Laboratory, University of California, Berkeley, Calif., or Alfred Bernhardt, Mülheim (Ruhr), West Germany. The phrase "worked up as usual" means that an ether–benzene solution of the products was washed with dilute alkali and/or acid, with water, and with saturated sodium chloride solution and dried over anhydrous sodium sulfate. After filtration the solvents were removed *in vacuo*.

(41) S. R. Landor, A. N. Patel, P. F. Whiter, and P. M. Greaves, *J. Chem. Soc. C*, 1223 (1966).
(42) Three components of shorter retention times, not affected by acetic anhydride, were observed but not identified. The ratios, yields, and relative retention times were as expected for analogs of ROCH(C≡CH)R', ROCH=C=CH—R', and ROCH₂C≡CR' (see Table I and ref 2).

Rearrangement Reactions of 9-Arylbicyclo[4.2.1]nona-2,4,7-trien-9-yl Cations[1,2]

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Abstract: The preparations of the *syn*-9-phenyl- and 9-*p*-anisylbicyclo[4.2.1]nona-2,4,7-trien-9-yl *p*-nitrobenzoate esters are reported. Rate comparisons of these compounds with their fully saturated analogs reveal a decrease in the amount of π participation accompanying the reaction as the positive charge at the 9-carbon is increasingly stabilized by the nature of the aryl group. The products are completely rearranged and consist of 78% *exo*- and 12% *endo,cis*-2-dihydroindenyl alcohol plus *ca.* 10% indene with the aryl group always on the 2-carbon of the indenyl system.

The ionization reactions of *syn*-bicyclo[4.2.1]nona-2,4,7-trienyl *p*-toluenesulfonate derivatives (I-OTs) have been reported to yield only rearranged products.[3,4] A quantitative study of the acetolysis of I-OTs (Z = H) revealed the highly specific nature of the reaction. Thus, *cis,exo*-dihydroindenyl acetate (II-OAc) is effectively the only product formed (99%), and in the deuterated analog (Z = D) the deuterium label is found exclusively at C-2 of II-OAc.[4] This same pathway is operative under nonsolvolytic conditions. The decomposition of 9-deuterio-I-OTs in DMSO yields 2-deuterioindene in 74% yield.[3a] Earlier reports on the reactions with the 9-phenyl derivatives of I in aprotic solvents also indicate the production of rearranged products only. However, in these cases not only is the 2-phenylindene formed but also 8-phenylindenyl derivatives which are generated by a rearrangement involving a simple 1,2 shift.[5] Presumably, this pathway becomes accessible when the incipient positive charge at C-9 of I becomes stabilized by the presence of the phenyl substituent. On the other hand, it is not clear as to what extent the variation in the rearranged products is due to the difference in the reaction conditions. In order to resolve this situation and further develop our understanding of these rearrangement reactions it seemed important to study quantitatively the reactions of 9-aryl derivatives of I in conditions which permit direct comparison of the results with those from the unsubstituted compounds.

Results

Synthesis. The bicyclo[4.2.1]nona-2,4,7-trienone was prepared in the reaction between cyclooctatetraene dianion and dimethylcarbamyl chloride as previously described.[3,4] Treatment of the ketone with NaBH₄ produced the endo-carbinol I-OH (Z = H). The endo-carbinol III-OH was produced in the reaction with LiAlH₄ as previously described.[4,6] Hydrogenation of I-OH on Pt produced (endo) IV-OH in high yields. Treatment of the ketone with NaBD₄ (99% D) produced I-OH (Z = D) in 77% yield. The corresponding alkyl toluenesulfonate esters were prepared with *p*-toluenesulfonyl chloride in pyridine in the usual way.

syn-9-Hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene (I-OH, Z = Ph) was similarly prepared in the reaction between cyclooctatetraene dianion and methyl benzoate. The purified carbinol was obtained in 46% yield, mp 104.8–105.2 (lit.[3b] 105–107°). Hydrogenation of the carbinol with Pd produced the fully reduced endo analog, IV-OH (Z = Ph), in 97% yield, mp 59.0–59.5° (lit.[3a] 59°). The *p*-anisyl substituted analog I-OH (Z = *p*-An) was prepared in a similar way starting with *p*-methoxybenzoic acid methyl ester. The endo-trienyl carbinol, mp 129.0–129.5°, was obtained in 48% yield. Hydrogenation of the trienyl carbinol with Pt produced the saturated endo carbinol IV-OH (Z = *p*-An) in 96% yield, mp 92.0–93.0°. The corresponding *p*-nitrobenzoate esters (ROPNB) were prepared in the usual manner. Structure proofs are based on nmr and glc analysis primarily.

I-OH
Z = H, Ph, *p*-An

exo-II-OH
Z = H, Ph, *p*-An

III-OH

IV-OH
Z = H, Ph, *p*-An
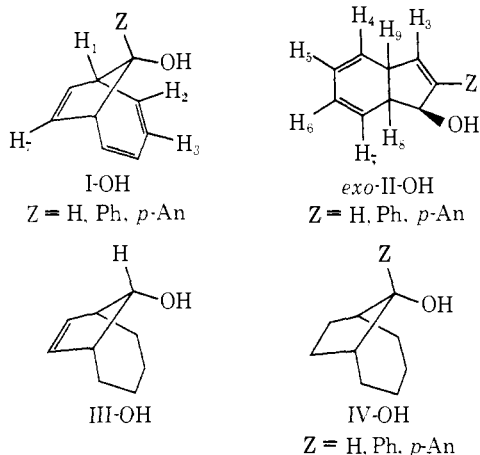
Rates. The rates of solvolysis of the various alkyl esters were followed by titration of the produced acid. Good first-order kinetics were observed in most cases, with the infinity titers being 99.5%. In the case of IV-OPNB (Z = Ph) the reaction is too slow to be practical, therefore the k value listed in Table I was estimated at 5% reaction and most likely reflects the acyl-oxygen cleavage reaction. At longer reaction times the k values increase rapidly, probably due to the H⁺-promoted reaction.

As previously discussed for the unsubstituted series, I-OTs is considerably more reactive than the more saturated analogs. On the other hand the presence of the anti double

bond in III-OTs has only a small effect on the measured reactivity of IV-OTs. Certainly it is not as large as the reactivity difference of 10^{11} observed between the *anti*-7-norbornenyl and 7-norbornyl derivatives.[7] In the present case the smaller rate difference is most probably due to the more open geometry of the 5-membered ring which reduces the effectiveness of π participation. The measured relative k's for I-OTs and IV-OTs are solvent sensitive where the greater difference appears in the more ionizing solvent acetic acid.

The presence of electron-releasing substituents at C-9 of the alkyl esters increases the solvolytic reactivity, where the saturated derivatives (IV) show a greater sensitivity toward aryl substitution. In combination with this effect the measured relative k ratio, $k(\text{unsat})/k(\text{sat})$, decreases from 3000 when Z = H to 0.2 when Z = *p*-An. Introduction of the *p*-anisyl substituent clearly changes the nature of the ionization mechanism. The reaction now proceeds without π participation where the relative k ratio of less than one reflects the inductive retardation of the double bonds.

Products. The products produced in the solvolysis of the trienyl derivatives are completely rearranged in every case. In the case of the unsubstituted esters the reaction is very clean producing only the *cis,exo*-dihydroindenyl acetate. No *endo*-II-OAc was observed where our procedure permits the detection of 0.15% acetate. The epimeric *cis*-dihydroindenyl products were shown to be stable (>99%) to the reaction work-up and analytical procedures used. But still it is not clear whether all of the few per cent of elimination product observed is primary product. The assignment of the exo,cis-fused dihydroindenyl structure is based on nmr analysis making primary use of the coupling constants. Thus for *exo*-II-OAc (Z = H) $J_{8,9}$ is 11.5 Hz and $J_{1,8}$ is 3 Hz, and for *exo*-II-OH (Z = aryl) $J_{1,8}$ is 3.5–3.8 Hz. The endo epimer is readily identified since the value for $J_{1,8}$ increases to 7 Hz. The singleness of the product formed is consistent with the rearranged intermediate structure being the bishomotropylium ion which is known to yield only *cis,exo*-dihydroindenyl product with stereoelectronic control.[8]
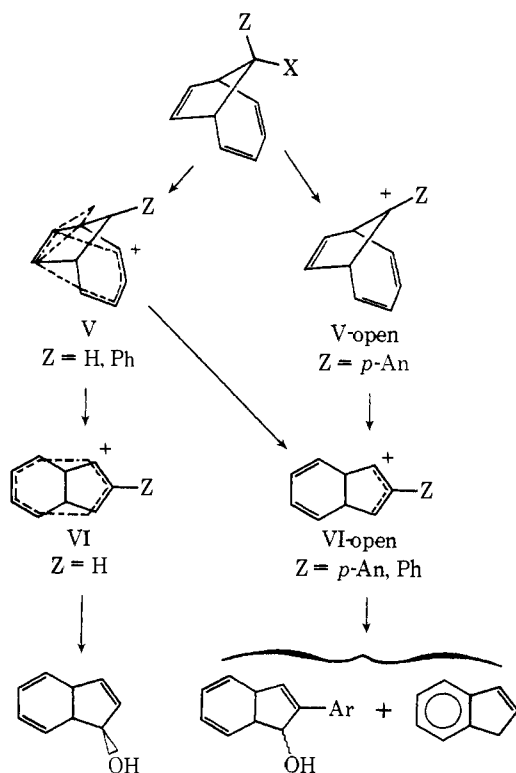

V
Z = H, Ph

V-open
Z = *p*-An

VI
Z = H

VI-open
Z = *p*-An, Ph

Table I. Summary of Solvolytic Rate Constants at 125°

Compd	Z	Solvent	$10^6 k$, sec^{-1}	$k(\text{unsat})/k(\text{sat})$
I-OTs	H	AcOH	68000	100,000
III-OTs	H	AcOH	7.5	11
IV-OTs	H	AcOH	3.4	
			0.7 (cor)[a]	(1)
I-OTs	H	80% acetone	6300	3,000
IV-OTs	H	80% acetone	2	
I-OPNB	H	80% acetone	~0.3[b]	
I-OPNB	Ph	80% acetone	21.2 ± 1.6	>100
IV-OPNB	Ph	80% acetone	0.2[b]	
I-OPNB	*p*-An	80% acetone	112 ± 5	0.2
IV-OPNB	*p*-An	80% acetone	565 ± 2	

[a] Corrected to that fraction of the reaction that proceeds without direct solvent interactions. [b] Initial k values.

Table II. Products Formed in the Solvolysis of the Various 9-Bicyclo[4.2.1]nona-2,4,7-trienyl Esters

Z	Conditions	Total recovery, %	exo-II-OH	endo-II-OH	Indene
H	NaOAc + HOAc, 50°	99	99		1
H	4 M NaBH$_4$ + 67% diglyme, 50°		98		2
Ph	NaOAc + 60% acetone, 125°	97	80	12	8
p-An	NaOAc + 80% acetone, 125°		80	10	10

Another result common to the trienyl derivatives studied is that the rearrangement process occurs always in a very specific manner where C-9 in I becomes C-2 in II-OH and indene products. In the case of the unsubstituted compound this became evident with the presence of deuterium label at C-9 of I-OTs. As was previously described[4] the 220-MHz nmr spectrum for *exo*-II-OAc-*d* (sample containing Eu(fod)$_3$) produced in the acetolysis of α-*d*-I-OTs is identical with that of the undeuterated material except that the peak at δ 7.18 assigned to H$_2$ disappears and the doublet at δ 6.21 for H$_3$ collapses to a singlet. This same specificity of the location of the label occurs in the reaction of 9-*d*-I-OTs in DMSO at 74° which produces 2-*d*-indene in 74% yield.[3a] Confirmation of the position of the deuterium label in *exo*-II-OAc is made available by comparing ^{13}C-nmr spectra. The spectra for the protio material measured in CDCl$_3$ shows signals, in ppm, at 171.06 for the carbonyl carbon, 138.66 for C$_3$, 128.83 for C$_2$, 126.53 and 125.13 for C$_4$ plus C$_7$, 121.86 and 121.31 for C$_5$ plus C$_6$, 87.52 for C$_1$, 43.16 for C$_8$ plus C$_9$, and 21.38 for the methyl carbon. The spectrum for the deuterated product is identical within ±0.06 ppm except that the signal at 128.83 is not visible.

Again the products formed in the solvolysis of the 9-aryl substituted alkyl *p*-nitrobenzoates are completely rearranged and the aryl group appears specifically at C-2 of the *cis*-dihydroindenyl alcohols. However, in contrast to the unsubstituted derivatives an epimeric mixture is produced consisting of 80% *exo*-II-OH, 11% *endo*-II-OH, plus 9% 2-arylindene. Experiments under controlled conditions show that all the products are stable to the reaction conditions. The nmr spectrum for the 2-aryl-*cis,exo*-dihydroindenyl alcohols is virtually identical with the spectrum for the 2-*d*-*cis,exo*-dihydroindenyl acetate with the exception that H$_1$ absorbs at slightly higher field. $J_{1,8}$ remains 3.5–3.8 Hz. Thus the presence of the aryl substituents has a dramatic effect on the nature of the product-forming step. These results are consistent with the rearranged cationic intermediate being an open allylic ion (VI-open) which can be

captured both exo and endo and can also produce elimination product.

The products formed in the solvolysis of the more saturated members in the series are more predictable. The acetolysis of III-OTs in sodium acetate buffered acetic acid produces III-OAc, which was recovered in 97% yield, and no other products were observed. Thus, the solvolysis of III-OTs must proceed *via* a bishomocyclopropenyl cation intermediate which is chemically captured to regenerate the starting structure as is the case with *anti*-7-norbornenyl derivatives.[7] The acetolysis of IV-OTs (Z = H) produces a four to one mixture of the epimeric *exo*-IV-OAc and an olefin with a rearranged carbon skeleton. It seems reasonable to make use of the nature of the products to adjust the measured k_t for IV-OTs for the purpose of comparing it with the k values for the other members in the series. Thus the k_t should be corrected by a factor of $\frac{1}{5}$ in order to generate the k for the reaction that proceeds without direct solvent intervention. This adjustment is listed in Table I. As for the 9-aryl-IV derivatives, products were determined only for the *p*-anisyl alkyl ester for practical reasons. In this case, the only product observed is the epimeric carbinol.

Discussion

The enhanced reactivity of I-OTs (Z = H) in spite of the rate-retarding inductive effect of the butadiene moiety is ascribed to a stabilizing interaction of this group with the incipient bishomocyclopropenyl cation (involving carbons 7, 8, and 9) in the rate-determining step to produce the bicyclo-conjugated cation V. However, the cation once formed is still less stable than the isomeric bishomotropylium ion VI and it therefore efficiently rearranges in a specific and symmetrical process. The stabilizing interaction of the butadiene moiety is further dramatized if one cross compares the contribution of bicycloconjugation to the total resonance energy stabilization for those structures where data are available. Thus in the norbornadienyl cation, the relative solvolytic reactivities of the various unsaturated members of the series suggest that only 25% of the stability is due to bicycloaromaticity and 75% is due to homoaromaticity.[7] Then in the bicyclo[3.2.2]nonatrienyl anion, the relative k's for base-catalyzed detritiation for the various unsaturated members of this series suggest that *ca.* 40% of the stability is due to bicycloaromaticity and ~60% is due to homoaromaticity.[9] Finally in the present case the stability of the incipient cation V is *ca.* 80% due to bicycloconjugation and 20% due to homoaromaticity.

The estimate for the present case is derived from a comparison of the relative rate ratios $k_{\text{I-OTs}}/k_{\text{III-OTs}}$ equal to 10^4 and $k_{\text{III-OTs}}/k_{\text{IV-OTs}}$ equal to 11, with the overall rate enhancement of 10^5 observed for the fully unsaturated I-OTs in this series. While inductive effects were not considered in these estimates, any corrections which are applied will expand the relative reactivity scale. The difficulty in attempting to apply these corrections is the quantitative assessment of the individual factors for the rate ratios $k_{\text{I-OTs}}/k_{\text{III-OTs}}$ and $k_{\text{III-OTs}}/k_{\text{IV-OTs}}$.

Some insight on the magnitude of these effects can be gained if one compares the solvolytic reactivities of the benzo analogs, VII and VIII *p*-bromobenzenesulfonate esters (ROBs), reported by Tanida and Irie,[10] with this series. The authors report rate constants in 60% aqueous diglyme at 190° of 23.2 × 10⁻⁵ sec⁻¹ for VII-OBs and 1.55 × 10⁻⁵ sec⁻¹ for VIII-OBs. The k value for VII-OBs can be adjusted to acetic acid solvent at 125° using the ΔH^* value of 33.1 kcal and the solvent reactivity difference [k(acetic acid)/k(aqueous diglyme)] value of 0.10 provided by the authors. Finally recognizing that ROBs esters solvolyze *ca.*

2–3 times faster than ROTs esters, the calculated k value for VII-OTs in acetic acid at 125° is 2.5 × 10⁻⁸ sec⁻¹ and can be compared directly with the k value for IV-OTs (Z = H). Thus the presence of the benzo group in VII depresses the solvolysis rate by a factor of *ca.* 130 as a result of the inductive effects. The net decrease in reactivity which is observed with the benzo group (VIII-OTs) and not the monoene moiety (III-OTs) is due to the reduced level of π participation resulting from the unfavorable configuration of the bicyclic system plus the poorer aptitude[11] of the benzo group for π participation. Consistently then, the presence of the additional butadiene system, as in VIII, further reduces the reactivity of the system by a factor of *ca.* 15. While there is no intent to use the estimates of inductive retardation from this series for correcting the relative reactivity series, IV-OTs (Z = H):III-OTs:I-OTs (Z = H), the comparison of the two series does help emphasize the importance of π participation in III-OTs and I-OTs (Z = H).


VII-OBs   VIII-OBs
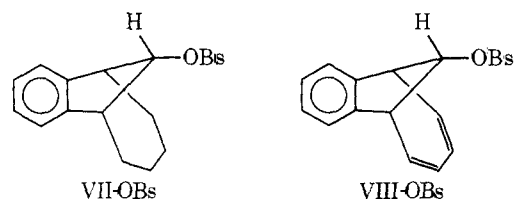
Since the photoelectron spectroscopy data reported by Heilbronner, *et al.*, suggest no interaction between the monoene and the diene in the bicyclo[4.2.1]nonatriene,[12] the interaction which occurs during the ionization of I-OTs must proceed with a considerable amount of motion of the atoms involved and little or no vertical stabilization. Because of the stereochemical orientation of the leaving group in I it seems that the initially formed cation or ion pair must involve laticyclic π interactions as in V. However, once the cation is fully formed, a structure which involves direct π interaction between the one-carbon bridge and the four-carbon bridge is certainly reasonable based on the photoelectron spectroscopy data for the bicyclo[4.2.1]nona-2,4,7-trien-9-one. In this case, the photoelectron data show no trace of bicycloconjugation but instead show the presence of a conjugative interaction between the nonbonded electron pair on the carbonyl group and butadiene group.[13]

While the initially formed cation from I-OTs efficiently rearranges to the homoaromatic ion, the additional stabilization due to the engagement of the butadiene is not as great in cation VI as it is in cation V. This fact can be appreciated by a cross comparison of the relative k's for the *exo*,- and *endo,cis*-8,9-dihydroindenyl *p*-nitrobenzoates ($k_{\text{exo}}/k_{\text{endo}}$ = 8)[8] with those for I-OTs (Z = H) and III-OTs (Z = H) where $k_{\text{triene}}/k_{\text{monoene}}$ = 10⁴.[4] In line with this observation a phenyl group, even on the 2-carbon of the allyl structure, is sufficient to open the bishomoaromatic ion (VI), while it takes the effect of the *p*-anisyl group to open the bicycloconjugated ion in structure V.

It seems contradictory that cation V (Z = H) which has more effective bicycloconjugation should rearrange to the bishomotropylium ion. However, the fact that even the open cation V (Z = *p*-An) rearranges to the open allylic cation VI (Z = *p*-An) suggests that the relative inherent stabilities of the carbon skeletons is the determining factor in the rearrangement process and not the resonance energy due to homoconjugation.

The rearrangement of the open cation V (Z = *p*-An) which occurs in a very specific manner is worth discussing briefly since it provides a particularly interesting situation. The rearrangement could proceed *via* a pathway which involves the formation of a biscyclopropylcarbinyl cation IX

as described by Shechter[3] or conversely *via* a cation like X which involves bond breaking between $C_1(C_6)$ and $C_2(C_5)$ with a corresponding increase in bond order between $C_2(C_5)$ and $C_8(C_7)$ and between $C_1(C_6)$ and C_9. The rearrangement process *via* a structure like X seems more reasonable than a process involving the formation of a highly strained cation like IX.

IX   X
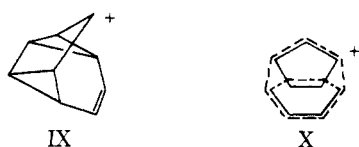
From a further consideration of the products formed with the aryl substituents some important conclusions may be drawn regarding homoaromaticity. These results show for the first time the chemical behavior of an open ion in a potential homoaromatic ion structure and as such help support the closed π-homoaromatic structure rather than the open allylic cation for the unsubstituted *cis*-dihydroindenyl cation.[8]

In conclusion, the ionization reactions of the *endo*-9-bicyclo[4.2.1]nonatrienyl derivatives proceed with rearrangement. Under normal solvolytic conditions the rearrangement process is efficient and is very specific both for the unsubstituted and the aryl-substituted derivatives. The results obtained with the *p*-anisyl derivative indicate that the high specificity of the rearrangement reaction is maintained even when an open cation is formed in the bicyclic structure as in V-open (Z = *p*-An) and that the driving force for the rearrangement is the relative stabilities of the basic carbon skeletons and not the amount of resonance energy due to homoconjugation.

Experimental Section

Bicyclo[4.2.1]nona-2,4,7-trien-9-one. The key intermediate for the preparation of the compounds used in this study is bicyclo[4.2.1]nona-2,4,7-trien-9-one. The procedure of Shechter[3c] was used. Dimethylcarbamyl chloride (11 g) in 170 ml of ether was added to a stirred solution of dilithium cyclooctatetraenide (from 10.2 g of cyclooctatetraene) in 1 l. of ether at 0° under nitrogen. After 4 hr of stirring, dilute sulfuric acid was added and the ether layer was washed with water and aqueous sodium bicarbonate, dried, and evaporated. The residue was distilled to give 6.1 g (47%) of pure ketone, bp 43–45° (0.2 mm) (lit.[3c] 46–47° (0.3 mm)): δ_{TMS} (CCl$_4$) 5.77–5.72 (m, 6, olefinic), 2.98 (d, J = 7.5 Hz, 2, bh); ν_{max} (neat) 1760 cm^{-1}. All nmr measurements were made on the Varian HR220.

syn-Bicyclo[4.2.1]nona-2,4,7-trien-9-ol (I-OH, Z = H). To a cold stirred suspension of 0.2 g of sodium borohydride in 5 ml of MeOH was added 0.41 g of bicyclo[4.2.1]nona-2,4,7-trien-9-one in 5 ml of MeOH. After 1 hr, the excess borohydride was destroyed and the solution was extracted with ether. After evaporation 0.37 g (89%) of residue was recrystallized in pentane to give pure I-OH, Z = H, mp 51–51.5° (lit.[3c] 51.0–52.5°): δ_{TMS} (CS$_2$) 6.07 (m, 2.1, butadiene), 5.83 (m, 2.2, butadiene), 5.17 (d, J = 0.8, 1.9, ethylene), 4.23 (doublet of triplets, J = 12.5 and 6 Hz, 0.9, α-H), 2.94 (doublet of doublets, J = 7 and 6 Hz, 1.9, bh), 1.36 (d, J = 12.5 Hz, 1.0, hydroxy).

syn-9-Deuteriobicyclo[4.2.1]nona-2,4,7-trien-9-ol (I-OH, Z = D). The carbinol I-OH (Z = D) was prepared as described for protio analog with the substitution of sodium borodeuteride (99%, Stohler Isotope). The deuterated carbinol was esterified without further purification.

syn-Bicyclo[4.2.1]nona-7-en-9-ol (III-OH). One gram of I-OH, 0.4 g of lithium aluminum hydride, and 10 ml of ether were refluxed 1 hr. The excess hydride was destroyed and the ether was washed with water and evaporated. The product contained 40% bicyclo[4.2.1]nona-2,7-dien-9-ol and 60% bicyclo[4.2.1]nona-3,7-dien-9-ol, as estimated by glpc.[6] The alcohols were separated by chromatography on silica gel. The pure unsymmetrical diene was

further reduced in refluxing THF containing lithium aluminum hydride for 3 days. Work-up and recrystallization from pentane gave 0.25 g of III-OH, mp 115–117°: δ_{TMS} (CS$_2$) 5.58 (d, J = 2 Hz, 2, olefinic), 4.34 (t, J = 7 Hz, 1, α-H), 2.58 (m, 2, bh), 2.42 (s, 1, hydroxy), 1.4–1.8 (m, 8, aliph).

syn-9-Hydroxybicyclo[4.2.1]nonane (IV-OH, Z = H). The carbinol I-OH, Z = H (0.445 g), 0.111 g of PtO$_2$, and 2 ml of 95% EtOH were stirred under a hydrogen atmosphere for 3 hr. The solution was filtered through Celite and evaporated to 0.44 g (99%) of a residue which was recrystallized in pentane, mp 176–177°: δ_{TMS} (CS$_2$) 4.14 (t, J = 7 Hz, 1.0, α-H), 2.20 (m, 1.9, bh), 1.4–2 (m, 12.7, hydroxy and aliph).

Alkyl *p*-Toluenesulfonate Esters. The alkyl tosylate esters of the carbinols were prepared using the procedure here described for I-OTs (Z = H).

The carbinol I-OH, Z = H (2.71 g), was dissolved in 8 ml of pyridine and cooled to 0°, and 4.56 g of tosyl chloride was added in small portions with stirring. After 8 hr at 0° the solution was poured into ether–water and washed with dilute hydrochloric acid, saturated aqueous sodium bicarbonate, and water. The solution was dried with potassium carbonate and evaporated to 4.6 g of crude alkyl tosylate, mp 83–85° (lit.[3c] 83–85°). Recrystallization in 9:1 hexane-chloroform gave 2.74 g of pure I-OTs, Z = H, as fine white needles, mp 85–85.5°: δ_{TMS} (CCl$_4$) 5.99 (m, butadiene), 5.65 (m, butadiene), 5.09 (d, J = 1.5 Hz, ethylene), 4.82 (t, J = 6.5 Hz, α-H), 3.02 (t, J = 6.5 Hz, bh).

The deuterio analog I-OTs, Z = D, was recrystallized in hexane-chloroform, mp 89–90°: no α-H could be detected and the bridgehead protons appeared as a doublet, J = 7 Hz, at δ 2.98 in CS$_2$.

The tosylate derivative of III was recrystallized from pentane at −78°, mp 49–52°: δ_{TMS} (CCl$_4$) 5.65 (d, J = 1.5 Hz, olefins), 4.89 (t, J = 7 Hz, α-H), 2.78 (m, bh).

The tosylate derivative of IV (Z = H) was recrystallized from pentane, mp 78–79°: δ_{TMS} (CS$_2$) 4.62 (t, J = 7 Hz, α-H), 2.25 (m, bh).

syn-9-Hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene (I-OH, Z = Ph). The method of Antkowiak and Shechter[3b] was used. To a stirred solution of dilithium cyclooctatetraenide (from 2.42 g of cyclooctatetraene) in 250 ml of ether at 0° was added 3.27 g of methyl benzoate in 100 ml of ether. After stirring 4 hr under nitrogen, 100 ml of 2% acetic acid was added. The ether layer was washed with water and aqueous sodium bicarbonate, dried, and evaporated. A yellow-orange solid (4.86 g) crystallized out of the ether and was chromatographed on activity III alumina. The pentane fraction was recrystallized in hexanes to give 2.27 g (46%) of pure I-OH, Z = Ph, as long white needles, mp 104.8–105.2° (lit.[3b] 105–107°): δ_{TMS} (CCl$_4$) 7.90 (d, 2.0, phenyl), 7.59 (m, 2.8, phenyl), 6.51 (m, 4.5, butadiene), 5.56 (d, 2.0, ethylene), 3.35 (d, 1.95, bh), 2.43 (s, 0.9, hydroxyl).

syn-9-Phenylbicyclo[4.2.1]nona-2,4,7-trien-9-yl *p*-Nitrobenzoate (I-OPNB, Z = Ph). A solution of 1.9 g of I-OH, Z = Ph, 1.77 g of *p*-nitrobenzoyl chloride, and 10 ml of pyridine was refluxed 10 hr. Usual work-up and recrystallization from ether–pentane gave 2.49 g of pure I-OPNB, Z = Ph, mp 173–173.5°: δ_{TMS} (CCl$_4$) 8.19 (d, 2.0, *p*-nitro), 8.00 (d, 2.0, *p*-nitro), 7.33 (d, 2.2, phenyl), 7.18 (d, 3.3, phenyl), 6.04 (s, 4.0, butadiene), 5.27 (d, 1.7, ethylene), 3.80 (broad s, 1.8, bh).

syn-9-Hydroxy-9-phenylbicyclo[4.2.1]nonane (IV-OH, Z = Ph). The carbinol I-OH, Z = Ph (0.356 g), 0.125 g of 5% Pd-C, and 50 ml of 95% EtOH were shaken at 25 psi of hydrogen for 20 hr. The solution was filtered through Celite and evaporated to give 0.356 g (97%) of white solid which was recrystallized in pentane to give pure IV-OH, Z = Ph, mp 59–59.5° (lit.[3c] 59°): δ_{TMS} (CCl$_4$) 7.55 (d, 2, phenyl), 7.29 (m, 3, phenyl), 2.48 (broad s, 2, bh), 1.32–2.11 (m, 12, aliph).

syn-9-Phenylbicyclo[4.2.1]nona-9-yl *p*-Nitrobenzoate (IV-OPNB, Z = Ph). A solution of 0.252 g of IV-OH, Z = Ph, 0.24 g of *p*-nitrobenzoyl chloride, and 2 ml of pyridine was refluxed 3 hr. Usual work-up and recrystallization from hexanes gave 0.21 g of pure IV-OPNB, Z = Ph, mp 140.5–141°: δ_{TMS} (CCl$_4$) 8.26 (d, 2, *p*-nitro), 8.16 (d, 2, *p*-nitro), 7.35 (d, 2, phenyl), 7.19 (m, 3, phenyl), 3.11 (broad s, 2, bh), 1.4–2 (m, 14.7, aliph).

syn-9-Hydroxy-9-*p*-anisylbicyclo[4.2.1]nona-2,4,7-triene (II-OH, Z = *p*-An). To a stirred solution of dilithium cyclooctatetrae-

nide (from 1.85 g of cyclooctatetraene) in 200 ml of ether at 0° was added 3.1 g of methyl anisate in 100 ml of ether. After stirring overnight under nitrogen, 50 ml of 4% acetic acid was added. The ether layer was washed with water and aqueous sodium bicarbonate, dried, and evaporated. A yellow solid crystallized out of the ether and was chromatographed on activity III alumina. The pentane fraction was recrystallized in hexanes to give 2.08 g, 48%, of pure I-OH, Z = p-An, as fine white needles, mp 129–130°: δ_{TMS} (CCl$_4$) 7.60 (d, 2.0, anisyl), 6.70 (d, 2.0, anisyl), 6.14 (m, 4.0, butadiene), 5.25 (d, 2.0, ethylene), 3.72 (s, 3.1, methoxy), 3.14 (d, 2.0, bh), 2.27 (s, 1.0, hydroxy).

syn-9-*p*-Anisylbicyclo[4.2.1]nona-2,4,7-trien-9-yl *p*-Nitrobenzoate (I-OPNB, Z = *p*-An). A solution of 0.4 g of I-OH, Z = *p*-An, 0.34 g of *p*-nitrobenzoyl chloride, and 2 ml of pyridine was refluxed for 5 hr. Usual work-up and recrystallization from CH$_2$Cl$_2$–pentane gave 0.48 g of pure I-OPNB, Z = *p*-An, mp 167.5–168°: δ_{TMS} (CCl$_4$) 8.17 (d, 2.0, *p*-nitro), 7.97 (d, 2.0, *p*-nitro), 7.22 (d, 2.0, anisyl), 6.68 (d, 2.1, anisyl), 6.01 (s, 4.0, butadiene), 5.25 (d, 2.1, ethylene), 3.78 (2.0, broad s, bh), 3.70 (3.0, s, methoxy).

syn-9-Hydroxy-9-*p*-anisylbicyclo[4.2.1]nonane (IV-OH, Z = *p*-An). A suspension of I-OH, Z = *p*-An (0.32 g), PtO$_2$ (0.08 g), and 4 ml of ethyl acetate was stirred in a hydrogen atmosphere for 2 hr. The solution was filtered and solvent was evaporated to give 0.31 g, 96%, of IV-OH, Z = *p*-An. The crude material had mp 92–93° and was esterified without further purification: δ_{TMS} (CCl$_4$) 8.28 (d, 2.0, anisyl), 7.67 (d, 2.0, anisyl), 4.26 (s, 3.2, methoxy), 2.75 (m, 2.0, bh), 1.55–2.34 (14.6, aliph).

syn-9-*p*-Anisylbicyclo[4.2.1]non-9-yl *p*-Nitrobenzoate (IV-OH, Z = *p*-An). A solution of 0.336 g of IV-OH, Z = *p*-An, 0.286 g of *p*-nitrobenzoyl chloride, and 2 ml of pyridine was refluxed 3 hr. After usual work-up and recrystallization from hexanes, 0.315 g of pure IV-OPNB, Z = *p*-An, was obtained, mp 145.8–146.4°: δ_{TMS} (CCl$_4$) 8.04 (d, 2.1, *p*-nitro), 7.95 (d, 2.0, *p*-nitro), 7.31 (d, 2.0, anisyl), 6.71 (d, 2.1, anisyl), 3.70 (s, 3.1, methoxy), 3.10 (m, 2.1, bh), 1.36–2.05 (complex m, 13.7, aliph).

Kinetic Measurements. The solvents used for kinetic measurements were purified and prepared as previously described.[14] All runs were with 0.006–0.01 *M* ROTs (or ROPNB) solutions using the sealed ampoule technique. In those runs with ROTs in acetic acid, aliquots from the reaction mixture were titrated with 0.010 *M* NaOAc in acetic acid titrant to the yellow end point of Bromo Phenol Blue. In those runs with ROPNB in mixed aqueous acetone solvent the samples were titrated with 0.00980 *M* NaOMe in methanol titrant to the blue end point of Bromo Thymol Blue (1% in ethanol). Infinity samples were analyzed after 10 reaction half-lives and the *k* values were calculated using the first-order integrated rate expression.

Product Analysis. A solution of 0.175 g of I-OTs, Z = H, 0.1 g of sodium acetate, and 5 ml of acetic acid was sealed in a glass ampoule and placed in a 50° bath for 35 hr. The contents were poured into ether and washed with water and aqueous sodium bicarbonate. Et$_2$O was carefully distilled through a 12-in. Vigreux column. Glpc analysis (2.5% KOH-Carbowax 20M on Chromosorb W, ⅛ in. × 2 m, 100°) showed only two products, indene (1%) and dihydroindene acetate (99%).

The remaining ether was removed under vacuum and the residue (0.1 g, 99%) was purified by preparative glpc (2.5% KOH-Carbowax 20M on Chromosorb W, 0.25 in. × 2 m, 100°).

Indene was identified by its nmr spectrum and glpc retention time. *cis,exo*-Dihydroindenyl acetate was identified spectroscopically: *m/e* 176; ν_{max} (neat) 1720 cm^{-1}; δ_{TMS} (CCl$_4$) 5.83 (broad s, 2.2, olefinic), 5.66 (broad s, 2.7, olefinic), 5.47 (m, 1.1, olefinic), 5.34 (m, 1.0, α-H), 3.64 (d, 1.0, bh), 2.89 (d, 1.0, bh), 1.92 (s, 2.95, methyl).

The *cis*-dihydroindenyl structure is indicated by the unsymmetrical allylic bridgehead protons. The coupling constant $J_{8,9} = 11.5$ Hz is characteristic of cis-fused dihydroindenes.[8,15,16] The $J_{1,8}$ of 3 Hz indicates exo stereochemistry for the acetate.[8]

The position of the deuterium label in the acetate product from I-OTs, Z = D, was determined by pmr using Eu(fod)$_3$[4] and by ^{13}C nmr.[17]

The ester III-OTs was solvolyzed in buffered acetic acid at 125° for 100 hr. Products were determined as described above for I-OTs, Z = H. The nmr spectrum of the only product detected was

identical with III-OAc, prepared in the usual manner from III-OH: δ_{TMS} (CS$_2$) 5.60 (d, 2, olefins), 5.01 (t, 1, α-H), 2.81 (m, 2, bh), 1.95 (s, 3, methyl), 0.8–1.6 (m, 8, aliph).

The ester IV-OTs, Z = H, was solvolyzed in buffered acetic acid at 125° for 300 hr. Products were determined as described above.

An nmr peak at δ 5.59 indicated the presence of a rearranged olefin, but it was not characterized further.

The α-H of the acetate product appeared as a singlet at δ 4.77 and the ester methyl at δ 2.10, which did not correspond to *endo*-bicyclo[4.2.1]nona-9-yl acetate. On treatment with lithium aluminum hydride an alcohol was obtained. This alcohol was found to be identical with that obtained by Na-isopropanol reduction of bicyclo[4.2.1]nona-9-one: δ_{TMS} (CS$_2$) 3.8 (s, 1.0, α-H), 3.36 (s, 1.0, hydroxy), 2.09 (broad s, 2.0, bh), 1.23–1.68 (m, 12, aliph) (identified as *exo*-bicyclo[4.2.1]nona-9-ol).

A solution of 0.25 g of I-OPNB, Z = Ph, 0.11 g of NaOAc, and 50 ml of 60% aqueous acetone were heated at 125° in a sealed tube for 15 hr. Acetone was removed on a rotary evaporator and the residue was extracted with ether, washed with water and sodium bicarbonate, and concentrated to 0.142 g of residue. Three components were found on tlc in benzene. The pure products were eluted with ether–pentane mixtures from activity III alumina.

cis,exo-2-Phenyldihydroindenyl alcohol was identified by the similarity of its nmr spectrum to II-OAc, Z = D: δ_{TMS} (CS$_2$) 7.34 (d, 2, phenyl), 7.20 (m, 3, phenyl), 5.86 (d, 1, olefinic), 5.66 (m, 3, olefinic), 5.53 (m, 1, olefinic), 4.80 (d, 1, α-H), 3.57 (m, 1, bh), 2.82 (m, 1, bh); $J_{1,8} = 3.8$ Hz, $J_{8,9} = 11.3$ Hz, $J_{3,9} = 2.6$ Hz.

cis,endo-2-Phenyldihydroindenyl alcohol was identified by the $J_{1,8}$ coupling constant of 7 Hz: δ_{TMS} (CS$_2$) 7.45 (d, 2, phenyl), 7.14 (m, 3, phenyl), 6.17 (d, 1, olefinic), 5.98 (m, 1, olefinic), 5.66 (m, 2, olefinic), 5.51 (m, 1, olefinic), 4.77 (d, 1, α-H), 3.32 (dd, 1, bh), 3.05 (dt, 1, bh); $J_{1,8} = 7$ Hz, $J_{8,9} = 11.3$ Hz, $J_{3,9} = 3.4$ Hz.

2-Phenylindene was identified by comparison of its nmr spectrum to the hydrocarbon produced in the reaction of I-OH, Z = Ph, with *p*-toluenesulfonic acid in chloroform:[5] δ_{TMS} (CS$_2$) 7.0–7.5 (aromatic and olefin), 2.52 (methylene).

Less than 0.5% of I-OH, Z = Ph, the expected product of acyl-oxygen fission, could be detected. Epimerization or elimination did not occur when pure II-OH, Z = Ph, was chromatographed on alumina, or when heated at 125° for 15 hr in buffered aqueous acetone.

The ester I-OPNB, Z = *p*-An, was solvolyzed in buffered 80% aqueous acetone for 17 hr at 125°. The products were isolated and purified as for I-OPNB, Z = Ph. Three spots were found on tlc in benzene. Product identification was simplified by the similarity to the phenyl-substituted products.

cis,exo-2-*p*-Anisyldihydroindenyl alcohol had: nmr δ_{TMS} (CS$_2$) 7.24 (d, 2, anisyl), 7.09 (d, 2, anisyl), 5.74 (d, 1, olefinic), 5.60 (m, 3, olefinic), 5.45 (m, 1, olefinic), 4.76 (m, 1, α-H), 3.65 (s, 3, anisyl methyl), 3.61 (m, 1, bh), 2.86 (m, 1, bh); $J_{1,8} = 3.5$ Hz, $J_{8,9} = 11.3$ Hz, $J_{3,9} = 2.2$ Hz.

cis,endo-2-*p*-Anisyldihydroindenyl alcohol had: nmr δ_{TMS} (CCl$_4$) 7.43 (d, 2, anisyl), 6.74 (d, 2, anisyl), 6.10 (d, 1, olefinic), 6.01 (m, 1, olefinic), 5.70 (m, 2, olefinic), 5.54 (m, 1, olefinic), 4.83 (d, 1, α-H), 3.71 (s, 3, anisyl methyl), 3.63 (m, 1, bh), 3.11 (m, 1, bh).

2-*p*-Anisylindene had: nmr δ_{TMS} (CCl$_4$) 6.73–7.5 (aromatic and olefinic), 3.78 (anisyl methyl), 3.61 (methylene).

IV-OPNB, Z = *p*-An, was solvolyzed in buffered aqueous acetone at 125° for 4 hr. The product had: nmr δ_{TMS} (CCl$_4$) 7.27 (d, anisyl), 6.74 (d, anisyl), 3.73 (s, anisyl methyl), 2.63 (m, bh). Less than 2% of any other product could be detected. The product is tentatively identified as *exo*-9-anisylbicyclo[4.2.1]nona-9-ol, as the carbonium ion is not expected to rearrange.

References and Notes

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Alkylations of 9-Lithio-9,10-dihydroanthracenes by Alkyl Halides, Alkyl Sulfates, and Alkyllithium Compounds. The Trapping of Radicals Generated by Lithium–Halogen Exchange Reactions

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Abstract: 10-*tert*-Butyl-9-lithio-9-methyl-9,10-dihydroanthracene (1) is alkylated stereospecifically trans to the 10-*tert*-butyl group by *n*-alkyl bromides, iodides, and sulfates. The protons on the β carbon of the new 9-alkyl group in these hydrocarbons appear upfield of tetramethylsilane as a result of diamagnetic anisotropic effects of the aromatic rings. Methylation of the 9-ethyl analog of 1 also occurs stereospecifically trans to the 10-*tert*-butyl group to yield the other diastereomer of the product obtained on ethylation of 1. The relative reactivities of alkyl iodides (Me > Et > *n*-Bu) and dialkyl sulfates (Me > Et) toward 1 are consistent with an SN2 mechanism for alkylation. Alkyl iodides can stimulate the alkylation of 1 by alkyllithium compounds. These indirect alkylations also occur stereospecifically trans to the 10-*tert*-butyl group. They occur only under conditions conducive for lithium–halogen exchange reactions, and the yields of indirect alkylation product increase with increasing temperatures. The concentration, temperature, and alkyl group effects on these reactions are consistent with a mechanism involving trapping of radical intermediates in the lithium–halogen exchange reaction by 1. These effects are not consistent with pathways in which the iodide derived from 1 or the alkyllithium compound by lithium–halogen exchange reaction is an important intermediate. The ethylations of 10-ethyl-9-lithio-9,10-dihydroanthracene by ethyl bromide and iodide and ethyllithium–methyl iodide all have cis stereoselectivity (99%).

The stereoselectivity of alkylation of 10-alkyl-9-lithio-9,10-dihydroanthracenes in tetrahydrofuran (THF) solution by alkyl iodides is a function of the size of both the 10-alkyl group and the iodide alkyl group.[1] When both groups are small, *e.g.*, methyl or ethyl, the cis hydrocarbon is the major or exclusive product,[2] and, when both groups are large, *e.g.*, isopropyl, the trans hydrocarbon is the major product.[1,3] The same alkylation stereoselectivity is obtained using alkyl bromides[2a,c,3b] and in liquid ammonia solution.[2a,c]

As part of a systematic study of solvent effects on the reactions of carbanions, we report here our studies on the stereoselectivity of alkylation of 10-*tert*-butyl-9-lithio-9-methyl-9,10-dihydroanthracene (1) and 10-*tert*-butyl-9-ethyl-9-lithio-9,10-dihydroanthracene (2). We have previously shown that the predominant ion-pair solvation complex of 1 and 2 present is different in diethyl ether, THF, and hexamethylphosphoramide (HMPA) solutions.[4] Unlike the protonation reactions of 1 and 2[4] or of 10-alkyl-9-lithio-9,10-dihydroanthracenes,[5] the solvent, temperature, or alkylating agent had no effect on the stereospecificity of alkylation. We have discovered that in reactions of mixtures of 1 and primary alkyllithium compounds with methyl iodide, the major product contains the alkyl group derived from the alkyllithium compound (indirect alkylations). The stereoselectivity of the direct and indirect alkylations of 1 are identical. The direct and indirect ethylations of 10-

ethyl-9-lithio-9,10-dihydroanthracene (3) also have identical stereoselectivity.

It has been proposed that the mechanism of reaction of alkyl iodides with these carbanions may be a SN2 displacement or may be a two-step sequence.[1] The first step is lithium–halogen exchange between the carbanion and the alkyl iodide. This is followed by coupling of the iodide derived from the carbanion and the alkyllithium compound formed in the first step. The relative reactivities of methyl, ethyl, and *n*-butyl iodide and dimethyl and diethyl sulfate toward 1 have been determined to distinguish between these possible mechanisms. The sulfates cannot react by a two-step sequence analogous to that proposed for the iodides. Similar relative reactivities for the iodides and sulfates will indicate that they react by the same mechanism. The relative reactivities in SN2 displacements are methyl > ethyl > *n*-butyl.[6] The relative reactivities expected for the two-step sequence would be difficult to predict. Possible mechanisms for the indirect alkylation reactions and their relation to the direct alkylation reactions are discussed.

Results

Alkylation Reactions. The carbanions 1 and 2 were prepared by reaction of *n*-butyl- or ethyllithium with diethyl ether, THF, HMPA, or 2,5,8,11-tetraoxadodecane (triglyme) solutions of *cis*- or *trans*-10-*tert*-butyl-9-methyl- or 10-*tert*-butyl-9-ethyl-9,10-dihydroanthracene, respec-