10% 1,2,3-tris-(2-cyanoethoxy)-propane on Celite at 170° showed only a single peak.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.87; H, 10.69.

The 2,4-dinitrophenylhydrazone, prepared in the usual manner, melted at 177.5–179.0° dec. (ethyl acetate–petroleum ether).

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 57.82; H, 6.07. Found: C, 58.09; H, 5.79.

The semicarbazone melted at 210–211° dec. (ethanol); $\lambda_{max}^{95\%\ EtOH}$ 229.8 mμ, ϵ_{max} 11,100.

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.13; H, 9.15; N, 20.08. Found: C, 63.32; H, 9.10; N, 20.17.

The oxime melted at 110.0–110.6° (ethanol–water).

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.25. Found: C, 71.90; H, 10.12.

cis-5-Cyclodecenone (VIII) was reduced to *cis*-5-cyclodecenol as follows. A solution of 0.53 g. (3.48 mmoles) of VIII in 30 ml. of ether was slowly added to a stirred slurry of 0.3 g. (7.9 mmoles) of lithium aluminum hydride in 35 ml. of ether. When addition was complete, the mixture was stirred for an hour. After the excess hydride was destroyed with saturated aqueous ammonium chloride, the mixture was extracted with ether in a continuous extractor for 18.5 hr. Evaporation of the ether yielded 0.537 g. (3.48 mmoles) of a solid alcohol, m.p. 43–44°. This product had an infrared spectrum (CCl₄ solution) identical with that of authentic *cis*-5-cyclodecenol.

Oxidation of *trans*-5-Cyclodecen-1-ol.—*trans*-5-Cyclodecen-1-ol (II, X = OH) was oxidized by the method described above for the *cis* isomer. A mixture of products (isomers) was obtained in 71% yield, b.p. 99–103° (15 mm.), $n^{25}D$ 1.4918–1.4923.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.50; H, 10.87.

Gas chromatographic analysis of this material with a 6-ft. column of 10% 1,2,3-tris-(2-cyanoethoxy)-propane on Celite (170°) showed it to consist of at least three components. The major component comprised about 80% of the total material. This was identified as *trans*-5-cyclodecenone (VII) by its infrared spectrum. A semicarbazone derivative was prepared by treating the crude ketone with semicarbazide hydrochloride and sodium acetate in aqueous ethanol; m.p. 179.5–180.5° (acetonitrile), $\lambda_{max}^{95\%\ EtOH}$ 232.3 mμ, ϵ_{max} 11,000.

Anal. Calcd. for $C_{11}H_{19}N_3O$: C, 63.13; H, 9.15. Found: C, 63.22; H, 8.94.

Attempts to prepare the 2,4-dinitrophenylhydrazone and the p-nitrophenylhydrazone failed.

Pure *trans*-5-cyclodecenone (VII) was obtained from the crude ketone (oxidation product) by gas chromatography (1,2,3-tris-(2-cyanoethoxy)-propane on Celite at 170°), followed by low temperature recrystallization from pentane.[18] Capillary gas chromatography (Ucon) showed this material to be over 99% pure. The infrared and ultraviolet spectra also indicated this material was homogeneous.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.80; H, 10.58.

Reduction of 0.521 g. (3.42 mmoles) of the crude ketone with lithium aluminum hydride by the method described for the reduction of the *cis* isomer VIII gave an almost quantitative yield of colorless oil. The infrared spectrum of this material was slightly different from that of *trans*-5-cyclodecenol. The material was dissolved in 15 ml. of olefin-free petroleum ether and shaken with 10 ml. of 10% aqueous silver nitrate. The two phases were separated and the petroleum ether solution evaporated, yielding 0.145 g. of material which was not investigated further. The silver nitrate solution was added to 20 ml. of ice-cold ammonium hydroxide and the resulting emulsion was extracted with ether. The yield of crude unsaturated alcohol was 0.220 g. (42%). This material was converted to 0.280 g. of p-nitrobenzoate, m.p. 108.0–109.0°, which was identical with authentic *trans*-5-cyclodecenyl p-nitrobenzoate.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

Transannular Interactions. IV. Products and Rates of Solvolysis of *cis*- and *trans*-5-Cyclodecen-1-yl *p*-Nitrobenzoate in Aqueous Acetone[1]

BY HARLAN L. GOERING AND WILLIAM D. CLOSSON[2]

Transannular participation by the double bond is involved in the solvolysis of *cis*- (Ia) and *trans*-5-cyclodecen-1-yl *p*-nitrobenzoate (II) in aqueous acetone. In each case the first-order rate is enhanced (alkyl–oxygen cleavage is involved) and only bicyclic products are formed. At 120° the *trans*-*p*-nitrobenzoate II is about 300 times more reactive than the *cis* isomer Ia which in turn is more reactive than the saturated analog, cyclodecyl *p*-nitrobenzoate. The *cis* isomer Ia is converted to *cis-cis*-1-decalol (V). Solvolysis of the *trans*-*p*-nitrobenzoate II is accompanied by an isomeric rearrangement (ca. 18%) to an unreactive product. The solvolysis product is *trans-trans*-1-decalol (IV) and the rearrangement product is mainly *trans-cis*-1-decalyl *p*-nitrobenzoate (III). The rearrangement product III formed from carbonyl-O¹⁸-*trans*-*p*-nitrobenzoate II has two-thirds of the label in the carbonyl position.

An investigation of the solvolysis of *cis*-5-cyclodecen-1-yl *p*-toluenesulfonate (Ib) was reported in an earlier paper.[3] In that work it was found that at 30° the unsaturated *cis*-*p*-toluenesulfonate Ib ethanolizes ten times faster and acetolyzes seven times faster than the saturated analog cyclodecyl *p*-toluenesulfonate. From the solvolytic behavior and the formation of bicyclic solvolytic and rearrangement products, it was concluded that ionization probably involves "transannular"[4] participation by the double bond.
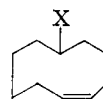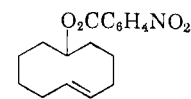
Ia, X = $O_2CC_6H_4NO_2$
b, X = OTs
c, X = OH

II

Transannular interactions involving carbon–carbon double bonds have been observed in other medium-sized ring systems. Pertinent examples

include the acid-catalyzed (a) hydration of caryophyllene oxide,[5] (b) cyclizations of the maleic anhydride "adduct" of caryophyllene[6] and (c) conversion of pyrethrosin to cyclopyrethrosin.[7] The rates and products of solvolysis of cis-4-cycloöcten-1-yl p-bromobenzenesulfonate in acetic acid and trifluoroacetic acid[8] indicate that transannular participation by the double bond is involved in this case also. Similarly the acid-catalyzed conversion of 6-ketocyclodecyl p-toluenesulfonate to bicyclo-[5.3.0]decan-2-one apparently involves enolization followed by a unimolecular cyclization of the enol, i.e., transannular participation by the enol double bond.[9]

In the present work the solvolytic reactivities of the cis- and trans-5-cyclodecen-1-yl systems were investigated. The trans system is far too reactive for preparation of the p-toluenesulfonate derivative and for this reason the p-nitrobenzoate derivative II was used. This paper describes an investigation of the products (stereochemistry) and rates of solvolysis (alkyl–oxygen cleavage) of cis-(Ia) and trans-5-cyclodecen-1-yl p-nitrobenzoate (II) in aqueous acetone. The stereochemistry of the cyclizations of these systems was of special interest in connection with recent suggestions that biogeneses of sesquiterpenes involve ionic cyclizations of unsaturated ten-membered ring intermediates.[10]

Results

Rate Measurements.—First-order rate constants for the solvolysis of cis-(Ia)[11] and trans-5-cyclodecen-1-yl p-nitrobenzoate (II)[11] are given in Table I. For comparison purposes, the reactivities of some other p-nitrobenzoates were measured and these data are also included in Table I. With two exceptions (cyclodecyl and trans-cis-1-decalyl p-nitrobenzoate, III) the constants given in the table are the average (and average deviation) of two independent kinetic experiments.

Solvolysis of trans-5-cyclodecen-1-yl p-nitrobenzoate (II) in 90% aqueous acetone at 100° and 120° resulted in the formation of about 0.82 equivalent of p-nitrobenzoic acid by a clean first-order process. The reactions were followed by titration of the p-nitrobenzoic acid and rate constants were determined from the rate of formation of acid. The "infinity" titers observed after ten half-periods at the reaction temperature were used to calculate the first-order constants. In each experiment the reaction was followed to about 80% completion. The rate was cleanly first-order and as can be seen from the small average deviations in Table I, the constants were reproducible. That alkyl-

(5) A. Aebi, D. H. R. Barton and A. S. Lindsey, J. Chem. Soc., 3124 (1953).

(6) A. Nickon, J. Am. Chem. Soc., 77, 1190 (1955).

(7) D. H. R. Barton, O. C. Böckman and P. de Mayo, J. Chem. Soc., 2263 (1960).

(8) A. C. Cope and P. E. Peterson, J. Am. Chem. Soc., 81, 1643 (1959); A. C. Cope, J. M. Grisar and P. E. Peterson, ibid., 82, 4299 (1960).

(9) H. L. Goering, A. C. Olson and H. H. Espy, ibid., 78, 5371 (1956).

(10) (a) J. B. Hendrickson, Tetrahedron, 7, 82 (1959); (b) D. H. R. Barton and P. de Mayo, Quart. Revs., 11, 189 (1957); L. Ruzicka, Experientia, 9, 357 (1953).

(11) H. L. Goering, W. D. Closson and A. C. Olson, J. Am. Chem. Soc., 83, 3507 (1961).

TABLE I

RATE CONSTANTS FOR SOLVOLYSIS OF p-NITROBENZOATE ESTERS (RX) IN AQUEOUS ACETONE[a]

p-Nitrobenzoate	Temp., °C.	[RX], 10^2 M	Solute, 10^2 M	10^5 k, sec.⁻¹
	90% aqueous acetone			
trans-5-Cyclo-decenyl (II)	119.42	2.47		75.4 ±0.2
	99.71	2.3		12.5 = .1
	99.68	2.3	2.6 HOPNB[c]	12.7 ± .4
	99.68	2.3	2.6 NaOPNB[c]	12.2 ± .2
cis-5-Cyclo-decenyl (Ia)	118.59	1.0	0.16 NaOPNB[c]	0.23 ± .01
Cyclodecyl	118.59	2.2	0.16 NaOPNB[c]	0.05[d]
trans-cis-1-Decalyl (III)	119.40	2.5		0.01[e]
α,α-Dimethylallyl	119.41	2.4		6.74 ±0.02
	80% aqueous acetone			
trans-5-Cyclo-decenyl (II)	99.71	2.2		38.7 ±0.05

[a] Indicated solvent composition based on volumes of pure components at 25° before mixing. [b] Except for cyclodecyl and trans-cis-1-decalyl p-nitrobenzoates all constants are average values for two independent kinetic experiments. [c] HOPNB and NaOPNB are p-nitrobenzoic acid and sodium p-nitrobenzoate, respectively. [d] Upper limit estimated from 7.4% reaction after 432 hr. [e] Upper limit estimated from 2.4% reaction after 528 hr.

oxygen rather than acyl–oxygen cleavage is involved in this reaction is shown by both the products and the rate—there is no apparent reason why acyl–oxygen cleavage should be more rapid for II (or Ia) than for cyclodecyl p-nitrobenzoate.

As shown in Table I, the presence of 0.025 M sodium p-nitrobenzoate or p-nitrobenzoic acid had no detectable effect on the rate of solvolysis. Solvolysis of the trans-p-nitrobenzoate II in 80% acetone was about three times faster than in 90% acetone and resulted in the formation of about 0.85 equivalent of p-nitrobenzoic acid.

The difference between the observed and calculated "infinity" titers results from partial rearrangement of the reactant to an unreactive isomer, i.e., solvolysis is accompanied by rearrangement as illustrated below. In this scheme k_s and k_r are first-order constants for solvolysis and rearrangement, respectively. The rate constants given in Table I are for the disappearance of II and thus correspond to $k_r + k_s$.

$$\text{II} \underset{k_r}{\overset{k_s}{\longrightarrow}} \begin{array}{l} \text{solvolysis product} \\ \text{rearrangement product} \end{array}$$
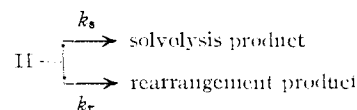
The rearrangement product is relatively unreactive and thus the rearrangement does not disturb the first-order rate of formation of p-nitrobenzoic acid. The ratio of rearrangement to solvolysis, k_r/k_s, can be determined readily from the observed and calculated "infinity" titers (i.e., k_r/k_s is the difference between the calculated and observed titers divided by the observed titer). Values of k_r/k_s for various conditions are given in Table II. These were determined from the calculated titers and those observed at about ten half-periods. Each value is an average (and average deviation) of two independent experiments.

The data show that k_r/k_s is not affected by the presence of sodium p-nitrobenzoate or p-nitrobenzoic acid. The ratio decreases slightly with tem-

TABLE II

RATIO OF REARRANGEMENT (k_r) TO SOLVOLYSIS (k_s) FOR 0.02 M trans-5-CYCLODECEN-1-YL p-NITROBENZOATE IN AQUEOUS ACETONE

Temp., °C.	Added solute, 10^2 M	$k_r/k_s{}^a$
	90% aqueous acetone	
118.6		0.226 ± 0.001
99.6		$.203 \pm .002$
118.6	2.47 NaOPNB^b	$.224 \pm .001$
99.6	2.47 NaOPNB^b	$.191 \pm .009$
118.6	2.54 HOPNB^c	$.235 \pm .001$
99.6	2.54 HOPNB^c	$.205 \pm .006$
	80% aqueous acetone	
118.6		0.170 ± 0.001
99.7		0.164 ± 0.001

^{a} Average value and average deviation of two independent experiments. ^{b} Sodium p-nitrobenzoate. ^{c} p-Nitrobenzoic acid.

perature (rearrangement is more sensitive to temperature changes than solvolysis) and is lower for 80% acetone than for 90% acetone.

A discrepancy between the observed and calculated infinity titers would result from contamination of the reactant with an unreactive isomer as well as from formation of such an isomer during solvolysis. In the present case the unreactive isomer is formed during the solvolysis. This was demonstrated by showing that when II is contaminated with isotopically labeled (O^{18}) trans-cis-1-decalyl p-nitrobenzoate (III), which is the major component of the unreactive rearrangement product, the contaminant is completely removed by the method[11] (recrystallization) used to purify II for the kinetic experiments. Also, the fact that k_r/k_s is solvent and temperature dependent and reproducible shows that the unreactive isomer is formed during solvolysis.

Rate constants for the solvolysis of cis-5-cyclodecen-1-yl p-nitrobenzoate (Ia),[11] α,γ-dimethylallyl p-nitrobenzoate,[12] trans-cis-1-decalyl p-nitrobenzoate (III) and cyclodecyl p-nitrobenzoate in 90% aqueous acetone at 120° are included in Table I. In the case of α,γ-dimethylallyl p-nitrobenzoate the reaction was followed to over 80% completion; no trends were observed and the infinity titer was in good agreement with the calculated value.

The kinetic experiments with cis-5-cyclodecen-1-yl p-nitrobenzoate (Ia) were complicated by the low solubility and reactivity in 90% aqueous acetone. The measurements were made with 0.01 M solutions and the reactions were followed to 30–50% completion. The rate constants, computed using the calculated infinity titers, did not show any trends. Since pure cis p-nitrobenzoate Ia can be isolated in good yields after partial solvolysis, it appears that solvolysis is not accompanied by isomerization. The solvolyses of cyclodecyl and trans-cis-1-decalyl p-nitrobenzoates (III) were so slow that only approximate values for the first-order constants were obtained. These were calculated from the small amounts (a few per cent.) of acid produced after long periods of time. In the latter two cases the reaction probably involves acyl–oxygen rather than alkyl–oxygen cleavage.

(12) H. L. Goering and M. M. Pombo, J. Am. Chem. Soc., 82, 2515 (1960).

Thus k for these compounds is a conservative upper limit for the carbonium-ion process (alkyl–oxygen cleavage).

Solvolysis Products.—The products resulting from the simultaneous solvolysis and rearrangement of 0.03 M trans-5-cyclodecen-1-yl p-nitrobenzoate (II) in 90% acetone at 100° were isolated after twelve half-periods. Vapor phase chromatography (v.p.c.) indicated that a volatile product, which was not identified, is formed in 10–20% yield. The product was separated into an alcohol (60–69% yield) and a p-nitrobenzoate (15–18% yield) fraction by either column chromatography or sublimation. The alcohol fraction was identified as trans-trans-1-decalol (IV) by comparison of the infrared spectrum and p-nitrobenzoate derivative with those of an authentic sample. Vapor phase chromatography showed that this fraction contained 1–2% of a contaminant that had the same retention time as trans-cis-1-decalol.

Recrystallization of the p-nitrobenzoate fraction (the rearrangement product) gave pure trans-cis-1-decalyl p-nitrobenzoate (III) which was identified by comparison with an authentic sample. Saponification of the p-nitrobenzoate fraction gave a binary mixture of alcohols consisting of 85% trans-cis-1-decalol (v.p.c.) and 15% of a material which was not identified but had the same retention time as trans-trans-1-decalol (IV).

Control experiments showed that from 93–95% of the alcohol and 97–99% of the p-nitrobenzoate are isolated by the techniques used in the product studies. It was also found that ester interchange does not occur under the conditions of the solvolysis reaction.

The solvolysis product of cis-5-cyclodecen-1-yl p-nitrobenzoate (Ia) was also isolated. In this case a 0.03 M solution of Ia in 90% aqueous acetone was heated to 120° for 545 hours. This corresponds to about 36% reaction. The product (alcohol) and unchanged p-nitrobenzoate were isolated and separated in the manner described above; 65% of the original Ia was recovered. The solvolysis product obtained in 33% yield (based on the original amount of Ia) was identified as cis-cis-1-decalol (V) by comparison of v.p.c. retention time, the phenylurethan derivative and infrared spectrum with those of an authentic sample. Vapor phase chromatography indicated that this fraction was homogeneous.

When cis-5-cyclodecen-1-ol (Ic) was heated in 90% aqueous acetone under the conditions of the solvolysis reaction it was recovered unchanged. Thus Ic is not a solvolysis product and evidently cis-cis-1-decalol (V) is the initially formed product. It is apparent from the product that the solvolysis of Ia involves alkyl–oxygen cleavage.

Rearrangement of Carbonyl-O^{18} trans-5-Cyclodecen-1-yl p-Nitrobenzoate (II).—To obtain additional information about the rearrangement of II to trans-cis-decalyl p-nitrobenzoate (III) which occurs during solvolysis, the relative positions of the carboxyl oxygen atoms in the reactant II and product III were established. Carbonyl-O^{18}-II was solvolyzed in 90% acetone at 100° and the major rearrangement product, III, was isolated

after ten half-periods. The distribution of O^{18} in III (and also in II) was determined by saponification (acyl–oxygen cleavage), followed by reconversion to the p-nitrobenzoate with unlabeled p-nitrobenzoyl chloride. The O^{18} content of the ester derived in this way corresponds to that of the ether–oxygen position of the original ester. The difference in O^{18} content before and after saponification and re-esterification corresponds to the O^{18} content of the carbonyl position of the original ester.

The results of the O^{18} experiments are summarized in Table III. Experiment 1 shows the O^{18} content of the reactant II. In the second experiment unreacted II was isolated after one half-life to determine if any scrambling occurs prior to reaction. Clearly there is little if any mixing of oxygen atoms in II during solvolysis. In experiment 3 the reaction was carried out in the presence of 0.05 M sodium p-nitrobenzoate. This experiment, in complete agreement with the kinetic results (i.e., k_r/k_s is not affected by p-nitrobenzoate ion), shows that the rearrangement is intramolecular and that none of the label is lost under the conditions of the rearrangement. Experiments 4 and 5 are duplicate experiments and show the O^{18} distribution in III derived from carbonyl-O^{18} II (3.98 atom % excess O^{18}). These experiments show that the III has about one-third of the O^{18} in the alkyl–oxygen position.

TABLE III

OXYGEN-18 DATA FOR CONVERSION OF CARBONYL-O^{18}
trans-5-CYCLODECEN-1-YL p-NITROBENZOATE (II) TO *trans*-*cis*-1-DECALYL p-NITROBENZOATE (III) IN 90% AQUEOUS ACETONE AT 99.6°

Expt.	Compound	Position	Atom % excess O^{18}
1	II[a]	Carbonyl-O	3.98 ± 0.04
2[b]	II	Alkyl-O	0.026 ± .012
3[c]	III	Total	3.99 ± .06
4	III	Alkyl-O	1.37 ± .01
5	III	Alkyl-O	1.33 ± .01

[a] Starting material. [b] The material was recovered from the solvolysis mixture after one half-life at 99.6°. [c] The experiment was carried out in the presence of 0.05 M sodium p-nitrobenzoate.

Discussion

The data in Table I show that in 90% aqueous acetone at 120° *trans*-5-cyclodecen-1-yl p-nitrobenzoate (II) solvolyzes over 300 times faster than the *cis* isomer Ia which in turn is about 5 times more reactive than the saturated analog, cyclodecyl p-nitrobenzoate. It is interesting to note that the *trans*-5-cyclodecen-1-yl system is even more reactive than the α,γ-dimethylallyl system by a factor of over ten. It was shown earlier that solvolysis of α,γ-dimethylallyl p-nitrobenzoate in aqueous acetone involves alkyl–oxygen cleavage.[12,13]

The high reactivities of Ia and II relative to cyclodecyl p-nitrobenzoate indicate that their rates of ionization (solvolysis) are accelerated by transannular participation by the double bond as illustrated for the two isomers by II′ and Ia′. In the absence of participation hydrolysis by acyl-oxygen cleavage would probably take over and the rates would be expected to be comparable with

those of p-nitrobenzoates of saturated secondary alcohols. Presumably the unassisted ionization rates for Ia and II would be substantially lower than the rate of solvolysis of cyclodecyl p-nitrobenzoate. Thus the present data indicate that the ionization rates of Ia and II are accelerated by factors of over 5 and 10^3, respectively.

For several reasons these estimates are lower limits. In the first place, for reasons that will be presented in the Experimental section, the rate constant for cyclodecyl p-nitrobenzoate in Table I is a rough upper limit and in fact may be too high. Secondly, solvolysis of cyclodecyl p-nitrobenzoate may well involve acyl–oxygen cleavage in which case the solvolysis rate exceeds the ionization rate. Finally, the unassisted ionization rate for Ia and II would be expected to be slower than that for the cyclodecyl system. Introduction of a double bond in a ten-membered ring should relieve "medium ring" strain which presumably is responsible for the relatively high reactivity of the cyclodecyl system— cyclodecyl p-toluenesulfonate acetolyzes about 500 times faster than cyclohexyl p-toluenesulfonate.[11] The inductive effect of the double bond would also tend to lower the unassisted ionization rate somewhat.

In connection with the large driving force observed with the *trans*-p-nitrobenzoate II it is interesting to note that the ultraviolet spectrum of the corresponding ketone, *trans*-5-cyclodecenone,[11] contains a solvent-dependent band (λ_{max} 214.5 mμ, ε 2300, in 2,2,3,3-tetrafluoropropanol) which has been assigned to the photodesmotic transition[15]
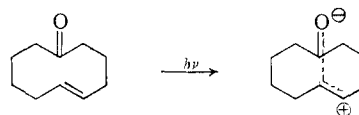
The ultraviolet spectrum of *cis*-5-cyclodecenone[11] does not contain this band.[16] The possibility of a correlation between absorption resulting from such interactions and anchimeric acceleration observed with derivatives of the corresponding alcohols has been noted previously.[17] Thus both the spectra of the isomeric ketones and the relative anchimeric accelerations observed with the isomeric p-nitrobenzoates (Ia and II) indicate that stereoelectronic factors are more favorable for transannular interactions between the double bond and C_1 in the *trans*-5-cyclodecen-1-yl system than in the *cis* isomer.

Solvolysis of *cis*-(Ia) and *trans*-5-cyclodecen-1-yl p-nitrobenzoate (II) results in bond formation between C_1 and C_6 as illustrated by II′ and Ia′. It is interesting that these cyclizations are stereospecific. The *trans* isomer II gives the *trans*-decalyl system and the *cis* isomer Ia gives the *cis*-decalyl system.[18]

(14) R. Heck and V. Prelog, *Helv. Chim. Acta*, **38**, 1541 (1955).

(15) E. M. Kosower, W. D. Closson, H. L. Goering and J. C. Gross. *J. Am. Chem. Soc.*, **83**, 2013 (1961).

(16) W. D. Closson, unpublished results.

(17) For leading references see S. Winstein, L. de Vries and R. Orloski, *J. Am. Chem. Soc.*, **83**, 2020 (1961).

(18) It is interesting that this is the same stereochemistry as that involved in (a) the transannular cyclization of pyrethrosin to cyclo-pyrethrosin[7] (conversion of a *cis*-cyclodecene system to a *cis*-decalin derivative) and (b) the proposed biogenesis of eudesmol[19a] (transan-

(13) H. L. Goering and R. W. Greiner, *J. Am. Chem. Soc.*, **79**, 3464 (1957).

In each case, solvolysis involves a *trans* addition of C_1 and solvent across the C_5,C_6-double bond. On the other hand, the isomeric rearrangement of II to III which accompanies solvolysis amounts to a *cis* addition of C_1 and the migrating p-nitrobenzoate group across the double bond. The isomeric rearrangement involved in the solvolysis of the cis-p-toluenesulfonate Ib is stereochemically analogous to the conversion of II to III; Ib isomerizes to cis-trans-1-decalyl p-toluenesulfonate during solvolysis (ethanolysis and acetolysis).[3]

H (OCOC₆H₄NO₂

II'   →   III, Ar = p-C₆H₄NO₂

H
10
H
9 OH
H
IV

H (OCOC₆H₄NO₂

Ia'   →   V
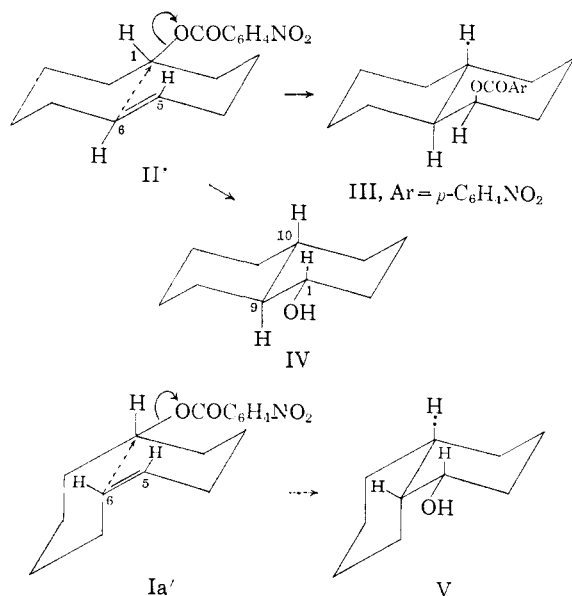
Evidently the rearrangement of II to III involves "ion pair return," probably "internal return."[19] That the process is ionic is indicated by the fact the rate shows about the same sensitivity toward varying the ionizing power of the solvent as does the rate of solvolysis (k_s); cf. k_r/k_s for 80% and 90% acetone. It is clear that the rearrangement is intramolecular because k_r/k_s is not affected by the addition of p-nitrobenzoate ion and the O^{18} experiments show that rearrangement does not result in exchange with either p-nitrobenzoic acid or p-nitrobenzoate ion. The fact that rearrangement results in only partial equilibration of the oxygen atoms (the carbonyl oxygen atom retains its identity in part) suggests that the process involves internal return. Return from a "solvent separated"[19] ion pair is believed to result in complete equilibration of the oxygen atoms in the anion portion of the molecule.[20] On the other hand, cases are known in which internal return results in no or only partial equilibration of the oxygen atoms in a p-nitrobenzoate.[12,20,21]

The observation that carbonyl-O^{18} trans-5-cyclodecen-1-yl p-nitrobenzoate (II) remains discretely labeled throughout the solvolysis indicates that the reactant is not reformed by internal return, i.e., it appears that the rate of solvolysis corresponds

nular cyclization involving a *trans* double bond to give a *trans*-decalin system).

(19) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, J. Am. Chem. Soc., 78, 328 (1956).

(20) S. Winstein and G. C. Robinson, ibid., 80, 169 (1958).

(21) M. M. Pombo and K. D. McMichael, unpublished work.

to the rate of ionization. Internal return to give rearrangement product III results in some oxygen mixing and if only one intimate ion pair intermediate is involved in the ionization–dissociation process, internal return to reactant II should also result in mixing of the oxygen atoms. Internal return has been observed to result in equilibration of carboxyl oxygen atoms during the solvolysis of allylic p-nitrobenzoates[12,21,22a] and benzhydryl p-nitrobenzoate.[22b] However, more than one internal ion pair intermediate may be involved and thus the absence of oxygen equilibration during solvolysis does not rule out the possibility of internal return.

One feature of the stereochemistry of the transannular cyclizations of cis- and trans-5-cyclodecen-1-yl derivatives remains obscure. This concerns the stereochemical change at C_1. If the reactive conformations of the reactants are those illustrated by II' and Ia', displacement of the leaving group at C_1 by C_6 proceeds with inversion of configuration. This arrangement, which allows for nucleophilic attack by the double bond from the rear, seems to be the best one for accounting for the rather large driving force—anchimerically accelerated ionizations evidently invariably involve back-side internal displacements.[23]

However, there is another possibility. This is illustrated for the *trans* isomer by II''. If this conformation is the one involved in the cyclization, C_1 is substituted (by C_6) with retention of configuration. Although there are many precedents for intramolecular front-side displacements, e.g., SNi reactions,[24] these usually occur when there is no alternative. Moreover, these probably often, if not generally, involve internal return from ion pair intermediates in which case front-side attack is not simultaneous with rupture of the original bond. It is not clear to what extent, if any, front-side nucleophilic attack can facilitate departure of a leaving group. Thus one is left with the dilemma that conformation II' nicely accounts for the accelerated ionization, but makes it difficult to rationalize the migration of the ester group from C_1 to C_5 without complete equilibration of the carboxyl oxygen atoms. On the other hand, II'' can nicely account for the stereochemistry[25] and O^{18} results of the rearrangement—the analogous conformation was used to rationalize the isomerization of Ib to cis-trans-1-decalyl p-toluenesulfonate[3]—but it is not clear if such an arrangement can accommodate the rate enhancement. In another problem we are attempting to establish the relative configurations of C_1 in the reactant II and C_{10} in the solvolysis IV and rearrangement products III to settle this point.

The large driving force indicates that ionization of the trans-p-nitrobenzoate II results in the direct

(22) (a) H. L. Goering and J. T. Doi, J. Am. Chem. Soc., 82, 5850 (1960); (b) J. F. Levy, unpublished results.

(23) For leading references see (a) A. Streitwieser, Jr., Chem. Revs., 56, 571 (1956), and (b) D. J. Cram, "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapt. 5.

(24) E. L. Eliel, ibid., Chapt. 2.

(25) The trans-1-decalyl isomer resulting from an intramolecular isomeric rearrangement of either II' or II'' would be expected to give the observed product III, i.e., if the reaction is intramolecular the product resulting from cis addition would be expected in any event.

OCOC$_6$H$_4$NO$_2$

$\longrightarrow$ III + IV

II''
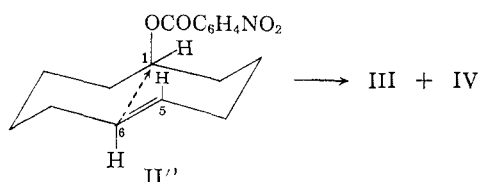
formation of an ion pair in which the cation is the *trans*-1-decalyl carbonium ion VI or the non-classical ion VII. Similarly, the initially formed cation from the *cis-p*-nitrobenzoate is either the classical "rearranged" ion VIII or the bridged non-classical ion IX. The anchimeric accelerations and probably also the stereochemistry are explicable in terms of either the classical or non-classical ions.
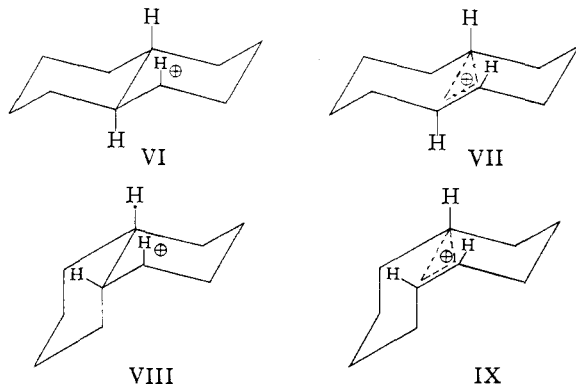
It is of interest in this connection that nitrous acid deaminations of *trans-trans*- and *cis-cis*-1-decalylamine give the corresponding alcohols as the only substitution products,[26] *i.e.*, in both cases there is complete retention of configuration. Presumably these reactions involve the same carbonium ions involved in the solvolysis-product forming step in the present work. The results of the deamination reactions have been interpreted in terms of the classical carbonium ions VI and VIII.[27] The reason proposed[27] for the retention of configuration was that solvent attacks the carbonium ion along the path of easiest approach, the approach to form equatorial alcohol being less hindered than that to form axial alcohol.[27] If this interpretation is correct the classical carbonium ions can similarly accommodate the present results. On the other hand, the non-classical structures for the *cis*-(IX) and *trans*-1-decalyl carbonium ions (VII) account for the products derived from these ions in an obvious way. Indeed, intermediates of this type (*i.e.*, bridged ions) are generally used to rationalize stereospecific *trans* addition reactions (which are observed with both isomers in the present case) and replacement reactions which involve retention of configuration.[23] In other problems we are investigating the structures of bicyclic carbonium ions of this type.

Experimental

Materials.—The *cis*-(Ia) and *trans*-5-cyclodecen-1-yl *p*-nitrobenzoates (II) used in the present work are described in the preceding paper.[11] Cyclodecyl *p*-nitrobenzoate, m.p. 114.5–115.0° (ethanol) (lit.[28] m.p. 116°), was prepared[11]

from cyclodecanol[9] in 93% yield. *trans-cis*-1-**Decalyl** *p*-**nitrobenzoate** (III), m.p. 116.0–116.5° (aqueous methanol) (lit.[26] m.p. 116°), was prepared[11] from *trans-cis*-1-decalol,[3] m.p. 48.0–48.5°, in 72% yield. α,γ-**Dimethylallyl-***p*-**nitrobenzoate**, m.p. 53–54° (lit.[29] m.p. 54°), was prepared from the pure alcohol[12] in 32% yield. *p*-Nitrobenzoic acid, m.p. 240.3–240.9°, was purified by recrystallization from methanol. Sodium *p*-nitrobenzoate was prepared by shaking a solution of 0.119 mole of *p*-nitrobenzoic acid in 200 ml. of ether with 50 ml. of 2.0 *M* aqueous sodium hydroxide. The aqueous layer containing the salt was extracted with ether in a continuous extractor to remove any traces of excess acid and then evaporated until the salt crystallized. The salt was separated by filtration and dried to constant weight at 140° under reduced pressure. An aqueous solution of this salt had a pH of about 8.

Aqueous acetone was prepared by mixing pure acetone (fractionated from calcium chloride) and conductivity water. The pure components were equilibrated at 25° prior to mixing. Solvent compositions are based on the volumes of the pure components at 25°.

Kinetic Experiments.—Standard solutions of the substrates in aqueous acetone were prepared and distributed into ampules. Ester concentrations of 0.020 *M* to 0.025 *M* were used except in the case of *cis*-5-cyclodecen-1-yl *p*-nitrobenzoate (Ia) where the limited solubility necessitated lower concentrations. All concentrations and volumes were measured at 25°.

Aqueous acetone solutions develop an acid titer slowly when heated in the presence of oxygen at high temperatures.[30] For example, the titer of a *0.01 M* solution of pure *p*-nitrobenzoic acid in 90% acetone increased about 35% in 200 hr. at 119° and then decreased slowly. The rate of production of acid by this process was too slow to affect the rate studies of the more reactive esters, *e.g.*, α,γ-dimethylallyl *p*-nitrobenzoate and II which at 119° have half-periods of 29 and 2.5 hr., respectively. However, it is obvious that it would seriously interfere with the less reactive esters. It was found that the acid-producing side reaction could be essentially eliminated by flushing the ampules several times with nitrogen before sealing them.[31] Titers of 0.01 *M* solutions of *p*-nitrobenzoic acid under nitrogen in ampules increased less than 1% when heated for 333 hr. at 119°. In all of the kinetic experiments, except those with the aforementioned reactive esters, ampules were flushed with nitrogen prior to sealing. Even so, it is clear that the acid-producing side reaction may be significant in experiments with cyclodecyl and *trans-cis*-1-decalyl *p*-nitrobenzoate (III), which at 119° react only to the extents of 7.4% in 432 hr. and 2.4% in 528 hr., respectively. Because of this complication the approximate constants in Table I for these two esters may be too high and thus should be considered to be rough upper limits.

The rate of acid formation was measured by potentiometric titration of aliquots with standard 0.025 *M* aqueous sodium hydroxide. A Beckman model G pH meter was used for the potential measurements. The first-order rate constants presented in Table I were calculated from the rate of acid formation in the usual manner.

Standard solutions of the *trans-p*-nitrobenzoate II under nitrogen in sealed ampules were heated for 10–12 half-lives to obtain the data presented in Table II.

Solvolysis Products. (A) *trans*-5-**Cyclodecen-1-yl** *p*-**Nitrobenzoate (II).**—A solution of 1.400 g. (4.61 mmoles) of II in 135 ml. of 90% aqueous acetone in a glass bomb was heated at 99.6° for 188 hr. (*ca.* 12 half-lives). The contents were diluted with 750 ml. of water and made basic to phenolphthalein with dilute sodium carbonate solution and the resulting solution was extracted with 40–60° petroleum ether in a continuous extractor for 71 hr. Gas chromatographic analysis of the petroleum ether solution with a 12-foot column of 20% saturated silver nitrate solution in polyethylene glycol (Carbowax 400) on Celite at 80° indicated the presence of olefin in amounts corresponding to 10–20% yield. The solution was concentrated and

(26) W. G. Dauben, R. C. Tweit and C. Mannerskantz, *J. Am. Chem. Soc.*, **76**, 4420 (1954).

(27) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957).

(28) M. Kobelt, P. Barman, V. Prelog and L. Ruzicka, *Helv. Chim. Acta*, **32**, 256 (1949).

(29) M. M. Pombo, Ph.D. Thesis, University of Wisconsin, 1960.

(30) This has also been noted by M. Silver, private communication, 1960.

(31) This same method has been used recently by M. Silver, *J. Am. Chem. Soc.*, **83**, 404 (1961), to suppress the acid-forming reaction.

separated by chromatography on a column of 52 g. of Merck "acid-washed" alumina. Elution with petroleum ether yielded 0.019 g. of a colorless oil, probably olefin. Elution with 50% benzene in petroleum ether produced 0.226 g. (0.745 mmole, 16.1%) of a mixture of *p*-nitrobenzoates (fraction A) consisting chiefly of *trans-cis*-1-decalyl *p*-nitrobenzoate (III). Elution with ethyl ether yielded 0.480 g. (3.110 mmoles, 67.4%) of solid alcohol (fraction B) which consisted almost entirely of *trans-trans*-1-decalol (IV). The product could also be separated into fractions A and B by sublimation. For example, sublimation of the product from 1.392 g. of II (after removal of the petroleum ether) at 80° and 0.3 mm. gave 0.490 g. (69.2%) of solid alcohol (fraction B) and 0.241 g. (17.3%) of unsublimable *p*-nitrobenzoate (fraction A). Control experiments with synthetic mixtures indicated that 93–95% of the alcohol fraction, and 97–99% of the *p*-nitrobenzoate fraction could be recovered by this procedure.

Recrystallization of a 0.226-g. portion of the *p*-nitrobenzoate fraction (fraction A) from methanol gave 0.111 g. of *trans-cis*-1-decalyl *p*-nitrobenzoate (III), m.p. 116.0–116.8°. This was identified by comparison with a known sample. Another sample of fraction A (0.206 g.) was saponified by refluxing it in 20 ml. of 5% methanolic potassium hydroxide for 3.5 hr. The solution was diluted with 20 ml. of water and extracted with 40–60° petroleum ether in a continuous extractor for 27 hr. Gas chromatography of the liquid alcohol (after evaporation of the petroleum ether) with a 6-foot column of 1,2,3-tris-(2-cyanoethoxy)-propane on Celite at 155° indicated its composition to be 85% *trans-cis*-1-decalol and 15% material having the same retention time as *trans-trans*-1-decalol (IV).

Treatment of 0.270 g. (1.75 mmoles) of fraction B with 0.36 g. (1.94 mmoles) of *p*-nitrobenzoyl chloride yielded 0.41 g. (77%) of *trans-trans*-1-decalyl *p*-nitrobenzoate, m.p. 83.7–84.8° (petroleum ether) (lit.[26] m.p. 86°). This proved to be identical with an authentic sample. Gas chromatographic analysis of fraction B with a 6-foot column of 20% 1,2,3-tris-(2-cyanoethoxy)-propane on Celite at 155° showed it to consist of 98–99% *trans-trans*-1-decalol (IV) and 1–2% of material having the same retention time as *trans-cis*-1-decalol.

In a control experiment a synthetic solvolysis mixture composed of 0.102 g. of *trans-cis*-1-decalyl *p*-nitrobenzoate (III), 0.260 g. of *trans-trans*-1-decalol (IV) and 0.323 g. of *p*-nitrobenzoic acid in 40 ml. of 90% aqueous acetone was heated at 100° for 240 hr. The mixture of alcohol and *p*-nitrobenzoate was isolated as described above and separated into fractions A and B by vacuum sublimation. Analysis of the alcohol fraction (fraction B) by gas chromatography showed it to be pure *trans-trans*-1-decalol (IV). The *p*-nitrobenzoate fraction (fraction A) was saponified and the alcohol thus obtained was shown by gas chromatography to be pure *trans-cis*-1-decalol. Thus, ester interchange does not occur under the conditions of the solvolysis reaction.

(B) *cis*-5-Cyclodecen-1-yl *p*-Nitrobenzoate (Ia).—A solution of 0.891 g. (2.94 mmoles) of Ia and 0.096 g. of sodium *p*-nitrobenzoate in 100 ml. of 90% aqueous acetone was placed in a glass bomb and heated at 118.6° for 545 hr. The solvolysis product and unchanged Ia were then isolated from the solution in the same manner as described for the isolation of the solvolysis products of II. The petroleum ether solution of solvolysis product and unreacted III was concentrated and chromatographed on 50 g. of Merck "acid-washed" alumina. Elution with 50% benzene in petroleum ether yielded 0.585 g. (1.93 mmoles, 66%) of *p*-nitrobenzoate, m.p. 147–152°. Recrystallization from ethanol–ethyl acetate gave 0.470 g. (1.55 mmoles) of *cis*-5-cyclodecenyl *p*-nitrobenzoate (Ia), m.p. 153.5–155° (identical with authentic material). Elution with 50% ether in benzene yielded 0.152 g. (0.985 mmole, 34%) of alcohol, m.p. 60–80°. Gas chromatography of this material with a 6-foot column of 20% 1,2,3-tris-(2-cyanoethoxy)-propane on Celite at 160° showed only a single peak which had the same retention time as *cis-cis*-1-decalol (V). Treatment of this material with phenyl isocyanate yielded the phenylurethan of *cis-cis*-1-decalol, m.p. 116–117°(petroleum ether) (lit.[32] m.p. 118°). This derivative was identical with a known sample.

To test the stability of *cis*-5-cyclodecenol (Ic) under the conditions of the solvolysis reaction, a solution of 0.080 g. of Ic, 0.079 g. of *p*-nitrobenzoic acid and 0.061 g. of sodium *p*-nitrobenzoate in 50 ml. of 90% aqueous acetone was heated at 118.6° for 455 hr. The alcohol fraction was isolated in the usual manner and analyzed by v.p.c. The alcohol was homogeneous and had a retention time corresponding to that of Ic. Treatment of the residual oil with phenyl isocyanate yielded a phenylurethan, m.p. 110.5–111.5°, which was identical (mixture melting point and infrared spectra in CHCl₃) with an authentic sample,[3] m.p. 111.5–112.5°.

Oxygen-18 Experiments.—Carbonyl-O¹⁸ labeled *trans*-5-cyclodecenyl *p*-nitrobenzoate (II) and *trans-cis*-1-decalyl *p*-nitrobenzoate (III) were prepared from the corresponding alcohols and *p*-nitrobenzoyl chloride-carbonyl-O¹⁸ in the usual manner.[12,22] Solvolysis of labeled II and isolation of the labeled III so produced were carried out as described above for unlabeled II.

To check for washout of O¹⁸ during isolation, synthetic mixtures of carbonyl-O¹⁸ labeled III (0.982 atom % excess O¹⁸), *trans-trans*-1-decalol and *p*-nitrobenzoic acid were isolated and separated in the manner described above. The O¹⁸ content of the recovered III was found to be identical, within the limits of experimental error (0.990 and 1.004 atom % excess O¹⁸), with that of the original material.[33]

To determine the O¹⁸ content of the alkyl–oxygen position of labeled III obtained from the rearrangement of labeled II it was saponified and reconverted to *p*-nitrobenzoate with unlabeled acid chloride as follows. To 20 ml. of 5% methanolic potassium hydroxide was added 0.226 g. (0.745 mmole) of labeled rearrangement product (fraction A) and 4 ml. of water. After 4 hr. of refluxing, the solution was diluted with 70 ml. of water and extracted with 40–60° petroleum ether in a continuous extractor for 20 hr. The petroleum ether was evaporated and the residue was dissolved in 4 ml. of pyridine. The resulting solution was treated with 0.166 g. (0.895 mmole) of unlabeled *p*-nitrobenzoyl chloride at 0°. The solution was stirred 3 hr. at room temperature and 0.209 g. (0.690 mmole) of crude *p*-nitrobenzoate mixture was obtained. Several recrystallizations from methanol gave 0.0913 g. (0.301 mmole) of III, m.p. 116.0–116.8°. This material contains the same alkyl–oxygen atom as the rearrangement product.

In experiment 2, Table III, the alkyl–oxygen position of unsolvolyzed II was investigated after one half-life at 99.6°. The total *p*-nitrobenzoate fraction (consisting of unsolvolyzed II and rearrangement products) from a 90% aqueous acetone solution, originally containing 0.2916 g. of carbonyl-O¹⁸ labeled II in 75 ml. of solution, was isolated by removing the solvent under aspirator vacuum. The remaining slurry was dissolved in 50 ml. of ether which was washed with 25 ml. of 3 *N* sodium carbonate solution and water and then dried with magnesium sulfate. Evaporation of the ether followed by recrystallization of the residue from 5 ml. of 60–68° petroleum ether gave 0.120 g. of crude *p*-nitrobenzoate mixture. This was saponified with methanolic potassium hydroxide and reconverted to the *p*-nitrobenzoate derivative. Three recrystallizations from 60–68° petroleum ether gave 0.087 g. of II, m.p. 108.7–109.8°, which contained the same alkyl–oxygen as the II recovered from the reaction mixture. This sample contained <1% of the original excess O¹⁸.

An isotope dilution experiment, designed to test for the presence of III in the samples of II used in the kinetic experiments, was carried out. To 0.4394 g. of II was added 0.0881 g. of carbonyl-O¹⁸ labeled III which contained 0.982 atom % excess O¹⁸. The solids were mixed, dissolved in ether, and recovered by evaporating the ether under an air stream. The m.p. of the solid was 90–104°. Five recrystallizations (60–68° petroleum ether) gave 0.13 g. of material melting at 108.2–109.6°, which was identical in every way with the original sample of II. This material did not contain any detectable excess O¹⁸. This experiment shows that the method used to purify the *trans p*-nitrobenzoate II would have removed any III and thus demonstrates that the II used in the kinetic experiments did not contain III.

(32) W. Hückel, R. Danneel, A. Gross and H. Naab, *Ann.*, **502**, 99 (1933).

(33) The O¹⁸ contents were determined by the method described in ref. 12.