15 min at 85°. Distillation gave dimethylphenyldifluorophosphorane[25,26] (**10**) in 91% yield. This substance had bp 30° (0.02 mm). The ^1H nmr spectrum of a fresh solution in $CDCl_3$ at 25° had six protons at τ 8.20 ppm, J_{HP} = 17.7 cps, J_{HF} = 12.5 cps (doublet of triplets), and five aromatic protons. For $(C_6H_5)(CH_3)_2P$: τ 8.75 ppm, J_{HP} = 2.7 cps. See ^{31}P nmr data in the Results section.

The residue from the above distillation solidified and was characterized as $(C_6H_5P)_5$ (**12**), mp 150–155°, $\partial^{31}P = +4.3$ ppm; the material was isolated in 85% yield.

(b) An equimolar mixture of dimethylphenylphosphine and difluorophenylphosphine was kept 5 min at 20°. The mixture was dissolved in CH_2Cl_2 and the solution was analyzed by ^{31}P nmr spectrometry. It contained unreacted tertiary phosphine and fluorophosphine and relatively small amounts of the phosphorane, **10**, and $(C_6H_5P)_5$, **12**, but no other intermediates or by-products.

Reaction with Methyldiphenylphosphine. Equimolar amounts of the reagents were kept 15 min at 20°. No reaction was detected. Reaction was complete after 7 days at 20°. The products were methyldiphenyldifluorophosphorane[25,26] (**11**) and $(C_6H_5P)_5$ (**12**).

Conformationally Isomeric Carbonium Ions in Condensed Ring Systems[1]

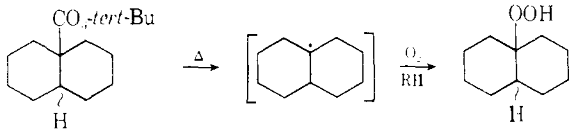
Raymond C. Fort, Jr.,[2] Rex E. Hornish,[3] and Gao A. Liang

Contribution from the Department of Chemistry, Kent State University, Kent, Ohio 44240. *Received May 2, 1970*

Abstract: The *p*-nitrobenzoate esters of cis- and trans-bridgehead alcohols in the decalin, hydrindan, and perhydropentalene systems have been synthesized stereospecifically and solvolyzed in aqueous acetone. The observed rates do not correspond to those expected if both stereoisomers of a given system lead to the same carbonium ion, and the product composition is a function of the stereochemistry of the starting material. When solvolysis is interrupted before completion, recovered *p*-nitrobenzoate has not isomerized. It is, therefore, concluded that solvolysis proceeds by way of conformationally isomeric carbonium ions.

Although many studies have been made of bridgehead carbonium ion reactivity in bridged polycyclic systems,[4–6] bridgeheads in condensed ring systems have received scant notice. There are many qualitative observations of carbonium ion formation at such sites,[7–16] but information of a quantitative sort bearing upon the ease of formation of these bridgehead carbonium ions and their subsequent behavior is lacking. The greater flexibility of the condensed rings offers the possibility that they will be of "normal" reactivity;[6] interesting stereochemical problems are raised by the existence of the condensed rings in diastereomeric forms.

An example of this latter point may be found in the radical chemistry of the decalins. When the *tert*-butyl peresters of the decalin-9-carboxylic acids are decomposed thermally in the presence of high pressures of oxygen (eq 1),[17] the stereochemistry of the hydroperoxide product is found to be a function of the stereochemistry of the perester precursor. This observation implies the brief existence of two discrete 9-decalyl radicals. A similar result was obtained when the isomeric 9-decalyl carbinyl hypochlorites were decomposed.[18] In each case, it was suggested that the distinction between the two radicals is a conformational one: a cis-like radical relaxing to a trans-like one.



(1)

It seemed to us that a search for such behavior in a carbonium ion process might well prove interesting, and it is thus that we report in this paper our results on the solvolysis of bridgehead derivatives of bicyclo[4.4.0]decane (decalin), bicyclo[4.3.0]nonane (hydrindane), and bicyclo[3.3.0]octane (perhydropentalene). Our aims are to place these systems in the general scheme of bridgehead reactivity and to demonstrate that their reactions are best rationalized by postulating the intervention of conformationally isomeric carbonium ions.

Results

The synthesis of the compounds studied is outlined in Chart I and detailed in the Experimental Section. The necessary alkenes were obtained by literature methods,[14,16,19–21] and their conversion to alcohols

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[1] Portions of this work have been reported previously: R. C. Fort, Jr., and R. E. Hornish, *Chem. Commun.*, 11 (1969); Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN 2.

[2] Author to whom inquiries should be addressed.

[3] University Fellow, 1969–1970; abstracted from the Ph.D. Dissertation of R. E. H., Kent State University, 1970.

[4] D. E. Applequist and J. D. Roberts, *Chem. Rev.*, **54**, 1065 (1954).

[5] U. Schollkopf, *Angew. Chem.*, **72**, 147 (1960).

[6] R. C. Fort, Jr., and P. von R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966).

[7] G. R. Clemo and J. Ormston, *J. Chem. Soc.*, 1778 (1932).

[8] A. Zlatkis and E. A. Smith, *Can. J. Chem.*, **29**, 162 (1951).

[9] F. E. Condon, *J. Amer. Chem. Soc.*, **73**, 3938 (1951).

[10] W. G. Dauben, R. C. Tweit, and R. L. MacLean, *ibid.*, **77**, 48 (1955).

[11] H. Köch and W. Haaf, *Angew. Chem.*, **70**, 311 (1958).

[12] G. Baddeley and E. Wrench, *J. Chem. Soc.*, 1324 (1959).

[13] R. E. Pincock, E. Grigat, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **81**, 6332 (1959).

[14] H. Christol and G. Solladié, *Bull. Soc. Chim. Fr.*, 1299 (1966).

[15] H. Christol and G. Solladié, *ibid.*, 3193 (1966).

[16] H. Christol and J.-M. Bessiere, *ibid.*, 2141, 2147 (1968).

[17] P. D. Bartlett, R. E. Pincock, J. Rolston, W. G. Schindel, and L. A. Singer, *J. Amer. Chem. Soc.*, **87**, 2590 (1965).

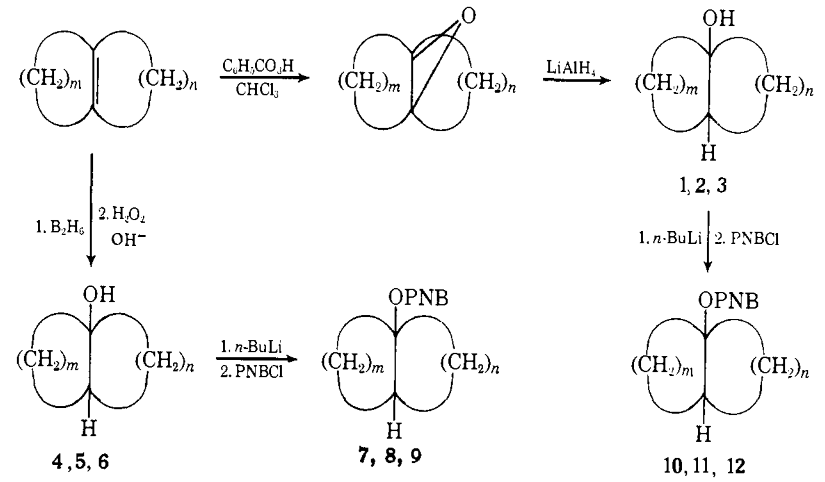
[18] F. D. Greene and B. R. Lowry, *J. Org. Chem.*, **32**, 875 (1967).

[19] W. P. Campbell and G. C. Harris, *J. Amer. Chem. Soc.*, **63**, 2721 (1941).

[20] E. J. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969).

[21] L. A. Paquette and R. W. Houser, *J. Amer. Chem. Soc.*, **91**, 3870 (1969).

Chart I. Synthesis of Condensed Ring *p*-Nitrobenzoates



1, 2, 3

4, 5, 6

7, 8, 9

10, 11, 12

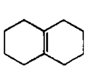
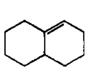
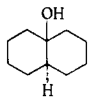
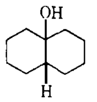
1, 4, 7, 10, $m = n = 4$
2, 5, 8, 16, $m = 4$, $n = 3$
3, 6, 9, 12, $m = n = 3$

follows routes of Dauben[10] and Mousseron.[22] This synthesis has the advantage of involving only reactions of clearly defined stereochemical course and, when coupled with Brown's[23] method for the preparation of *p*-nitrobenzoates, provides esters free of any trace of stereoisomeric impurities and of suitable reactivity for solvolytic studies.

Table I. Rates of Solvolysis of Condensed Ring Bridgehead *p*-Nitrobenzoates in 60% Acetone

p-Nitrobenzoate	*T*, °C	Buffer	$k_1 \times 10^{-6}$, sec^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
cis-9-Decalyl	100	None	22.1	27.6	−11.0
	100	NaOAc (2 equiv)	22.2	29.5	−1.1
trans-9-Decalyl	100	None	6.90	28.1	−9.0
	100	NaOAc (2 equiv)	7.05	31.5	+1.8
cis-8-Hydrindanyl	80	None	21.1	27.0	−3.7
	80	NaOAc (2 equiv)	22.0	27.1	−3.6
trans-8-Hydrindanyl	80	None	79.3	26.4	−2.9
	80	NaOAc (2 equiv)	85.9	27.8	+1.2
cis-Bicyclo[3.3.0]octyl-1	100	None	0.86	29.9	−2.1
trans-Bicyclo[3.3.0]-octyl-1	50	None	61.8	23.1	−2.1

Table II. Decalyl Solvolysis Products, 60% Acetone, 100°, Ten Half-Lives[a]

		Per cent of			
p-Nitrobenzoate	Buffer				
cis-9-Decalyl	None	62.3	33.2	1.4	0.0
	NaOAc (2 equiv)	45.0	48.0	4.0	2.0
trans-9-Decalyl	None	55.5	36.3	4.8	0.0
	NaOAc (2 equiv)	39.0	59.0	2.0	0.0

[a] All percentages ±0.5% reproducibility.

The kinetic data and product analyses obtained upon solvolysis of the *p*-nitrobenzoates (PNB's) in 60% aqueous acetone are collected in Tables I–IV. Data for some model systems are shown in Table V. All rates were followed for at least three half-lives, and strictly first-order behavior was observed in both the buffered and unbuffered solutions. Product analyses were by capillary gas chromatograph, employing authentic comparison samples, and are reproducible to ±0.5%. A control experiment showed that the rather large effect of added sodium acetate upon the product ratio during solvolysis of the *cis*-1-bicyclo[3.3.0]octyl *p*-nitrobenzoate results from interruption of acid-catalyzed hydration of the $\Delta^{1,5}$-bicyclo[3.3.0]octene.

In the hydrindanyl series, pure samples of the alkenes **13** and **14** were not available readily, and the following approach was employed to distinguish between them in the solvolysis product mixture. Dehydration of commercially available 7-hydrindanol (eq 2) with phosphorus oxychloride in pyridine (nonequilibrating condi-

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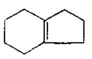
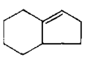
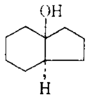
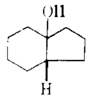
(22) M. Mousseron, M. Mousseron-Canet, G. Phillippe, and J. Wylde, *C. R. Acad. Sci., Paris*, **256**, 51 (1963).

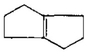
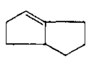
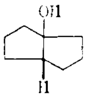
(23) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Amer. Chem. Soc.*, **86**, 1248 (1964).

Table III. Hydrindanyl Solvolysis Products, 60% Acetone, 100°, Ten Half-Lives[a]

		Per cent of			
p-Nitrobenzoate	Buffer				
cis-8-Hydrindanyl	None	73.2	23.5	0.0	3.3
	NaOAc (2 equiv)	60.7	30.4	3.5	5.4
trans-8-Hydrindanyl	None	45.0	51.3	0.0	3.7
	NaOAc (2 equiv)	21.0	76.0	1.0	2.0

[a] All percentages ±0.5% reproducibility.

Table IV. Bicyclo[3.3.0]octyl Solvolysis Products, 60% Acetone, 100°, Ten Half-Lives[a]

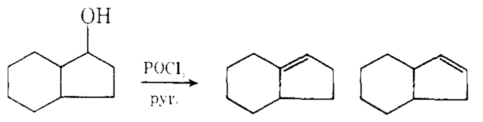
		Per cent of[b]		
p-Nitrobenzoate	Buffer			
cis-1-Bicyclo[3.3.0]octyl	None	10	2	88
	NaOAc (2 equiv)	88	7	5
trans-1-Bicyclo[3.3.0]octyl	None	13	72	15
	NaOAc (1.5 equiv)	14	83	3

[a] All percentages ±0.5% reproducibility. [b] No trans alcohol detected (<0.5%).

Table V. Solvolysis of Some Model *p*-Nitrobenzoates in 60% Acetone

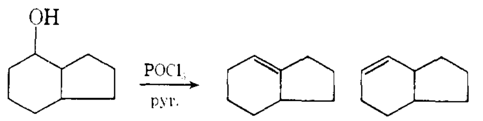
p-Nitrobenzoate	*T*, °C	$k_1 \times 10^6$, $\sec^{-1}$	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
$(CH_3)_3C-$	100	18.5	28.0	−5.7
$(CH_3CH_2)_3C-$	100	99.1	27.3	−4.0
1-Methylcyclopentyl	80	23.1	25.9	−6.7
1-*n*-Butylcyclopentyl	80	42.2	25.7	−6.0
1-Methylcyclohexyl	100	15.3	29.5	−2.0

tions) must give a mixture of **13** and **15**. Since **15** is unlikely to be a solvolysis product, that component of the solvolysis product mixture which is identical with one of the two components of the dehydration mixture must be **13**.



13 **15** (2)

A sample containing **14** was prepared as shown in eq 3. Gas chromatographic comparison then established that **13** only was present in the solvolysis product mixture; **14** was shown to be present in the mixture obtained when the bicyclo[4.3.0]nonenes are equilibrated[24] over P_2O_5 and among the products of the silane trapping experiments.



14 **16** (3)

A number of attempts were made to "trap" the carbonium ion intermediates in the solvolyses. The first of these, solvolysis of the decalyl *p*-nitrobenzoates in aqueous dioxane in the presence of sodium borohydride, led only to the formation of an orange solid which is assumed to be the product of reductive coupling of two ester moieties through the nitro groups.

Samples of the 9-decalyl chlorides and bromides, rich in either the cis or the trans isomers, were then prepared by reaction of the alcohols with thionyl chloride or bromide. Solvolysis of these compounds in aqueous dioxane or diglyme, with sodium borohydride present, produced no detectable decalin (as little as 1% could have been found). Similarly, solvolysis of the halides in the presence of sodium azide yielded no decalyl azides, although small amounts of alcohol were formed. Attention was therefore turned to what promised to be a more efficient method of trapping.

Carey and Tremper[25,26] have reported that carbonium ions of reasonable stability can be reduced readily to the corresponding hydrocarbons by hydride transfer from organosilanes. The cation is generated from the alcohol and trifluoroacetic acid in a methylene chloride solution containing the organosilane. This method was applied to the isomeric 9-decalols and 8-hydrindanols with the results presented in Tables VI and VII. No attempt was made to trap the bridgehead perhydropentalenyl cation because of the limited amounts of alcohols available.

Discussion

Kinetic Data. The relative rate data collected in Chart II show that the condensed ring derivatives of this study display "normal" reactivity in comparison to other simple tertiary systems. This is not surprising, since the bridgehead cations can be easily constructed with Drieding models, an observation which implies the presence of only minimal strain. One notes particularly the similarity between the decalins and 1-

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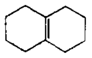
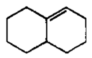
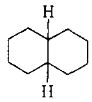
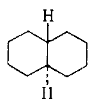
[24] Studies of the equilibrium composition of bicyclo[4.3.0]nonene mixtures will be reported elsewhere.

[25] F. A. Carey and H. S. Tremper, *J. Amer. Chem. Soc.*, 90, 2578 (1968).

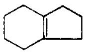
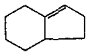
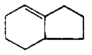
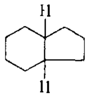
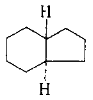
[26] F. A. Carey and H. S. Tremper, *J. Org. Chem.*, 34, 4 (1969).

Table VI. Decalyl Carbonium Ion Trapping[a]

		Per cent of			
Alcohol	Organosilane				
cis 9-Decalol	$(C_6H_5)_3SiH$	75	25	0	0
	Et_3SiH	70	20	10	0
trans-9-Decalol	$(C_6H_5)_3SiH$	60	40	0	0
	Et_3SiH	35	39	1	25

[a] With R_3SiH in $CF_3CO_2H-CH_2Cl_2$.

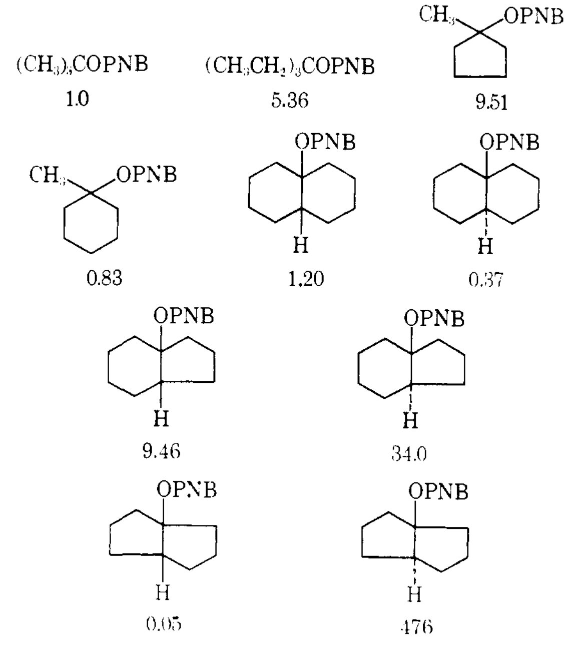
Table VII. Hydrindanyl Carbonium Ion Trapping[a]

		Per cent of				
Alcohol	Organosilane					
cis-8-Hydrindanol	$(C_6H_5)_3SiH$	95.0	5.0	0.0	0.0	0.0
	Et_3SiH	83.0	7.0	0.0	6.0	4.0
trans-8-Hydrindanol	$(C_6H_5)_3SiH$	90.0	6.0	3.0	0.0	1.0
	Et_3SiH	62.0	13.0	7.0	3.0	15.0

[a] With R_3SiH in $CF_3CO_2H-CH_2Cl_2$.

methylcyclohexyl and between the hydrindans and 1-methylcyclopentyl.

Chart II. Relative Solvolysis Rates of *p*-Nitrobenzoate Esters in 60% Aqueous Acetone at 100°



It is, however, the cis/trans rate ratios for the condensed rings which are important to further discussion. Condon[9] pointed out in 1951 that if the decalins (or their derivatives) ionized to a common carbonium ion, then the relative rates of ionization should be governed by the relative ground-state energies. This reasoning only holds true, of course, insofar as the transition state for ionization resembles the carbonium ion; the assumption that it does is a common and reasonable one.[27]

Analysis of the condensed ring solvolysis rates in these terms is fairly straightforward, since ground-state energies for such molecules may be estimated readily. The Arrhenius equation then allows conversion of the calculated energy difference into an appropriate rate ratio. The results of such an analysis are given in Table VIII; the manner in which they are obtained is outlined below.

Table VIII. Predicted Rate Ratios for Condensed Ring Solvolyses

System	ΔE_a, kcal[a]	k_{cis}/k_{trans} (calcd)	k_{cis}/k_{trans} (obsd)
Decalyl	1.7	18	3.2
Hydrindanyl	0.05	~1	0.27
Perhydropentalenyl	−6.9	8.8×10^{-6}	9.8×10^{-6}

[a] $E_{cis} - E_{trans}$.

In order to estimate the ground-state energy differences, two factors must be considered: the intrinsic energy differences between the isomeric hydrocarbon skeletons, and the excess energy resulting from interactions involving the bridgehead substituent—in this case, the PNB ester substituent. It is well known that *cis*-decalin is of higher energy than *trans*-decalin; both direct equilibration[28] and heats of combustion[29] yield a value of 2.7 kcal/mol for the difference, in good agreement with the excess of three *gauche*-butane interactions in *cis*-decalin. The ester function in the trans isomer is axial to only one ring. The *A* value for the *p*-nitrobenzoate group is known to be 1.0 kcal/mol,[30] and thus 2.0 kcal is to be added to the energy of the trans isomer and 1.0 kcal to the energy of the cis. The overall energy difference is then 3.7 −

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(27) G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967).

(28) N. L. Allinger and J. L. Coke, *ibid.*, **81**, 4080 (1959).

(29) D. M. Speros and F. D. Rossini, *J. Phys. Chem.*, 64, 1723 (1960).

(30) G. F. Hennion and F. X. O'Shea, *J. Amer. Chem. Soc.*, **80**, 614 (1958).

2.0 = 1.7 kcal/mol, favoring the *trans*-PNB. Equating this value with the difference in activation energies for solvolysis (Table I indicates that the rate difference is entirely in the activation enthalpy), one estimates that *cis*-decalyl PNB should solvolyze about 18 times more rapidly than the trans isomer at 25°, if both yield the same carbonium ion.

For analysis of the remaining two systems it is necessary to know the energy of a pseudoaxial group on a cyclopentane ring, an interaction which has not been identified unambiguously. The rough estimate that such interactions average $\sim 90\%$ of their value in cyclohexanes can be made by comparing the energy differences between the 1,2-dimethylcyclopentanes[31] and the cyclopentane-1,2-dicarboxylic acids[32] with the values for their cyclohexyl counterparts. A value of 0.9 kcal/mol has therefore been employed for the PNB substituent pseudoaxial on a cyclopentane. (Should the actual value be smaller, the more realistic direction of error,[33] the conclusions of the analysis remain unaltered.) Coupled with a value of 1.0 kcal/mol for the excess energy of *cis*- over *trans*-hydrindan,[28,34,35] and 6.0 kcal/mol for that of *trans*-perhydropentalene over the cis isomer,[36] this estimate yields the energies and predicted rate rations in Table VIII.

On comparison of the predicted and observed rate ratios, one may see that *in no case* are the observed ratios as large as those predicted. It follows, therefore, that a single carbonium ion is *not* the intermediate in the solvolysis of a given pair of isomers. While recognizing that such an argument, in view of the assumptions and inaccuracies necessarily inherent, is at best indicative, one may feel that as part of the overall picture of these solvolyses, it is useful. The suggestions derived from it are confirmed by examination of the product distributions.

Product Data. Substantial variations are observed in the product distribution (Tables II–IV) as a function of initial stereochemistry when the PNB's are solvolyzed in buffered media. Three explanations would seem to be available for consideration: (1) that solvolysis is actually bimolecular, the major reaction being an E2 elimination; (2) solvolysis leads initially to a tight ion pair, with the product composition being determined by the position of the *gegenion;* and (3) unencumbered, conformationally distinct cations are the product determining intermediates.[37] Let us consider each of these possibilities in turn.

It is a dictum of the dichotomy between unimolecular and bimolecular substitution or elimination that the rate of the bimolecular process shall be a function of the concentration of nucleophile or base. Table I shows that the rates of reaction of the condensed ring PNB's are virtually unchanged (5% or less) in the presence of a molar excess of sodium acetate. Furthermore, the preferred trans-anti-parallel arrangement[38-41] of leaving group and proton obtains between the PNB leaving group and the remaining bridgehead hydrogen in all three of the trans isomers studied. The resulting alkene would be tetrasubstituted, and thus more stable than any other possibility; yet in no case is that alkene the major product of buffered solvolysis of a *trans*-PNB. Thus it is clear that the bimolecular process is not of consequence.

Ion pair or gegenion control of product formation cannot be definitely ruled out, but there are several lines of reasoning which suggest that it is probably unimportant.

In the classic experiments of Goering on ion pair formation from *p*-nitrobenzoates,[42-44] these intermediates revealed themselves by equilibration of label in the ester portion of the molecule, and by racemization of the alkyl portion. In the condensed rings, the equivalent of racemization is interconversion of geometrical isomers. We therefore interrupted solvolyses of the decalyl and hydrindanyl PNB's after one half-life had elapsed, and recovered the unreacted ester. Proton magnetic resonance analysis (see Experimental Section) indicated that within the limits of the method, ±5%, no isomerization had occurred with any of the four PNB's.

This result strongly suggests, but by no means conclusively proves, that tight ion pairs are not significant product-determining intermediates. The qualification is necessary since it is possible that for steric reasons the *p*-nitrobenzoate anion may be unable to move readily from one side of the cation to the other.[45,46] Solvent separated ion pairs are not, of course, ruled out by this test.

The trapping data of Tables VI and VII also bear upon the ion pair question. Reaction of the isomeric alcohols with trifluoroacetic acid cannot involve ion pairs, since the leaving group (H_2O) is neutral. Nonetheless, significant differences in the stereochemistry of the saturated hydrocarbon are observed within a given isomeric pair of alcohols. It would seem clear, then, that some internal factor in the cation is controlling the nature of the products.

A strong tendency toward retention is observed in these trapping experiments. Probably this can be attributed to rapid hydride transfer from the silanes, which would limit interconversion of the cis-like and trans-like cations. Differences in product composition as a function of the nature of the silane are expected[26] since by virtue of lesser steric interactions, triethylsilane is a more efficient hydride donor than triphenylsilane. One might also note that the olefin composi-

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tion will also depend somewhat upon the exact reaction time, for the olefins are equilibrated by the CF_3COOH.

Finally, one must consider whether a conformational distinction between two cations could persist long enough to be the responsible factor. Interconversion of two condensed ring cations, or their relaxation to some common species, would serve to smooth out the product differences. Such a question can be answered in two ways.

The molecular relaxations which would be required to equilibrate these types of systems are known to have rate constants of the order of 10^6–10^8 sec^{-1}.[47,48] On the other hand, carbonium ion capture by solvent, or loss of a proton to solvent, is most likely a diffusion-controlled process, having a rate constant of the order of 10^9–10^{11} sec^{-1}.[49,50] Thus reaction of the cations with solvent may be expected to be much faster than any process which would serve to remove the conformational distinction.

Experimental affirmatives to this question are also to be found, for example, in the elegant work of Collins[51] on the 1,2,2-triphenylethyl system, and in the studies of Murr in the diphenylnaphthyl series.[52,53] In each of these cases a reasonable explanation requires that the cations be able to maintain conformational integrity.

Conclusions

Taken altogether, the evidence presented seems to weigh strongly on the side of conformationally isomeric cations as intermediates in the solvolysis of these condensed ring derivatives. A consistent interpretation of the rates, the product variations, and the trapping experiments would seem to require the intervention of these species. If ion pairs are to play a part, it would seem to be a minor one, perhaps just a small modification of the conformational effect. The cations from a given system are pictured as differing by retaining something of the ring geometry of their precursors. Speculation as to their exact "shapes" is presently fruitless since no evidence bearing upon this point is available aside from the notoriously inaccurate method of inspection of models. Further experiments designed to shed more light on these solvolyses are in progress.

Experimental Section

Melting and boiling points are uncorrected. Pmr spectra were recorded with a Varian A-60 spectrometer. Gas chromatographic analyses employed a Perkin-Elmer 810 chromatograph with flame ionization detector; the column was a 150-ft capillary column, coated with DC-550 silicone. Elemental analyses are by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Kinetic Measurements. These were carried out employing the ampoule technique. Duplicate runs were made in all cases; in no case was the difference greater than ±5%, and more than half the runs agreed to within ±2%.

Product Analyses. Approximately 0.5 g of ester was solvolyzed in 60% acetone for at least five half-lives. The resulting solution was diluted with water and extracted three times with small portions of ether. The combined extracts were washed with 10% sodium carbonate to remove *p*-nitrobenzoic acid, with water, with brine, and dried over anhydrous Na_2SO_4. The volume of the solution was reduced to 3–5 ml by carefully distilling off the ether, and the residue was analyzed by gas chromatography. At least two runs were made, and the results were reproducible to ±0.5%.

Trapping Experiments. These were carried out according to the procedure of Carey and Tremper.[26,26] About 1 mmol of the alcohol was added to 4 ml of methylene chloride containing 2–6 mmol of the organosilane. (Below 2 mmol of silane, trapping is inefficient; from 2 to 6 mmol, little effect on product composition is observed.) Trifluoroacetic acid (2 mmol) was added dropwise, and the solution was allowed to stand at room temperature for 30–40 min with occasional swirling. Excess solid sodium carbonate was added to neutralize the solution, which was then filtered and analyzed on the gas chromatograph.

Bicyclo[4.4.0]decene was prepared by the method of Christol and Solladié.[14]

Bicyclo[4.4.0]decene Oxide. A solution of 0.2 ml of perbenzoic acid in chloroform was prepared according to the procedure of Braun.[54] To this solution is added 19 g (0.145 mol) of bicyclodecene in 100 ml of chloroform. The mixture was allowed to stand for 2 days at 4°, and for 2 days at room temperature. The solution was then washed four times with 1 *N* sodium hydroxide, with water, and with brine. After drying over sodium sulfate, the solvent was stripped on a rotary evaporator. Distillation of the residue gave 14.2 g (65%) of epoxide, bp 90–93° (14 mm) (lit.[14] bp 88° (16 mm)).

trans-**9-Decalol (1).** Bicyclodecene oxide (14.0 g, 0.092 mol) was added dropwise over a period of 2 hr to a suspension of 6.0 g (0.16 mol) of lithium aluminum hydride in 200 ml of dry tetrahydrofuran (distilled from calcium hydride). The resulting mixture was stirred at reflux for 12 hr, then cooled, and saturated sodium sulfate solution added dropwise until the powdery salts settled out quickly when stirring was stopped. The salts were filtered off with suction, the solvent evaporated, and the residue distilled. There was obtained 5.6 g (40%) of alcohol, bp 98–102° (18 mm) (lit.[10] bp 60–61° (1.4 mm)), solidifying to a waxy solid in the receiver.

cis-**9-Decalol (4).** Bicyclodecene (25.0 g, 0.184 mol) was added all at once to a suspension of 2.27 g (0.06 mol) of sodium borohydride in 150 ml of dry diglyme contained in a 500-ml three-necked flask equipped with a mechanical stirrer, pressure-equalizing addition funnel, and nitrogen inlet and outlet. The system was thoroughly flushed with dry nitrogen and a slight positive pressure maintained. Boron trifluoride etherate (11.5 g, 0.08 mol) was added dropwise over 1 hr. The resulting solution was stirred at room temperature for 3 hr. Crushed ice (25 g) was then added, followed by 40 ml of 3 *N* sodium hydroxide, and 30 ml of cold 30% hydrogen peroxide (added dropwise). Stirring was continued an additional 2 hr, after which the mixture was poured into water and extracted with ether. The extracts were washed with water and brine, and dried over sodium sulfate. Removal of solvent and distillation gave 10.2 g (60%) of alcohol, bp 118° (18 mm), solidifying in the receiver.

trans-**9-Decalyl** ***p*****-Nitrobenzoate (10).** *trans*-9-Decalol (3.86 g, 0.025 mol) was dissolved in 75 ml of dry hexane and placed in a 250-ml three-necked flask fitted with a reflux condenser, an injection septum, and nitrogen inlet. The solution was stirred magnetically, and thoroughly flushed with dry nitrogen. *n*-Butyllithium in hexane (8.6 ml of 2.9 *M* solution = 0.026 mol) was injected through the septum. The resulting champagne-colored solution was heated at reflux for 20 min. The septum was replaced by a pressure-equalizing addition funnel and a suspension of 4.65 g (0.025 mol) of freshly recrystallized *p*-nitrobenzoyl chloride in 70 ml of dry hexane was added over 10 min. The mixture was stirred at reflux for 3 hr and then filtered while hot to remove the lithium chloride. Upon cooling the *p*-nitrobenzoate deposited as pale yellow crystals. Recrystallization from hexane gave 2.7 g (34%) of pure ester, mp 166.0–167.3°.

Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98. Found: C, 67.25; H, 6.98.

cis-**9-Decalyl** ***p*****-Nitrobenzoate (7).** The procedure was identical with that used in the preparation of the trans isomer **10**. The yield was 41%, mp 129.0–130.0°.

Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98. Found: C, 67.25; H, 7.01.

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Bicyclo[4.3.0]nonene was prepared according to the method of Christol and Solladié.[15]

Bicyclo[4.3.0]nonene oxide was prepared by the same method as the decene oxide; since the alkene was impure, the oxide was also, bp 60–68° (15 mm) (lit.[15] bp 70–76° (20 mm)). No attempt was made at further purification.

trans-**8-Hydrindanol (2).** This alcohol was prepared by the lithium aluminum hydride reduction of the epoxide, as above. The yield was 85% of product, bp 82–85° (11 mm).

cis-**8-Hydrindanol (5).** This alcohol was prepared by the same hydroboration–oxidation sequence used for **4**. It had bp 85–88° (4.5 mm). Since gas chromatography indicated that it was only about 75% pure (contamination with secondary alcohols), it was further purified by column chromatography on alumina.

trans-**8-Hydrindanyl *p*-nitrobenzoate (11)**, prepared as above, had mp 138.5–139.5°. The yield was 65%.

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62. Found: C, 66.56; H, 6.56.

cis-**8-Hydrindanyl *p*-nitrobenzoate (8)**, obtained in 62% yield, had mp 100.5–101.5°.

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62. Found: C, 66.58; H, 6.70.

Bicyclo[3.3.0]octene. The method of Corey[20] and Paquette[21] was employed. In our hands the yield was 65% of a substance having ir and pmr spectra identical with those reported.

Bicyclo[3.3.0]octene Oxide. This epoxide was prepared as described above. The yield was 78% of epoxide, bp 55–60° (20 mm) (lit.[55] bp 92° (74 mm)).

trans-**Bicyclo[3.3.0]octan-1-ol (8).** This preparation followed that of 1. There was obtained 61% product, bp 75–78° (20 mm), solidifying to a waxy solid in the receiver.

cis-**Bicyclo[3.3.0]octan-1-ol (6).** This alcohol was prepared by the hydroboration–oxidation method. Yield was 65% of material with bp 85–87° (16 mm) which solidified in the receiver. The ir was identical with that reported by Cope.[55]

trans-**1-Bicyclo[3.3.0]octyl *p*-nitrobenzoate (12)** was obtained in only 25% yield. It had a pseudo melting point at 135–136° and decomposed at 235°.

Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; Found: C, 65.48; H, 6.17.

cis-**1-Bicyclo[3.3.0]octyl *p*-nitrobenzoate (9)** was obtained in 65% yield and had mp 124.0–124.8°.

Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22. Found: C, 65.59; H, 6.21.

Test for Ion Pair Formation. A 100-mg portion of ester was refluxed in 15 ml of 60% acetone for one half-life. The resulting solution was poured into water and extracted four times with small portions of ether. The combined extracts were washed with 10% sodium carbonate to remove *p*-nitrobenzoic acid, with water, and with brine, and dried over sodium sulfate. After removal of solvent, the entire residue was dissolved in deuteriochloroform and its pmr spectrum obtained. Spectra of authentic mixtures were employed for comparison, and it was shown that as little as 5% of one isomer in the other could be detected.

Resonances important for characterization were the *p*-nitrobenzoate absorption which differed by about 4 Hz between isomers and an absorption at 2.2 ppm in the cis isomers which was entirely lacking in the trans isomers.

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Ether Cleavage and 1,3-Hydride Shifts in Reactions Involving Unsaturated Carbonium Ions[1a]

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Abstract: High yields of anisole and 2-methoxyethyl 2-methyl-1-propenyl ether (III) are obtained when a solution of 5,5-dimethyl-*N*-nitrosooxazolidone (I) and phenol in 1,2-dimethoxyethane is treated with sodium phenoxide. A mechanism involving formation of an oxonium salt from solvent and an unsaturated carbonium ion is proposed to account for the results. Treatment of I with sodium phenoxide in benzene containing phenol yields a mixture of 2-methyl-1-propenyl phenyl ether (IV) and 2-methallyl phenyl ether (V) which are not interconverted under the experimental conditions. Mechanisms involving a 1,3-hydride shift are proposed to account for the results. An isotope effect is apparent in the 1,3-hydride shift.

The reaction of 5,5-dialkyl-*N*-nitrosooxazolidones with alkoxides in alcohols leads to the formation of a variety of vinyl ethers in good to high yields.[2] The present work was undertaken to see if aryl vinyl ethers could be prepared by a similar route.

When a solution of 5,5-dimethyl-*N*-nitrosooxazolidone (I) in glyme (1,2-dimethoxyethane) was added to a solution of sodium phenoxide and phenol in glyme an exothermic reaction took place and approximately the theoretical yield of nitrogen was evolved. By suitable work-up and glpc analysis of the products 79% anisole (II), 74% 2-methoxyethyl 2-methyl-1-propenyl ether (III), and only 11% of the expected 2-methyl-1-propenyl phenyl ether (IV) were shown to be present. The unexpected cleavage of the solvent in this reaction can be explained by postulating that an unsaturated carbonium ion (A) is formed from I and complexes with an ether linkage of glyme to yield the oxonium salt (B) which is attacked by phenoxide ion to yield anisole (II) and the vinyl ether III as shown in Scheme I.[3]

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