimeric tricyclo[5.3.1.0^{4,11}]undeca-2,5,8-trien-10-yl (**10** and **11**) and tricyclo[5.3.1.0^{4,11}]undec-8-en-10-yl derivatives (**17** and **18**) and their solvolytic behavior are described. In methanol solution, the multiply unsaturated *p*-nitrobenzoates **10b** and **11b** gave an essentially identical mixture of unrearranged exo and endo methyl ethers (exo/endo = 6.6–6.8). In the more polar 60% acetone solvent, the relative proportions of unrearranged alcohols were more disparate (exo/endo = 3.6–5.8) owing to greater solvation factors. The greater steric hindrance on the endo face of **17b** and **18b** was adequate to provide only the corresponding exo alcohol from solvolysis. Kinetic measurements revealed the rate of ionization of the four *p*-nitrobenzoates to differ by a factor of only 43 at 111 °C, with the more highly unsaturated molecules being the less reactive! These data are interpreted in terms of the total absence of neighboring double bond participation and a reflection merely of inductive contributions on simple allylic cation formation. Neither could evidence for "anchored" trishomotropylium ion character be gained from studies in superacidic media. The impact of electronic factors and molecular topology on trishomotropylium ion generation is discussed.

Pursuant to the discovery by Pettit in 1962 of the monohomotropylium cation,[3] several 1,3- (**1**)[4] and 1,4-bishomotropylium ions (**2**)[5] have been generated and their electronic structures analyzed. Importantly, such twofold interruptions of the 6π7C topology were shown not to seriously disrupt charge delocalization, as long as the pair of bridges maintain a syn disposition.[4b,6] Mutual bonding of the bridge carbons to each other or to atom X as in **1** and **2** serves particularly well



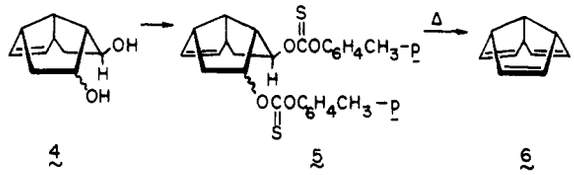
1 **2** **3**

to maintain a rather rigid geometry suitable for orbital interaction. In this paper, attention is given to the trishomotropylium cation defined by **3** in which the three bridges are suitably "anchored" to an apical carbon in order to guarantee a reasonable pericyclic topology.

The question of cyclic delocalization in **3** gains particular interest when attention is called to its pivotal position relative to the classical Hückel approach to aromaticity and the newer concept of ribbon interactions.[7] As detailed in Table I, simple HMO calculations[8] predict (as with **1** and **2**) that any interaction between the allylic cation and olefinic segments in **3** will be stabilizing, even when ($\beta_{3,5}/\beta_0$) is as low as 0.3. Similarly, perturbation theory suggests that such a $3^+2^02^0$ pericyclic arrangement lends itself to a favorable combination of symmetry imposed HOMO–LUMO interactions. Although stabilization of **3** is thereby implied, this conclusion is necessarily contingent upon suitable weighted consideration of several other factors (vide infra).

We herein examine the solvolytic reactivity of the *exo*- and *endo*-tricyclo[5.3.1.0^{4,11}]undeca-2,5,8-trien-10-yl *p*-nitrobenzoates and their tetrahydro counterparts and the behavior of the corresponding alcohols and chlorides in various superacidic media at low temperatures.

Synthesis. Triquinacene (**6**) seemed a logical starting point for the proposed synthesis, especially since diol **4**, which had previously been prepared by Deslongchamps and co-workers,[9] could now be more reliably and efficiently (60–70%) dehydrated by pyrolysis (230 °C) of bisthiocarbonate **5**.[10,11] This



4 **5** **6**

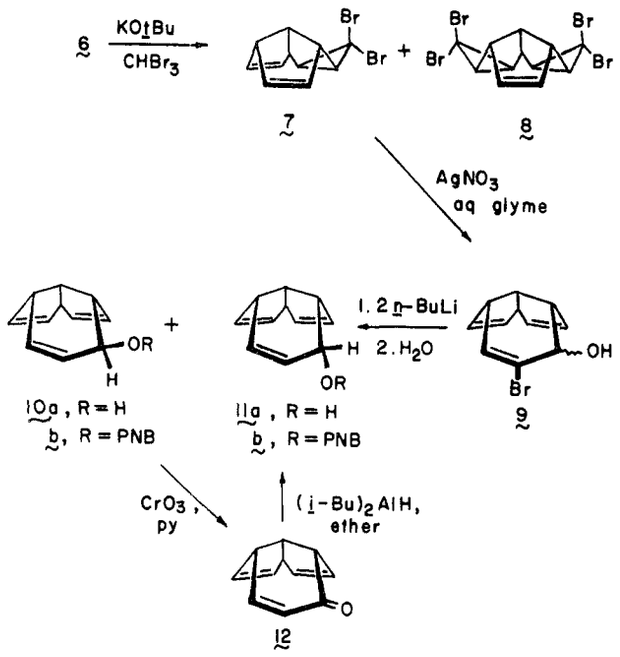
procedural modification, which substantially improves the overall yield, allows for convenient extraction of the nongaseous, nonsulfuraceous by-product (*p*-cresol) into 5% sodium

Table I. HMO Calculations for 3

Case A: $\beta_{2,10} = \beta_{3,5} = \beta_{6,8}$						Case B: $\beta_{2,10} = \beta_{6,8}$; $\beta_{3,5} = 0$					
	E_π-6_α	Electronic charge					E_π-6_α	Electronic charge			
$\beta_{2,10}/\beta_0$	(β_0)	$C_{2,6}$	$C_{3,5}$	$C_{8,10}$	C_9	$\beta_{2,10}/\beta_0$	(β_0)	$C_{2,6}$	$C_{3,5}$	$C_{8,10}$	C_9
0.0	6.828	1.000	1.000	0.500	1.000						
0.3	7.026	0.989	0.953	0.560	0.995	0.3	6.954	1.000	9.959	0.541	1.000
0.5	7.398	0.955	0.897	0.659	0.979	0.5	7.166	1.000	0.900	0.600	1.000
0.75	8.100	0.900	0.857	0.777	0.933	0.75	7.556	1.000	0.820	0.680	1.000

hydroxide solution while providing pure **6** in the organic phase. Reaction of triquinacene with potassium *tert*-butoxide and bromoform in pentane at −30 °C gave the mono (**7**) and bis adducts (**8**) in 50 and 15% yields, respectively (Scheme I).

Scheme I

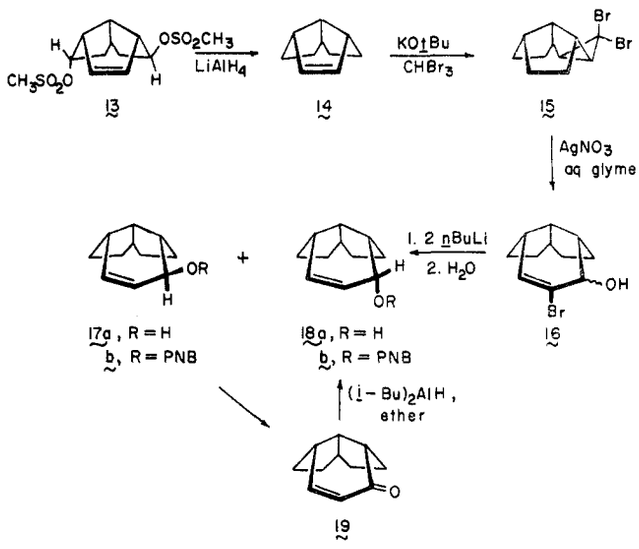


The major portion of **7** could be isolated by trituration with pentane, while the remainder was obtained by HPLC methods. Exposure of **7** to silver nitrate in aqueous dimethoxyethane resulted in efficient conversion to the isomeric mixture **9** which, because of its apparent instability, was directly reduced. For this purpose, the preferred procedure consisted of its inverse addition to 2 equiv of *n*-butyllithium in hexane followed by quenching with water. Under these conditions, a 90% conversion to **10a** and **11a** (ratio 1.6:1.0)[12] could be realized. These epimeric alcohols were separated by preparative HPLC on Florisil and converted to their respective *p*-nitrobenzoate derivatives. The stereochemical assignments, initially made on the basis of the ^{1}H NMR spectra, were confirmed by oxidation of the **10a/11a** mixture to **12** and reduction of this ketone with diisobutylaluminum hydride. Highly stereoselective conversion to **11a** was observed. This result is readily accommodated on steric grounds and further supported by the presence of intramolecular hydrogen bonding in **11a** (ν 3560 cm^{-1}) which is possible only when the hydroxyl group is endo oriented.

For the preparation of **17a** and **18a**, diol **4** was converted to its dimesylate (**13**), subsequent hydride reduction of which comprised a very serviceable route to tetrahydrotriquinacene[13] (**14**, Scheme II). As is evident, the remaining transformations parallel those utilized in Scheme I.

Kinetic Measurements. In Table II are summarized the rate data at three temperatures for the hydrolysis of the four *p*-nitrobenzoates (**10b**, **11b**, **17b**, and **18b**) as determined

Scheme II



conductometrically on 0.30–0.40 mM solutions in 60% aqueous acetone. With the aid of a calibration curve showing the conductance to be a linear function of the concentration of *p*-nitrobenzoic acid, all four reactions were found to exhibit clean first-order behavior.

If trishomotropylium cation **3** with delocalized charge is more stable than its simpler localized "classical" allylic counterpart, then the transition state having double bond assisted ionization might reflect itself in rate enhancement. Should **3** be destabilized, the opposite effect would be called for. However, the energy gap between homoaromatic and classical ions may be sufficiently small that the inductive rate-retarding effect of the two 2π bridges and the rather nucleophilic properties of 60% aqueous acetone may disguise either effect. In actuality, **10b** solvolyzes ten times more slowly than **17b** at 111.2 °C and the exo:endo rate ratio for **17b/18b** (6.9) exceeds that for **10b/11b** (4.2). Clearly, the kinetic data do not provide evidence for the intervention of **3** under solvolytic conditions, a not unprecedented finding in this area. For example, although **2** (X = nil) has been observed by NMR spectroscopy, the solvolysis of **21** in 80% acetone–water is

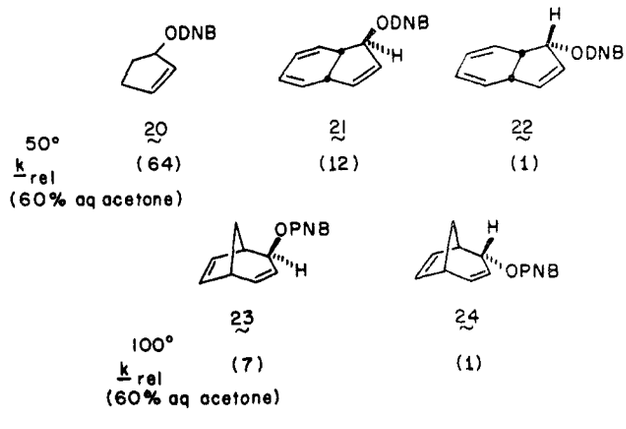


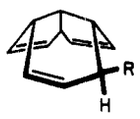
Table II. Kinetic Data for Solvolysis of *p*-Nitrobenzoates in 60% (v/v) Aqueous Acetone

Registry no.	Compd	Temp, °C	$k \times 10^4$, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel}, 111.20 °C
62609-41-0	**10b**	99.22	0.315	28.5	−3	4.2
			0.335			
		111.20	0.959			
			1.09			
		124.40	3.96			
			3.97			
62653-17-2	**11b**	111.20	0.243	29.3	−4	1.0
			0.230			
		124.40	1.05			
			1.01			
		136.50	2.68			
			2.55			
62609-42-1	**17b**	85.15	0.843	26.0	−5	43.2
			0.840			
		99.22	4.25			
			4.19			
		111.20	10.9			
			10.2			
62653-18-3	**18b**	99.22	0.407	27.6	−5	6.3
			0.404			
		111.20	1.52			
			1.45			
		124.40	4.50			
			4.68			

slower by a factor of 5 than that of cyclopentenyl 3,5-dinitrobenzoate (**20**) and only a factor of 12 faster than that of the endo isomer **22**.[5i] This behavior is to be contrasted with that of the bicyclo[3.2.1]octa-2,6-dienyl *p*-nitrobenzoate pair **23** and **24** where the exo:endo reactivity ratio does not become inverse despite strong destabilization (antihomoaromatic character) anticipated between the developing allylic cation and the olefinic moiety during ionization of **23**.[14] In line with our findings, the effect of the 6,7 double bond in both isomers is rate retarding relative to their bicyclo[3.2.1]octen-2-yl counterparts.[14]

Given these difficulties in quantitatively assessing relative reactivities, trishomoaromatic ion **3** could still be the product-determining species under such short-lived conditions. Further insight into the nature of the solvolytic intermediates was therefore next sought along the lines of product analysis.

Product Studies. In 60% acetone which was buffered with 2,6-lutidine and heated to 135 °C, exo *p*-nitrobenzoate **10b** was converted in good yield to a mixture of the unrearranged alcohols **10a** and **11a**. Determination of the product composition was achieved through methylation (KH, CH_3I) of the crude product, quantitative VPC analysis of the resulting mixture, and spectral analysis of the individual pure ethers **25a** and **26**. This showed the exo/endo ratio to be 5.8. In the



25 a, R = OCH_3
b, R = Cl

26

case of endo *p*-nitrobenzoate **11b**, the same two alcohols were again produced free of other possible products. After conversion to the epimeric ethers, VPC showed **25a** to dominate over **26** by the somewhat lower factor of 3.6.

A comparable product analysis was made under conditions of methanolysis. In both instances, the same epimeric ethers were formed and the partitioning between **25a** and **26** was now virtually identical. For **10b**, the exo/endo ratio was determined to be 6.8, while for **11b** the value was 6.6. Small amounts of methyl *p*-nitrobenzoate were also detected.

The solvolyses of **17b** and **18b** were likewise very clean. In buffered 60% acetone, both of these *p*-nitrobenzoates gave rise uniquely to exo alcohol **17a**.

Ionization Studies in Superacidic Media. Treatment of **10a** under a variety of those conditions customarily utilized for the generation of allylic cations (FSO_3H–SbF_5–SO_2ClF, FSO_3H, FSO_3H–SO_2ClF, FSO_3H–SbF_5–SO_2, etc.)[15] at temperatures as low as −120 °C led to its rapid decomposition. Comparable handling of **11a** in magic acid (FSO_3H-SbF_5)[16] showed it to be less acid sensitive. The clear orange-colored solution obtained at −120 °C exhibited a ^1H NMR spectrum which, while subject to some variation at temperatures up to −50 °C, could not be interpreted in terms of **3** or its simpler allylic cation equivalent. The spectra bear a great number of similarities to those recently described by Schröder and coworkers who have independently examined the reactivity of **25a** toward FSO_3H in SO_2ClF/CD_2Cl_2 (1:1) solution at low temperatures.[17] Our spectra are therefore not illustrated here, nor do we wish to speculate at the present time on the nature of the species produced. Suffice it to say that neither **3** nor its lesser delocalized form was thereby generated. Attempted quenching ($NaOCH_3$, CH_3OH) of such solutions at −78 °C and below afforded only polymeric material.

In contrast, dissolution of **17a** in SbF_5–SO_2ClF at −120 °C gave an orange-colored solution, the ^1H NMR spectrum of which at −86 °C displayed precisely those features anticipated for cation **27**: δ 9.35 (dd, J = 7.0 and 1.5 Hz, 2), 8.15 (t, J = 7.0 Hz, 1), and a complex envelope of peaks at 4.69–1.27 (12 H). When such solutions were quenched by addition to methanolic sodium methoxide at −78 °C, exo methyl ether **28a** could be isolated in addition to considerable quantities of polymer.

Because of a suggestion that chlorides can sometimes serve

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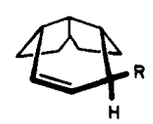
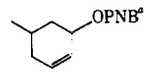
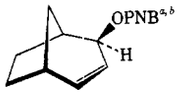
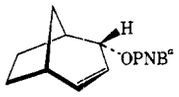
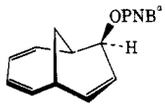
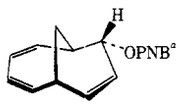


28 a, R = OCH_3
b, R = Cl

Table III. Summary of Kinetic Behavior of Bridged Cyclohexen-2-yl *p*-Nitrobenzoates in Aqueous Acetone at 100 °C

Compd	k, s^{-1}, 80% acetone	k_{rel} in 80% acetone	k, s^{-1}, 60% acetone	k_{rel} in 60% acetone
		0.2		
 29	1.76×10^{-5}	1.0	3.23×10^{-4}	10
 30	4.67×10^{-6}	0.3		
23[a]	2.76×10^{-7}	0.02	1.53×10^{-5}	0.47
24[a]	2.65×10^{-7}	0.02	2.21×10^{-6}	0.07
 31	2.20×10^{-2}	3000		
 32	6.60×10^{-7}	0.09		
10b[b]			3.24×10^{-5}	1.0
11b[b]			7.35×10^{-6}	0.2
17b[b]			3.82×10^{-4}	12
18b[b]			4.19×10^{-5}	1.3

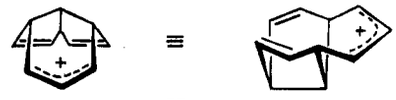
[a] References 5i and 14. [b] The present work.

as preferred precursors to carbocations,[18] the synthesis of **25b** and **28b** was effected by reaction of the corresponding alcohols with thionyl chloride and pyridine in benzene solution. Although these chlorides were somewhat labile and difficult to purify, access to samples of adequate purity was eventually gained. When treated with SbF_5–SO_2ClF at −120 °C, both chlorides apparently experienced complete decomposition since no recognizable spectra could be recorded.

Discussion

The available kinetic data (Table II) show the ionization of exo *p*-nitrobenzoate **10b** not to be significantly accelerated. That no interaction is incurred between the two vinyl bridges and the developing allylic cation moiety at the rate-determining transition state is further suggested by the exo/endo rate ratio of 4.2 (at 110 °C). Endo epimer **11b** clearly cannot avail itself of long-range interaction with either vinyl bridge at the onset of ionization and therefore bond heterolysis must be nonassisted in this instance. An assumption-free independent assessment of the prevailing state of affairs can be gained by a comparison of the reactivities of the tetrahydro derivatives **17b** and **18b**. Here an exo/endo rate ratio of approximately 7 was observed at 111 °C. The fact that **17b** ionizes ten times more rapidly than **10b** can be understood simply in terms of the adverse inductive effects contributed by the remote olefinic centers. With regard to this question, comparison with such isomer pairs as **29/30** and **23/24** is informative (Table III). Here exo derivatives **29** and **23** differ in reactivity by a factor of 64, perhaps as a direct consequence of the more proximal attachment of the ethylenic bridge in **23**. The related endo pair **30** and **24** is expectedly less sensitive to such influences (factor of 17).

Given the above data, kinetic criteria are seen to provide absolutely no support for the conclusion that delocalization between the π bridges gains importance. However, it may be argued that such an analysis does not provide adequate insight into the nature of the intermediates formed during solvolysis.[19] But strong negative support is also derivable from the nature of the solvolysis products. Thus, in methanol both **10b** and **11b** gave an identical distribution of methyl ethers **25a** and **26**, a result suggesting that the two systems do in fact pass through the common intermediate **33**. When solvolyzed in 60%



33

aqueous acetone, a solvent system of higher nucleophilicity, exo alcohol **10a** again predominates to a significant, but somewhat varied, extent. However, the larger percentage of **10a** formed from **10b** can be reasonably attributed to solvation factors. Equally enlightening with regard to this question is the behavior of **17b** and **18b** under these conditions. Their total conversion to exo alcohol **17a** is in line with expectations based on the substantially enhanced steric congestion on the underside of the molecular "cup" arising from the presence of four additional "axial" hydrogens. On this basis, we conclude that trishomoaromatic stabilization of the type depicted by **3** is not operational.

Does the inability of **3** to be generated under either long- (negative evidence only) or short-lived conditions arise because of electron destabilization or geometric factors? Haddon, in his perturbational MO treatment of homoaromaticity,[22] concluded that the upper limit to ring size for a monohomoaromatic ion should be relatively low (≤16 members). The properties of the homo[15]annulenium cation are in harmony with this particular assessment.[23] Although the number of key constituent carbon atoms in **3** falls well below this assumed upper limit, its tropylium-like skeleton is now

fractured at three sites. Although theoretical evaluation of such extensive interruption of an aromatic core has generally not been considered,[22,24] it would seem likely that multiple fracturing can only further diminish orbital overlap relative to the aromatic nucleus. In other words, just as homoaromatic delocalization is less stabilizing than its classical aromatic counterpart, so one can anticipate a trishomoaromatic arrangement to cause yet a further fall-off in intrinsic capability to support a ring current. This is not to say that suitable HOMO–LUMO interactions do not exist,[7] but only that their impact on the total energy of the system must be less when trishomoaromatic character is involved. As visualized by us, therefore, a capacity for ground-state electronic stabilization does in principle exist for **3**; however, its manifestation is likely to be substantially reduced from presently known standards.[25]

Finally, we examine the question of topology. Our interest in **3** and related species was aroused because molecular models revealed their "anchored" nature to be capable of maintaining a rigid geometry having properly canted pπ orbitals, an arrangement seemingly conducive to overlap. However, each of the "homo" bridges necessarily introduces an aperture which must directly affect this π orbital arrangement. At issue, therefore, is the question of whether the limit of practicality for reasonable orbital interaction is exceeded when three sites of interruption are introduced into a core as small as that of the 6π7C cation. It is obviously important to establish whether such limitations do indeed exist. Several attempts to establish this in the case of **3** have been to no avail.[26] But in a preceding paper[1] experimental data are provided which reveal the anchored trishomocyclopentadienide anion to be so structurally encumbered that cyclic delocalization is not observable. For this reason, it appears entirely plausible that geometric factors inhibit pericyclic stabilization[7] in **3** as well.

Experimental Section

Melting points and boiling points are uncorrected. Proton magnetic resonance spectra were obtained with Varian A-60A and HA-100 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined on Perkin-Elmer Model 137 and 467 instruments. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Preparative VPC work was done on a Varian-Aerograph A90-P3 instrument equipped with a thermal conductivity detector.

Triquinacene (6). A. Preparation of Bis(thiocarbonate) *O*-Ester 5. A solution of diol **4**[9] (24.79 g, 0.15 mol) and pyridine (29.20 g, 0.37 mol) in methylene chloride (150 mL) was cooled to 0 °C and *O*-4-methylphenyl chlorothioformate[27] (64.0 g, 0.34 mol) dissolved in 200 mL of methylene chloride was added dropwise during 1.5 h. The reaction mixture was stirred at room temperature for 5 h, transferred to a separatory funnel, and washed several times with 10% hydrochloric acid, water, and sodium bicarbonate solution before drying. Evaporation of solvent left 56.6 g (82%) of a brown, viscous oil which was employed directly in the pyrolysis. Chromatography of a small sample on Florisil (1:1 pentane–ether elution) gave a colorless oil which crystallized from 5% ether in pentane: mp 117.5–121 °C; δ_{Me_4Si} ($CDCl_3$) 6.75–7.30 (m, 8), 5.35–5.90 (m, 2), 1.50–3.55 (m, 10), and 2.32 (br s, 6).

B. Pyrolysis of 5. The unpurified bisthiocarbonate ester (10 g, 0.02 mol) was pyrolyzed at 230 °C in a 40 × 3 cm column packed with glass beads. The pyrolysis was conducted under reduced pressure (100 mm) while a small stream of N_2 gas passed through the column and the products were collected in a series of three traps. The first trap was cooled with ice water, the second with dry ice–isopropyl alcohol, and the third with liquid nitrogen. Most of the *p*-cresol was collected in the first trap while triquinacene condensed in the next two traps. The products in all three traps were combined, dissolved in pentane, and washed four times with 5% sodium hydroxide solution and water before drying. Fractional distillation of the solvent at room temperature followed by flash distillation of the residue at 40–60 °C (0.3 mm) afforded 1.8 g (65%) of pure triquinacene (**6**).

Dibromocarbene Addition to 6. A slurry of potassium *tert*-butoxide (15.8 g, 0.141 mol) in 100 mL of dry pentane was cooled to −30 °C and 9.19 g (0.071 mol) of triquinacene in 100 mL of pentane was added under nitrogen. While the reaction mixture was maintained at −30 °C, 18.0 g (0.071 mol) of bromoform in 50 mL of pentane was added dropwise with vigorous stirring during 45 min. After the stirred mixture had been kept at room temperature for 2 h, water was added and the products were extracted with ether. The combined organic layers were washed with water and saturated brine and dried. The solvent was removed at atmospheric pressure by distillation through a 12-in. Vigreux column. Vacuum distillation of the residue at 30–40 °C (0.1 mm) afforded 1.7 g (18.4%) of unreacted **6**. The residue was leached with warm pentane to remove the major portion of **7**. The remainder was subjected to high-pressure liquid chromatography on a 24 ft × 0.75 in. silica gel column using pentane as the eluent. Mono adduct **7** which eluted first was recrystallized from cold pentane to give a total of 8.76 g (50.5%) of white crystals: mp 69–70 °C; δ_{Me_4Si} ($CDCl_3$) 5.45–6.91 (m, 4), 3.63–3.95 (m, 1), 3.16–3.47 (m, 3), and 2.19 (s, 2); calcd *m/e* 299.91502, found 299.91548.

Anal. Calcd for $C_{11}H_{10}Br_2$: C, 43.74; H, 3.34. Found: C, 43.68; H, 3.34.

Bis adduct **8** was recrystallized from ethyl ether to give 4.79 g (14.6%) of white crystals: mp 160–161 °C; δ_{Me_4Si} ($CDCl_3$) 5.63 (s, 2), 3.07–3.37 (m, 2), 2.76–3.02 (m, 2), and 2.25 (s, 4); calcd *m/e* 469.7518, found 469.7526.

Anal. Calcd for $C_{12}H_{10}Br_4$: C, 30.42; H, 2.13. Found: C, 30.52; H, 2.16.

***exo*- and *endo*-9-Bromotricyclo[5.3.1.0^{4,11}]undeca-2,5,8-trien-10-ol (9).** To a solution of **7** (8.76 g, 0.029 mol) in 150 mL of dimethoxyethane was added 7.35 g (0.044 mol) of silver nitrate in 100 mL of water. The mixture, which was refluxed for 1.5 h in the absence of light, turned immediately cloudy. After cooling, 50 mL of brine was added followed by 100 mL of saturated sodium bicarbonate solution. The precipitated silver salts were separated by filtration and the filtrate was evaporated until an aqueous residue remained. The residue was extracted with methylene chloride and the combined extracts were washed with water and dried. Evaporation of solvent furnished 6.60 g (95.2%) of **9**, a yellowish oil which proved unstable to prolonged standing at room temperature or in the freezer. This product was therefore used in the ensuing reaction without further purification. A small sample of **9**, subjected to column chromatography on Florisil (20% ether in hexane as eluent), was isolated as a colorless oil: δ_{Me_4Si} ($CDCl_3$) 6.15 (d, J = 3.0 Hz, 1), 5.37–5.95 (m, 4), 4.24 (d, J = 3.0 Hz, 1), 3.14–3.98 (m, 4), and 2.47 (br s, 1); calcd *m/e* 237.9994, found 237.9997.

***exo*- and *endo*-Tricyclo[5.3.1.0^{4,11}]undeca-2,5,8-trien-10-ol (10a and 11a).** A cold (0 °C) solution containing 6.60 g (0.028 mol) of **9** in 150 mL of anhydrous ethyl ether was treated dropwise via syringe with 36.5 mL (0.087 mol) of 2.4 M *n*-butyllithium in hexane during 0.5 h under nitrogen. The reaction mixture was allowed to warm to room temperature, stirred for 1 h, and treated carefully with 30 mL of water. The organic layer was separated and the aqueous phase extracted with ether. The combined ether extracts were washed with water, dried, and evaporated. Chromatography of the residue on Florisil (30% ether in pentane as eluent) gave 4.19 g (90.3%) of light yellow oil. Conversion of a small amount of this mixture to the methyl ethers followed by VPC analysis (4 ft × 0.25 in. 5% FFAP on 60/80 Chromosorb G, 150 °C) revealed a 1.6:1.0 mixture of exo/endo isomers. The exo and endo alcohols were separated by high-pressure liquid chromatography on a 12 ft × 0.75 in. Florisil column (30% ether in hexane elution). Minor component **11a** eluted first and crystallized from pentane as white crystals: mp 105–106 °C; δ_{Me_4Si} ($CDCl_3$) 5.22–6.12 (m, 6), 4.48 (br d, J = 5.0 Hz, 1), 3.65–3.93 (m, 1), 2.98–3.59 (m, 3), and 2.27 (br s, 1); IR (CCl_4) 3635, 3560, 3500, 3060, 2950, and 2870 cm^{-1}; calcd *m/e* 160.0888, found 160.0890.

The *p*-nitrobenzoate (**11b**) was obtained as colorless crystals, mp 117–118 °C (from ethanol), 90% yield.

Anal. Calcd for $C_{18}H_{15}NO_4$:, C, 69.89; H, 4.89; N, 4.53. Found: C, 69.88; H, 4.95; N, 4.40.

Exo alcohol **10a** failed to crystallize from pentane and was obtained as a clear oil: δ_{Me_4Si} ($CDCl_3$) 5.31–6.26 (m, 6), 3.96 (d of d, J = 5.5 and 2.5 Hz, 1), 2.81–3.87 (m, 4), and 2.48 (br s, 1); IR (CCl_4) 3630, 3500, 3060, 2960, and 2880 cm^{-1}; calcd *m/e* 160.0888, found 160.0890.

The *p*-nitrobenzoate (**10b**) was obtained as colorless crystals, mp 102–103 °C (from ethanol), 86% yield.

Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53. Found: C, 69.74; H, 5.01; N, 4.46.

Tricyclo[5.3.1.0^{4,11}]undeca-2,5,8-trien-10-one (12). Chromium trioxide (0.70 g, 7.0 mmol) was added to a mechanically stirred solution of 1.1 g (14.0 mmol) of pyridine in 30 mL of methylene chloride at 0 °C. After 0.5 h at room temperature, a mixture of alcohols **10a** and

11a (0.310 g, 1.94 mmol) in 5 mL of methylene chloride was added in one portion. A tarry black deposit separated immediately. After 15 min, the solution was decanted from this residue which was washed again with ether. The combined organic layers were diluted with an additional 30 mL of ether and washed successively with 5% sodium hydroxide solution, 15% hydrochloric acid, saturated sodium bicarbonate solution, and brine before drying. Solvent removal gave 235 mg (76.8%) of a light yellow oil, chromatography of which on Florisil (10–20% ether in pentane as eluent) afforded 180 mg of pure ketone **12**: δ_{Me_4Si} ($CDCl_3$) 6.92 (ABX, J_{AB} = 10.0, J_{BX} = 2.5 Hz, 1), 5.55–6.27 (m, 5), 3.93–4.25 (m, 1), and 3.48–3.82 (m, 3); IR (neat) 1680 cm^{-1}; λ_{max} (C_2H_5OH) 228 nm (ϵ 7750).

The semicarbazone was obtained as colorless crystals: mp 180–182 °C dec; calcd *m/e* 215.1058, found 215.1060.

Anal. Calcd for $C_{12}H_{13}N_3O$: C, 66.95; H, 6.09; N, 19.52. Found: C, 66.78; H, 6.18; N, 19.70.

Hydride Reduction of 12. A solution of ketone **12** (157 mg, 0.994 mmol) in 10 mL of dry ether under nitrogen was cooled in an ice–water bath and treated via syringe with 1.25 mL (2.0 mmol) of a 20% solution of diisobutylaluminum hydride in hexane. The mixture was stirred at room temperature for 2 h, cooled to 0 °C, and treated dropwise with 3 mL of a methanol–water solution (1:1). During 0.5 h a light yellow precipitate formed. The solution was decanted and the residual salts were thoroughly washed with ether. The combined organic phases were washed successively with 5% sodium hydroxide solution, water, and brine prior to drying. Evaporation of solvent gave 118 mg (74.2%) of a light yellow oil, the ^1H NMR spectrum of which revealed the presence only of endo alcohol **11b**. Conversion of this crude product to the methyl ether followed by VPC analysis (4 ft × 0.25 in. 5% FFAP on 60/80 Chromosorb G, 150 °C) showed less than 5% of exo methyl ether to be present.

Tetrahydrotriquinacene (14). To a suspension of lithium aluminum hydride (1.2 g, 31.6 mmol) in 25 mL of anhydrous tetrahydrofuran was added 2.00 g (6.22 mmol) of dimesylate **13**[9] dissolved in 10 mL of tetrahydrofuran. The reaction mixture was refluxed overnight under a nitrogen atmosphere and the excess hydride was destroyed by addition of a saturated ammonium chloride solution. The resulting salts were washed with tetrahydrofuran and the organic solutions were combined, diluted to 300 mL with water, and extracted with pentane. The pentane extracts were combined, washed with water, and dried prior to careful fractional distillation. Flash distillation of the residue (35–45 °C, 0.5 mm) with the receiver cooled in a dry ice–isopropyl alcohol bath gave 600 mg (71.8%) of **14**: δ_{Me_4Si} ($CDCl_3$) 5.38 (s, 2), 2.78–3.26 (m, 3), 2.11–2.53 (m, 1), and 1.10–1.95 (m, 8); calcd *m/e* 134.1095, found 134.1097.

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.61; H, 10.63.

Dibromocarbene Addition to 14. To a solution of **14** (2.60 g, 19.6 mmol) in 50 mL of pentane cooled to −30 °C was added in one portion 4.50 g (40.0 mmol) of potassium *tert*-butoxide. The resulting slurry was then treated dropwise with 5.45 g (21.5 mmol) of bromoform dissolved in 10 mL of pentane. The reaction mixture was allowed to warm to room temperature and stirred for 3 h before dilution with water and extraction with pentane. The pentane extracts were combined, washed with water and brine, and dried prior to evaporation of pentane and chromatography on Florisil (pentane elution). There was obtained 4.50 g (75.2%) of dibromide **15** as a clear oil: δ_{Me_4Si} ($CDCl_3$) 2.37–2.91 (m, 4), 2.05 (s, 2), and 1.18–1.98 (m, 8).

Anal. Calcd for $C_{11}H_{14}Br_2$: C, 43.17; H, 4.61. Found: C, 43.15; H, 4.64.

Alternate Synthesis of 15 by Catalytic Reduction of 7. Dibromide **7** (2.2 g, 7.3 mmol) was dissolved in 100 mL of cyclohexane and hydrogenated at atmospheric pressure over 10% palladium on carbon (300 mg). After 6 h, the solution was filtered and evaporated to give 2.2 g (99%) of **15** as a colorless oil.

***exo*- and *endo*-9-Bromotricyclo[5.3.1.0^{4,11}]undec-8-en-10-ol (16).** To a solution of **15** (2.50 g, 8.17 mmol) in 100 mL of dimethoxyethane was added 2.90 g (17.0 mmol) of silver nitrate in 50 mL of water. The mixture was refluxed for 1 h in the absence of light and processed in the predescribed fashion. Chromatography of the crude product on Florisil (15% ether in hexane as eluent) afforded 1.50 g (75.7%) of **16** as a clear oil: δ_{Me_4Si} ($CDCl_3$) 6.04–6.28 and 5.47–5.55 (m, 1), 4.42–4.61 and 4.06–4.22 (m, 1), 2.60 (br m, 5), and 1.02–2.08 (m, 8). The signals at δ 4.06–4.22 and 4.42–4.61 in a ratio of 4:1 correspond to the >CHOH protons of the exo and endo isomers, respectively. The same applies to the signals at δ 6.04–6.28 and 5.47–5.55. IR (neat) 3350, 2950, and 2870 cm^{-1}; calcd *m/e* 242.0307, found 242.0310.

***exo*- and *endo*-Tricyclo[5.3.1.0^{4,11}]undec-8-en-10-ol (17a and 18a).** A cold (0 °C) solution containing 3.00 g (12.4 mmol) of **16** in 80 mL of anhydrous ether was treated dropwise via syringe with 15.5 mL (36.2 mmol) of 2.4 M *n*-butyllithium in hexane. The reaction mixture was then allowed to warm to room temperature, stirred for 45 min, and treated carefully with 20 mL of water. Workup as before and chromatography on Florisil (30% ether in hexane as eluent) gave 1.70 g (83.6%) of a clear oil. The ^1H NMR spectrum ($CDCl_3$) showed two sets of vinyl protons at δ 5.80–5.88 and 5.53 in a ratio of 4:1 corresponding to the exo and endo alcohols, respectively. The two isomers were separated by high-pressure liquid chromatography on a 12 ft × 0.25 in. Florisil column using 7% ether in hexane as the eluent. Major component **17a** which eluted last was obtained as white crystals: mp 37–38.5 °C (from pentane); δ_{Me_4Si} ($CDCl_3$) 5.80–5.88 (m, 2), 3.88–4.00 (m, 1), 2.36–2.72 (m, 3), 2.00–2.24 (m, 1), and 0.95–1.95 (m, 9); IR (neat film) 3340, 3030, 2940, and 2870 cm^{-1}; calcd *m/e* 164.1201, found 164.1204.

The *p*-nitrobenzoate (**17b**) was obtained as colorless crystals, mp 123–124 °C (from ethanol), 92% yield.

Anal. Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11; N, 4.47. Found: C, 68.62; H, 6.19; N, 4.48.

Endo alcohol **18a** melts near room temperature and was obtained as a clear oil: δ_{Me_4Si} ($CDCl_3$) 5.53 (s, 2), 4.42–4.54 (m, 1), 2.14–2.72 (m, 4), and 1.04–1.92 (m, 9); IR (neat film) 3350, 3030, 2940, and 2870 cm^{-1}; calcd *m/e* 164.1201, found 164.1204.

The *p*-nitrobenzoate (**18b**) was obtained as colorless crystals, mp 97.5–98 °C (from ethanol), 87% yield.

Anal. Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11; N, 4.47. Found: C, 68.25; H, 6.38; N, 4.43.

Tricyclo[5.3.1.0^{4,11}]undec-8-en-10-one (19). Chromium trioxide (2.7 g, 27.0 mmol) was added to a mechanically stirred solution of 4.3 g (54.0 mmol) of pyridine in 50 mL of dry CH_2Cl_2 at 0 ° C. After 0.5 h at room temperature, a mixture of alcohols **17a** and **18a** (0.64 g, 3.9 mmol) in 5 mL of methylene chloride was added in one portion. The predescribed workup afforded 0.54 g (85.6%) of **19** as a light yellow oil. The product was purified by VPC (4 ft × 0.25 in. 5% FFAP on Chromosorb G, 150 °C): δ_{Me_4Si} ($CDCl_3$) 6.67 (d of d, 1), 5.85 (d, J = 10.0 Hz, 1), 2.30–3.10 (m, 4), and 1.06–1.22 (m, 8); IR (neat) 1670 cm^{-1}; UV (95% ethanol) λ_{max} 231 nm (ϵ 8900) and 301 (176); calcd *m/e* 162.1044, found 162.1047.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70: Found: C, 81.46; H, 8.89.

Hydride Reduction of 19. A solution of **19** (0.40 g, 2.47 mmol) in 10 mL of anhydrous ether under nitrogen was cooled in ice while treated with 3 mL (4.20 mmol) of a 20% solution of diisobutylaluminum hydride in hexane. Processing in the predescribed manner gave 350 mg (86.5%) of light yellow oil, the ^1H NMR spectrum of which was identical with that of **18a**.

Kinetic Procedure. The *p*-nitrobenzoates (1.5–2.0 mg) and 20 mL of 60% acetone–water (acetone purified by heating over $KMnO_4$, drying over $CaSO_4$, and distillation; water was demineralized and doubly distilled) were individually sealed under reduced pressure (20 mm) in a medium-walled conductivity cell, the cell was placed in a constant-temperature oil bath (all temperatures ±0.1 °C or better), and the solvolyses were followed by a self-balancing, recording Wheatstone bridge.

The rate data were obtained by Guggenheim treatment of the first-order percent resistance vs. time plot.[28] The rate constants and activation parameters were obtained by the method of least squares.

Solvolysis of 17b and 18b. The *p*-nitrobenzoate (200 mg) and 2,6-lutidine (47 mg) dissolved in 60% aqueous acetone (25 mL) were sealed in a thick-wall glass tube and heated in a cylindrical oven at 135 °C for a period of at least 10 half-lives. After cooling, most of the acetone was removed in vacuo. The resulting residue was diluted to 70 mL with water and extracted into ether. The combined organic layers were washed successively with water, 5% hydrochloric acid, and saturated sodium bicarbonate solution prior to drying. Solvent removal left colorless or slightly yellow oils, the ^1H NMR and IR of which identified them as **17a** (90–95% yields).

Solvolysis of 10b and 11b. The procedure followed was identical with that described above. The product mixtures, isolated in 85–90% yield, were immediately methylated as follows. A given sample (ca. 200 mg) dissolved in anhydrous ether (2 mL) was introduced via syringe into a stirred slurry of potassium hydride (130 mg, 3.2 mmol) in ether (10 mL) cooled to 0 °C. After 30 min, methyl iodide (570 mg, 4.0 mmol) was added and the mixture was stirred at room temperature for 4 h. Methanol (2 mL) addition was followed by aqueous hydrolysis (5 mL) and extraction with ether. The combined ether extracts were dried, carefully concentrated, and analyzed on a 4 ft × 0.25 in. 5% FFAP column (Chromosorb G) at 150 °C. The product ratios were determined by integration of the traces (flame ionization detectors; identical response of **25a** and **26** assumed).

For exo isomer **25a**: δ_{Me_4Si} ($CDCl_3$) 5.35–5.97 (m, 6), 3.36 (s, 3), and 2.96–3.90 (m, 5); calcd *m/e* 174.1045, found 174.1048.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.79; H, 8.28.

For endo isomer **26**: δ_{Me_4Si} ($CDCl_3$) 5.39–5.93 (m, 6), 3.43 (s, 3), and 2.95–4.15 (m, 5); calcd *m/e* 174.1045, found 174.1048.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.84; H, 8.30.

10-Chlorotricyclo[5.3.1.0^{4,11}]undeca-2,5,8-triene (25b). A sample of **10a** and **11a** (150 mg, 0.92 mmol) as obtained from reductive dehalogenation of **9** was dissolved in dry benzene (10 mL) and cooled to 10 °C while pyridine (280 mg, 3.50 mmol) and then thionyl chloride (328 mg, 2.76 mmol) were added by syringe. After 10 min, the mixture was poured into a slurry of ice and water and extracted with benzene (10 mL). The organic layer was washed successively with cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and water prior to drying and evaporation. There was obtained 111 mg (67.8%) of **25b** as a light yellow oil. Kugelrohr distillation at 40–45 °C (0.01 mm) afforded the chloride as a colorless oil: δ_{Me_4Si} ($CDCl_3$) 5.33–6.40 (m, 6), 4.63–4.39 (m, 1), 3.98–3.65 (m, 1), and 3.30–3.53 (m, 3); additionally, a weak intensity absorption at δ 4.77 was evident (relative intensity 8%) which could be due to the >CHCl proton in the endo isomer; ν_{max} (neat) 3030, 2920, 2830, 1190, 825, and 810 cm^{-1}.

10-Chlorotricyclo[5.3.1.0^{4,11}]undec-8-ene (28b). Treatment of a **17a/18a** mixture (130 mg, 0.79 mmol) in 10 mL of benzene with 219 mg (2.78 mmol) of pyridine and 283 mg (2.38 mmol) of thionyl chloride in the predescribed fashion afforded 123 mg (85%) of **28b** as a colorless oil after distillation in the Kugelrohr apparatus (40–45 °C, 0.01 mm): δ_{Me_4Si} ($CDCl_3$) 5.80–5.93 (m, 2), 4.38–4.60 (m, 1), 2.38–2.94 (m, 4), and 1.09–2.19 (m, 8); additionally, absorptions at δ 4.90 and 5.33 (relative intensities ~10%) attributable to the endo epimer were in evidence; ν_{max} (neat) 3030, 2945, 2865, 1470, 1450, 1215, and 780 cm^{-1}.

***exo*-10-Methoxytricyclo[5.3.1.0^{4,11}]undec-8-ene (28a).** A solution of **17a** (200 mg, 1.22 mmol) in 3 mL of anhydrous ether was added to a suspension of potassium hydride (100 mg, 2.5 mmol) in 10 mL of the same solvent. Formation of the alkoxide as before, reaction with methyl iodide (400 mg, 2.8 mmol), and workup afforded 193 mg (88.9%) of a yellowish oil. Preparative VPC purification (12 ft × 0.25 in. 15% Carbowax 20M on Chromosorb P, 170 °C) gave pure **28a** as a colorless oil: ν_{max} (neat) 2940, 2870, 1520, and 1090 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.75–5.88 (m, 2), 3.42–3.63 (m, 1), 3.33 (s, 3), 2.17–2.72 (m, 4), and 0.97–2.03 (m, 8); calcd *m/e* 178.1358, found 178.1362.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.86; H, 10.16.

***endo*-10-Methoxytricyclo[5.3.1.0^{4,11}]undec-8-ene (26).** Treatment of **18a** (60 mg, 0.35 mmol) with potassium hydride (30 mg, 0.70 mmol) and methyl iodide (119 mg, 0.84 mmol) in the above manner and isolation by preparative VPC afforded 45 mg (72.3%) of the endo methyl ether as a colorless oil: ν_{max} (neat) 2940, 2870, 2820, 1520, 1320, 1200, 1105, and 980 cm^{-1}; δ_{Me_4Si} ($CDCl_3$) 5.57 (s, 2), 3.87–4.08 (m, 1), 3.35 (s, 3), 2.23–2.75 (m, 4), and 1.07–1.87 (m, 8); calcd *m/e* 178.1358, found 178.1362.

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Registry No.—**4**, 57636-89-2; **5**, 62609-43-2; **6**, 6053-74-3; **7**, 60714-87-6; **8**, 62637-57-4; *exo*-**9**, 62609-44-3; *endo*-**9**, 62653-19-4; **10a**, 62609-45-4; **11a**, 62653-20-7; **12**, 62609-46-5; **12** semicarbazone, 62609-47-6; **13**, 62637-58-5; **14**, 57595-39-8; **15**, 62609-48-7; *exo*-**16**, 62609-49-8; *endo*-**16**, 62653-21-8; **17a**, 62609-50-1; **18a**, 62653-22-9; **19**, 62609-51-2; **25a**, 60714-89-8; *exo*-**25b**, 62609-52-3; *endo*-**25b**, 62653-23-0; **26**, 60761-29-7; **28a**, 62609-53-4; *exo*-**28b**, 62609-54-5; *endo*-**28b**, 62653-24-1; *O*-4-methylphenyl chlorothioformate, 937-63-3; bromoform, 75-25-2; thionyl chloride, 7719-09-7.

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