

Anal. Calcd. for C_8H_8S : C, 70.5; H, 5.92; S, 23.5. Found: C, 70.1; H, 5.71; S, 23.2.

The infrared spectrum included absorption bands at 2564 cm^{-1} (SH) and 1613 cm^{-1} (C=C), as well as the usual aromatic and monosubstituted benzene absorptions. An attempt to prepare a derivative by reaction with 2,4-dinitrobenzenesulfonyl chloride gave a gum that failed to crystallize.

Oxidation of Bis-(β -phenylvinyl) Sulfide to Bis-(β -phenylvinyl) Sulfone.—Bis-(β -phenylvinyl) sulfide (3.5 g.) was stirred with 16 ml. each of glacial acetic acid and acetic anhydride. The mixture was cooled to 0–5° while 5 ml. of 30% hydrogen peroxide was added dropwise during 20 minutes, and the reaction mixture was then allowed to warm up slowly. After standing overnight, the mixture was poured into ice-water and the crystalline sulfone filtered off (3.1 g., 78% yield). Recrystallization from methanol gave white needles, m.p. 90–91°. The infrared spectrum included the expected absorptions at 1613 cm^{-1} (—C=C—) and at 1316 and 1124 cm^{-1} (SO_2).

Anal. Calcd. for $C_{16}H_{14}SO_2$: C, 71.1; H, 5.22; S, 12.8. Found: C, 71.4; H, 5.30; S, 12.8.

The X-Ray-induced Addition of Hydrogen Sulfide to 3,3,3-Trifluoropropyne.—A mixture of trifluoropropyne (20 g., 0.21 mole) and hydrogen sulfide (25 g., 0.73 mole) in a stainless-steel pressure vessel was irradiated with X-rays for 4 hours at an average dose rate of $\sim 20,000$ rads/minute. After the excess volatiles were bled off, there remained 3.1 g. of a vile-smelling, yellow liquid.

The products from several such runs were combined (19 g.) and distilled through a low-temperature, helices-packed column. Two major fractions were obtained; the first (9.5 g.) appeared to boil at 6–8° (70 mm.) ($n_D^{25} 1.3879$ – 1.3931). The higher-boiling fraction (5 g.) was pumped over into a trap under oil-pump vacuum (~ 0.25 mm.) without an accurate boiling point being recorded ($n_D^{25} 1.4408$).

Redistillation of the lower-boiling fraction through a spinning-band column gave a center cut (4 g.) boiling at 21–22° (138 mm.) ($n_D^{25} 1.3889$ – 1.3899). The infrared spectrum included the expected absorptions for 3,3,3-trifluoropropenethiol; viz., 2564 cm^{-1} (SH), 3125–3030 cm^{-1} (CH), 1639 cm^{-1} (C=C) and 1430–1100 cm^{-1} region (CF_3).

Anal. Calcd. for $C_3H_3SF_3$: F, 44.5; S, 25.0. Found: F, 44.2; S, 25.0.

The higher-boiling product included decreased but significant C=C absorption (1639 cm^{-1}), together with increased CH (2940 cm^{-1}) and SH (2564 cm^{-1}) absorptions in the infrared. Redistillation gave as the principal fraction 1.7 g. boiling at 33° (15 mm.). Its infrared spectrum was essentially the same as that of the crude material.

Anal. Calcd. for $C_3H_3S_2F_3$ (2:1): S, 39.4; F, 35.2; mol. wt., 161. Calcd. for $C_3H_4SF_6$ (1:2): S, 14.4; F, 51.3; mol. wt., 222. Found: S, 36.0; F, 37.3; mol. wt., 173.

The analysis and infrared spectrum suggest a mixture of the 2:1 adduct, probably $CF_3CH(SH)CH_2SH$, and the 1:2 adduct ($CF_3CH=CH$)₂S in a ratio of about 85:15. The data calculated for such a mixture are: S, 35.6; F, 37.6; mol. wt., 171.

X-Ray-induced Addition of Hydrogen Sulfide to Hexafluoro-2-butyne.—A mixture of hexafluoro-2-butyne (96.0 g.) and hydrogen sulfide (62 g., 1.8 moles) was irradiated with X-rays for 5 hours at an average dose rate of about 15,000 rads/minute. Volatiles were bled off, collected in a -80° trap, and subsequently reirradiated. The liquid product from four such runs (20 g.) was distilled through a spinning-band column to give 9.5 g. of hexafluoro-2-butene-2-thiol (b.p. 57–58°, $n_D^{25} 1.339$).

Anal. Calcd. for $C_4F_6H_2S$: S, 16.4; F, 58.1. Found: S, 16.3; F, 58.1.

There was also obtained a small fraction (2 g.) of material boiling over the range 58° (90 mm.) to 53° (45 mm.) ($n_D^{25} 1.360$), which is probably a mixture of hexafluorobutanedithiol and bis-(hexafluorobutenyl) sulfide. There remained, following removal of this material, about 5 g. of viscous, oily residue.

Addition of Hydrogen Sulfide to Dimethylacetylene.—A mixture of 28 g. (0.52 mole) of dimethylacetylene and 29 g. (0.85 mole) of hydrogen sulfide in a 300-ml. stainless-steel cylinder was irradiated with X-rays for 3.5 hours at an average dose rate of about 20,000 rads/minute. Volatiles were bled off by immersing the cylinder in warm water (35–40°). There remained 3.8 g. of pale yellow liquid. The products from two runs were combined and distilled through an 8 in. Vigreux column. After removing dissolved dimethylacetylene, the following fractions were obtained.

1, $\sim 25^\circ$ (65 mm.)	0.7 g.	$n_D^{25} 1.4782$
2, 45–46° (12 mm.)	1.2 g.	1.5182
3, 37° (~ 1 mm.)	0.6 g.	1.5189
4, Residue	~ 1.0 g.	1.556

The infrared spectrum of 1 included the expected bands for a 1:1 adduct, $CH_3C(SH)=CHCH_3$; viz., 2564 cm^{-1} (SH) and 1639–1613 cm^{-1} (C=C; doublet), in addition to the usual C—H absorptions.

Anal. Calcd. for C_4H_8S : C, 54.5; H, 9.15; S, 36.3. Found: C, 56.5; H, 9.34; S, 34.8.

Fraction 2 was shown to be butane-2,3-dithiol¹⁰ by its infrared spectrum (strong SH absorption and no C=C absorption) and by preparation of a derivative with 2,4-dinitrobenzenesulfonyl chloride. A mixture of 0.2 g. of the dithiol and 0.8 g. of 2,4-dinitrobenzenesulfonyl chloride in 60 ml. of anhydrous ether on standing for 15 hours gave 0.4 g. (40% yield) of the bis-disulfide derivative. It was recrystallized from benzene to a constant melting point of 169–170°.

Anal. Calcd. for $C_6H_{14}N_4O_8S_4$: N, 10.8; S, 24.7. Found: N, 10.8; S, 24.9.

Nuclear Magnetic Resonance Spectra.—Proton spectra were obtained with an A-60 nuclear magnetic resonance spectrometer manufactured by Varian Associates, Palo Alto, Calif. The standard was tetramethylsilane. F^{19} spectra (56.4 Mc.) were obtained by means of a high resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates. The standard was *sym*-1,2-difluoro-tetrachloroethane.

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

Stereochemistry of Allylic Rearrangements. XIII. The Racemization, Carboxyl-oxygen Equilibration and Solvolysis of trans- α,γ -Dimethylallyl *p*-Nitrobenzoate in Aqueous Acetone¹

By HARLAN L. GOERING, MELVIN M. POMBO² AND KIRK D. McMICHAEL

RECEIVED NOVEMBER 7, 1962

Rate constants for the following four first-order processes associated with the solvolysis of optically active trans- α,γ -dimethylallyl *p*-nitrobenzoate (I) in 60% aqueous acetone have been determined: (a) racemization of the unsolvolyzed ester (k_{rac} eq. 1), (b) solvolysis of the ester (k_t), (c) equilibration of the carboxyl-oxygen atoms in the unsolvolyzed ester (k_{eq} eq. 2) and (d) scrambling of carboxyl-oxygen atoms in each enantiomer starting with discretely ¹⁸O-labeled optically pure I (k_s eq. 3). Comparison of these constants with those reported earlier (ref. 3) for 90% acetone shows that solvent effects are consistent with the view that racemization and oxygen equilibration result from reformation of substrate (racemic and oxygen-equilibrated) by internal return from an internal ion-pair intermediate (II); $k_{rac} = k_{eq}$ for both solvents. The rate at which the oxygen atoms in the enantiomers become scrambled (k_s) relative to the rate of interconversion of the enantiomers ($k_{rac}/2$) provides information concerning the nature of the ion-pair intermediate II.

Introduction

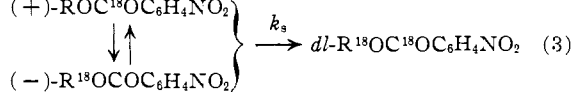
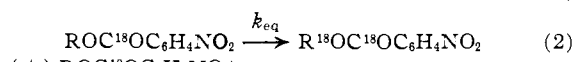
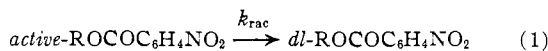
Internal return associated with the solvolysis of optically active and ¹⁸O-labeled trans- α,γ -dimethylallyl *p*-

nitrobenzoate (I) in aqueous acetone results in the following first-order changes in the unsolvolyzed ester.³ In these equations R represents the trans- α,γ -dimeth-

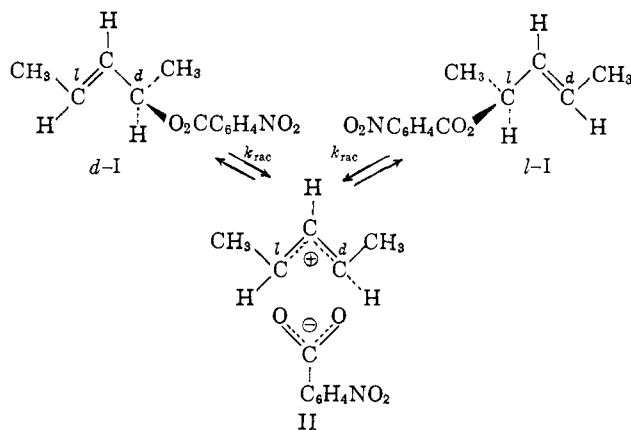
(1) This work was supported by the National Science Foundation, Grant G-19244.

(2) Du Pont summer research assistant, 1958 and 1959; Procter and Gamble Fellow, 1959–1960.

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



ylallyl group and $\text{dl-R}^{18}\text{OC}^{18}\text{OC}_6\text{H}_4\text{NO}_2$ represents ester with the label equally distributed between the two positions in each optical isomer. In this system the most favorable conformation for ionization (alkyl-oxygen cleavage) is such that a symmetrical carbonium ion is produced.³⁻⁶ Thus the internal⁷ ion-pair intermediate II is symmetrical and internal return amounts to a simple first-order interconversion of enantiomers. This paper is concerned only with internal return (*i.e.*, that fraction of II that returns) and thus solvolysis has not been included in the accompanying scheme. Solvolysis does not interfere with the intramolecular equilibration of enantiomers (internal return) but does consume substrate and limit the period that equilibration can be studied. Solvolyzing conditions are necessary to isolate internal return from external return (the fraction of II that dissociates is intercepted by solvent).³



The relative rates of the various changes in the unsolvolyzed ester provide considerable information about the structure and behavior of II. The rate of reaction 1 corresponds to the rate of production of that fraction of II that returns. Or to put it another way, this is the rate at which the allylic carbon atoms in the unsolvolyzed ester become equivalent. In an earlier investigation it was found that in 90% aqueous acetone at 100° carbonyl-¹⁸O-I undergoes equilibration of the label (eq. 2) at the same rate as active I racemizes (eq. 1), *i.e.*, $k_{\text{eq}} = k_{\text{rac}}$. This shows that in II the carboxyl oxygen atoms in the anion as well as the allylic carbon atoms in the cation are equivalent. Thus both k_{rac} and k_{eq} measure total internal return.⁸

The transformation summarized by eq. 3 can be followed using ether-¹⁸O or carbonyl-¹⁸O labeled optically pure I and determining the distribution of the label in each enantiomer at various times. In effect, this amounts to using double labeling—the allylic carbon atoms are distinguishable because they are related to different enantiomers—and determining the relative

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

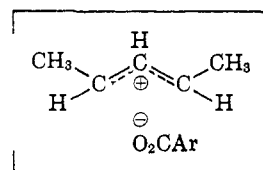
(5) H. L. Goering, *Rec. Chem. Progr.*, **21**, 109 (1960).

(6) H. L. Goering and J. T. Doi, *J. Am. Chem. Soc.*, **82**, 5850 (1960).

(7) S. Winstein, E. Clippinger, A. Fainberg, R. Heck and G. Robinson, *ibid.*, **78**, 328 (1956).

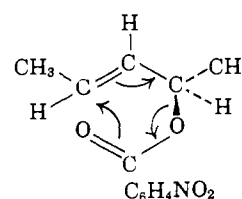
(8) The ion-pair return observed under these conditions has been termed "internal return" because it is completely intramolecular—there is no exchange with common-ion salts (ref. 3). Moreover, in similar systems ion-pair return observed under these conditions is completely stereospecific (ref. 5 and 6).

locations of the allylic carbon atoms and carboxyl oxygen atoms in the original substrate and substrate reformed by internal return. The rate of reaction 3 (k_s) relative to that of production of the intermediate (k_{rac}) is particularly informative about the arrangement of the ions in the intermediate. If the ions are arranged as indicated by II and if there is a tendency for the oxygen atoms to bond preferentially with the nearest carbon atom, k_s/k_{rac} will be less than unity (in this case some interconversions will not result in the type of scrambling defined by eq. 3). In fact, if the equivalent oxygen atoms bond exclusively with the nearest carbon atom the enantiomers will remain discretely labeled and k_s will be zero. On the other hand, if both oxygen atoms are equivalent with respect to both carbon atoms, as illustrated by III, both enantiomers reformed by internal return will have the oxygen atoms completely scrambled and k_s will equal k_{rac} .



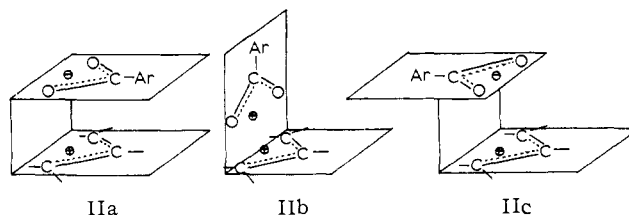
III

For the solvolysis of I in 90% aqueous acetone at 100° $k_s/k_{\text{rac}} = 0.34$.³ This means that 34% of the product of internal return has the carboxyl oxygen atoms scrambled in each enantiomer (17% of the enantiomers formed by internal return are labeled inversely). Thus in 83% of the interconversions the carboxyl oxygen atom in the reactant (one enantiomer) becomes the ether-oxygen atom in the product (the other enantiomer) as summarized by IV. Or to put it another way, in II the equivalent carboxyl oxygen atoms bond with the nearest carbon atom 4.9 times faster than with the more remote one. Thus, under these conditions the arrangement of the ions in the ion-pair intermediate corresponds to II rather than III. For each of these k_{eq} is equal to k_{rac} ; there is an equal probability that the intermediate will be converted to either enantiomer and there is the same probability that either oxygen atom will bond to carbon.



IV

As has been pointed out,^{3,5} the cation and anion in II are not coplanar. Rather, presumably the carboxyl oxygen atoms and the two allylic carbon atoms form a plane perpendicular to that of the cation. The plane of the carboxyl group relative to that of the cation may be parallel *endo*-IIa, perpendicular IIb⁶ or parallel *exo*-IIc. There is an indication that the arrangement represented by IIc is the most favorable one (*vide infra*).



In the present work the rates of reactions 1-3 associated with the solvolysis of *trans*- α,γ -dimethylallyl *p*-nitrobenzoate (I) in 60% aqueous acetone have been determined. Comparison of these data with those reported earlier³ for 90% aqueous acetone shows the effect of varying solvent polarity on the rates and relative rates of these three processes. The sensitivity of these rates to ionizing power of the solvent was of interest for several reasons. First, it was desirable to obtain additional evidence that reactions 1-3 are indeed manifestations of internal return from a polar intermediate rather than resulting from a process independent of ionization. The effect of varying solvent polarity on the k_s/k_{rac} ratio was also of considerable interest because according to the present interpretation this ratio is a measure of the tightness of the ion-pair intermediate. Finally, it was of interest to determine if the two independent methods for measuring internal return, racemization (eq. 1) and carboxyloxygen equilibration (eq. 2),⁹ would show good agreement for 60% as well as for 90% aqueous acetone.

Results

The polarimetric (k_α) and titrimetric (k_t) first-order rate constants for the solvolysis of *trans*- α,γ -dimethylallyl *p*-nitrobenzoate (I) in 60% aqueous acetone¹⁰ are shown in Table I together with data taken from reference 3 for solvolysis in 90% aqueous acetone. Rate constants for racemization of the unsolvolyzed ester (eq. 1), $k_{rac} = (k_\alpha - k_t)$, and k_α/k_t ratios are included in the table.

TABLE I

RATE CONSTANTS FOR LOSS OF OPTICAL ACTIVITY (k_α), SOLVOLYSIS (k_t) AND RACEMIZATION OF UNSOLVOLYZED ESTER (k_{rac}) FOR SOLVOLYSIS OF *trans*- α,γ -DIMETHYLALLYL *p*-NITROBENZOATE IN AQUEOUS ACETONE

Temp., °C.	$10^3 k_\alpha$, ^a hr. ⁻¹	$10^3 k_t$, ^a hr. ⁻¹	k_α/k_t	$10^3 k_{rac}$, ^b hr. ⁻¹
A. 60% aqueous acetone ^c				
59.94		9.42 ± 0.05	2.17 ± 0.1	11.0 ± 0.3
59.94		9.42 ± 0.08		
59.94	20.4 ± 0.3			
59.94	20.4 ± 0.3			
79.63		79.1 ± 0.8		
79.62		78.5 ± 0.6		
99.61		541 ^d		
B. 90% aqueous acetone ^{e,f}				
99.61		4.23 ± 0.01 ^g	5.4 ± 0.1	18.6 ± 0.3
99.61	22.8 ± 0.3 ^h			

^a The indicated uncertainty is the average deviation of 7 to 12 values for each experiment. ^b Indicated uncertainties determined from the limiting values of k_α and k_t . ^c Substrate concentration 0.05 M. ^d Value obtained by extrapolation using data for 59.94° and 79.62°. ^e Substrate concentration 0.05 M for titrimetric and 0.06 M for polarimetric experiments. ^f Data taken from ref. 3. ^g Average (and average deviation) of two independent kinetic experiments.

These constants were determined by methods used earlier.³ Reactions were followed to about 80% completion and in all cases good first-order behavior was observed. In the titrimetric experiments the titers observed after ten half-periods were within 1% of the calculated values. For the polarimetric experiments the infinity rotations, measured after ten half-periods, were about 1% of the original values. The cause of this residual activity remains obscure³; however, it is clear that this minor disturbance does not affect these or the ¹⁸O-experiments. A control experiment, which demonstrates that solvolysis involves exclusive alkyl-oxygen cleavage, was reported previously.³

(9) H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, **84**, 3853 (1962).

(10) Solvent compositions are based on volumes of pure components at 25° before mixing.

The data presented in Table I show that ionization (k_α), solvolysis (k_t) and internal return (k_{rac}) increase and the k_α/k_t ratio decreases with solvent polarity. Such behavior has been observed earlier for similar systems.^{4,11} Comparison of k_t for the two solvents at 99.6° shows that solvolysis is 128 times faster in 60% acetone than in 90% acetone. A satisfactory estimate of k_α for 60% acetone at 99.6° can be made as follows. It has been observed¹¹ that for a similar allylic system in aqueous acetone k_α/k_t is quite insensitive to change in temperature. Thus, for 60% aqueous acetone at 99.6° k_α presumably will equal 2.17 k_t , which is 1.2 hr.⁻¹. It is significant that a one-point kinetic experiment was in good agreement with this estimate. Thus at 100°, k_α and k_{rac} are larger in 60% acetone than in 90% acetone by factors of about 52 and 34, respectively.

The rate of equilibration of the carboxyl oxygen atoms (eq. 2) which accompanies solvolysis was determined by the method described earlier.⁶ This involves using carbonyl-¹⁸O-labeled I and determining the distribution of the label at appropriate times in the unsolvolyzed ester. Data for 60% and 90% aqueous acetone are presented in Table II. This table includes the extent of solvolysis (calculated from k_t) at the time of isolation of the ester and the extent of oxygen equilibration of the unsolvolyzed ester as well as the rate constants. Oxygen-18 contents were determined in triplicate; the average deviation from the mean is included with each value.

TABLE II

RATES OF ¹⁸O-EQUILIBRATION DURING SOLVOLYSIS OF *trans*- α,γ -DIMETHYLALLYL *p*-NITROBENZOATE-CARBONYL-¹⁸O

Time, hr.	Sol- volysis, ^a %	X, ^b atom % excess	Equilibra- tion ^c %	$10^3 k_{eq}$, hr. ⁻¹
A. 60% aqueous acetone, 59.93°, $a = 2.15 \pm 0.01$ ^d				
0	0	0	0	..
20.3	17	0.42 ± 0.00	19.5	10.8
46.5	36	0.84 ± .02	39	10.7
81.3	54	1.22 ± .01	57	10.3
				Av. 10.6 ± 0.2
B. 90% aqueous acetone, 99.61°, $a = 2.31 \pm 0.03$ ^d				
0		0	0	
12	5	0.43 ± 0.01	19	17.2
27.5	11	0.93 ± .01	40	18.7
49.3	19	1.35 ± .04	58	17.8
				Av. 17.9 ± 0.6

^a Percentage of ester solvolysed at time t (calculated from k_t). ^b Oxygen-18 abundance of ether oxygen atom in unsolvolyzed ester. ^c Percentage of unsolvolyzed ester with label equally distributed between two positions. ^d Final (infinity) ¹⁸O-content (one-half of the ¹⁸O-content of the carboxyl group).

From these data it is clear that oxygen equilibration in the unsolvolyzed ester (reaction 1) is clearly first order. Moreover, within the combined experimental uncertainties $k_{eq} = k_{rac}$ for both solvents (*cf.* Tables I and II). This shows that substrate reformed by internal return is completely racemic (the allylic carbon atoms are equilibrated) and oxygen equilibrated. Or in other words, k_{eq} as well as k_{rac} measures total internal return. This observation is of considerable significance in connection with the use of carboxyl-oxygen equilibration (eq. 2) as a method for measuring internal return in systems which do not rearrange (racemize).⁹

The rate of scrambling of the carboxyl oxygen atoms in the enantiomers (eq. 3) was also determined by the

(11) H. L. Goering and E. F. Silversmith, *J. Am. Chem. Soc.*, **77**, 1129 (1955).

method described earlier.³ This involves using optically pure carbonyl- or ether-¹⁸O-I, isolating the unsolvolyzed ester at appropriate times, and determining the distribution of the label in each optical isomer. This distribution was determined as follows. The unsolvolyzed partially racemic ester (I) was reduced with lithium aluminum hydride and the resulting *trans*- α,γ -dimethylallyl alcohol was re-resolved as the acid phthalate derivative. The ¹⁸O-contents of both optical isomers of this derivative were determined. These isomers contain the same ether oxygen atom as the corresponding enantiomers in the unsolvolyzed ester; *i.e.*, the ¹⁸O-contents of the enantiomeric acid phthalates correspond to the ether ¹⁸O-contents of the enantiomeric *p*-nitrobenzoates. Since the total ¹⁸O-content of the carboxyl group in I remains constant throughout the solvolysis, the carbonyl ¹⁸O-contents for the enantiomers can be obtained by difference.

In the present work both carbonyl-¹⁸O and ether-¹⁸O optically pure I were used to determine k_s associated with internal return in 60% aqueous acetone at 60°. It is necessary for the ester to be optically pure because the allylic carbon atoms as well as the carboxyl oxygen atoms must be discretely labeled. Carbonyl-¹⁸O-(+)-I was prepared from optically pure *trans*- α,γ -dimethylallyl alcohol and *p*-nitrobenzoyl chloride-carbonyl-¹⁸O.³ The alcohol was derived from its acid phthalate derivative which was shown to be optically pure by an isotope dilution method.⁶

Ether-¹⁸O-(+)-I was prepared from optically pure *trans*- α,γ -dimethylallyl alcohol-¹⁸O which was prepared as follows. Crotonaldehyde-carbonyl-¹⁸O was prepared by equilibration of crotonaldehyde with ¹⁸O-enriched water. The labeled aldehyde was converted⁴ to *trans*- α,γ -dimethylallyl alcohol which was resolved as the acid phthalate derivative. That the ¹⁸O-label was exclusively in the ether position was shown as follows. Labeled *p*-nitrobenzoate (I) containing 2.51% ¹⁸O¹² was reduced with lithium aluminum hydride. The resulting α,γ -dimethylallyl alcohol was reconverted to its *p*-nitrobenzoate derivative. The observed ¹⁸O-content of this derivative was 2.52%.

In the experiment summarized in part A of Table III a 0.0504 molar solution of carbonyl-¹⁸O-(+)-I was distributed into two ampoules which were placed in a 59.93° thermostat. One ampoule was heated for 63 hr. From k_t and k_{rac} (Table I) it can be calculated that at this time 45% of the ester is solvolyzed and the remaining ester is 50% racemic (*i.e.*, 75% (+)-isomer). The second ampoule was heated for 147.2 hr.; this corresponds to 75% solvolysis and 80% racemization. In each case the unsolvolyzed ester was isolated and converted to its acid phthalate derivative which was resolved and the ¹⁸O-contents of each isomer determined. The optical purities of the (+)- and (-)-acid phthalates obtained from this resolution and the observed ¹⁸O-contents of these samples are given in the third and fourth columns in Table III. These data provide two linear equations which can be solved for the ¹⁸O-contents of the pure enantiomers.³ These values are shown in the fifth column. From these values and the total carboxyl ¹⁸O-content of the isolated I, the distribution of the isotope in each enantiomer can be determined.

The total ¹⁸O-content of the carboxyl group in the unsolvolyzed ester can be determined as follows. Internal return results in equilibration of the carboxyl oxygen atoms and the allylic carbon atoms at equal rates ($k_{rac} = k_{eq}$). This means that at any instant the sum of the ether ¹⁸O-contents of the (+)- and (-)-I produced by internal return must correspond to the

total carboxyl ¹⁸O-content.³ The ether ¹⁸O-contents for the enantiomers produced by internal return are shown in column six of Table III. All of the (-)-isomer of the unsolvolyzed ester is formed by internal return and in this case the observed ¹⁸O-content (column 5) corresponds to the ether ¹⁸O-content of the (-)-I produced by internal return. The same is not true for the (+)-isomer because some of this material has not been reformed by internal return; the isolated ester was not completely racemic. For example, at 63 hr. (50% racemization) the composition of the unsolvolyzed ester I is 50% (+)-isomer and 50% *dl*-isomer. Only one-third of the (+)-isomer has been reformed by internal return. The rest is unreacted starting material and still discretely labeled in the carbonyl position. Hence, the ether ¹⁸O-content of that fraction of (+)-isomer formed by internal return is 3 times that of the total (+)-isomer [(75/25) \times 0.35% = 1.05%]. Thus the carboxyl ¹⁸O-content of I derived from the data for 63 hr. is 1.05 + 3.43% = 4.48%. A similar treatment of the data for 147.2 hr. gives an ether ¹⁸O-content of 1.40% for the (+)-isomer produced by internal return and a value of 1.40 + 3.18% = 4.58% for the carboxyl group.¹³

Part B of Table III shows the results of a similar experiment using ether-¹⁸O-(+)-I. In this experi-

TABLE III
OXYGEN-18 DATA FOR INTERNAL RETURN DURING SOLVOLYSIS OF CARBONYL- AND ETHER-¹⁸O-(+)-*trans*- α,γ -DIMETHYLALLYL *p*-NITROBENZOATE IN 60% AQUEOUS ACETONE AT 59.93°

Acid phthalate	Time, hr. ⁻¹	Optical ^a purity, %	¹⁸ O-Content ^b		
			Obsd. ^c	Pure isomer ^d	Corrected ^e
A. Carbonyl- ¹⁸ O-(+)-I					
(+)	63	87.6	0.54	0.35	1.05
(-)		3.4	1.94	3.43	3.43
(+)	147.2	79.8	1.17	0.94	1.40
(-)		11.6	2.19	3.18	3.18
B. Ether- ¹⁸ O-(+)-I					
(+)	63	82.5	2.19	2.29	1.89
(-)		53.0	1.09	0.69	0.69
(+)	140	90	1.92	1.98	1.70
(-)		56.3	1.05	0.79	0.79

^a Optical purity of (+)- and (-)-acid phthalate obtained by resolution of alcohol derived from unsolvolyzed ester. ^b ¹⁸O-Contents given as atom % excess ¹⁸O. ^c Observed ¹⁸O-contents of enantiomeric acid phthalates. ^d Calculated ¹⁸O-contents for optically pure enantiomeric acid phthalates. ^e ¹⁸O-Contents of pure enantiomers derived from I which has been reformed by internal return.

ment the initial ester concentration was 0.048 molar and samples of the unsolvolyzed ester were isolated after 63 hr. (50% racemization) and 140 hr. (78% racemization). The ether-oxygen labeled substrate offers the advantage that the ¹⁸O-content of the *p*-nitrobenzoate (I) is the same as that of the optically pure acid phthalate from which it is derived. Thus the carboxyl ¹⁸O-content can be determined by analysis of the acid phthalate derivative. In the present experiment the ¹⁸O-content of this derivative was 2.49%.¹³ This agrees well with the sums of the ether ¹⁸O-contents of the enantiomers (column 6, Table III) for the 63-hr.

(13) Unlike in the earlier work (ref. 3) the ¹⁸O-content of the carboxyl group determined by analysis of the enantiomeric acid phthalates (4.53 \pm 0.05%) does not agree with the value obtained by analysis of the starting *p*-nitrobenzoate I (3.70%). We have observed that often the reproducible apparent ¹⁸O-contents of *p*-nitrobenzoate derivatives of ¹⁸O-labeled alcohols are lower than those of the acid phthalate derivatives. The magnitude of the discrepancy seems to depend on the history of the pyrolysis train used for the ¹⁸O-determinations. Because of such discrepancies it is desirable to use the same derivative when comparing relative ¹⁸O-contents. In the present work all ¹⁸O-contents refer to the apparent content of the acid phthalate derivative.

(12) All ¹⁸O-values are atom % excess ¹⁸O.

sample (2.58%) and 140-hr. sample (2.49%). This not only represents a most important test for internal consistency of the data but also shows that the carboxyl ^{18}O -content remains steady during solvolysis. This was also found to be the case for solvolysis in 90% aqueous acetone.³ The constancy of the carbonyl ^{18}O -content shows that for this system the ^{18}O -isotope effect for alkyl-oxygen cleavage is negligible. Otherwise the isotope would be enriched in the unsolvolyzed ester because of selective solvolysis of the unlabeled ester.¹⁴

The first-order rate constant for scrambling (reaction 3) was determined using the relationship; $k_s = (1/t) \ln 100/Z$ where Z is the percentage of enantiomers which remain discretely labeled at time t . The values of Z were determined from the data in Table III and the enantiomeric composition of the unsolvolyzed ester by the method outlined earlier.³ First-order constants for scrambling (k_s) are presented in Table IV together with the percentage of unreacted substrate (Z) for each point. Because of a less favorable ratio of internal

TABLE IV
FIRST-ORDER RATE CONSTANT FOR SCRAMBLING OF CARBOXYL OXYGEN ATOMS IN ENANTIOMERS OF I IN 60% ACETONE AT 59.93°

Time, hr.	$Z, \%$	$10^3 k_s, \text{hr.}^{-1}$
A. Carbonyl- ^{18}O (+)-I		
63.0	76.8	4.2
147.2	50.4	4.6
B. Ether- ^{18}O (+)-I		
63.0	74.1	4.7
140.0	50.2	4.9

Av. 4.6 ± 0.2

^a Percentage of optical isomers remaining discretely labeled at time t . Calculated from: (i) enantiomeric composition of ester at time of isolation, (ii) ^{18}O -contents given in column 5 (Table III) and (iii) total carbonyl ^{18}O -contents for isolated ester (4.53% for A and 2.49% for B).

return to solvolysis for 60% acetone than for 90% acetone (cf. k_a/k_t ratios, Table I) this reaction could not be followed to as near completion as was possible in the earlier work.³ As indicated by final values of Z the reactions were followed to about 50% completion. The agreement between the two experiments in Table IV is rather good considering that these experiments were carried out by different investigators using different batches of solvent, reactants and facilities. These data clearly show that scrambling of oxygen atoms in the enantiomers (eq. 3) is a first-order process and less than half as fast as the rate of production of II (k_{rac}).

Discussion

Comparison of the data for 60% and 90% aqueous acetone shows that all of the rates are much faster in the more polar solvent; the differences in the rate constants vary from factors of about 34 (k_{rac}) to 128 (k_t). The largest difference in relative rates concerns the ratio of return (k_{rac}) to solvolysis (k_t). The k_{rac}/k_t ratio decreases from 4.4 (90% acetone) to 1.2 (60% acetone), an amount that would be expected from our earlier work with similar systems.^{4,11}

The observed solvent effects are consistent with the view that reactions 1-3 are manifestations of internal return, *i.e.*, the internal ion-pair intermediate is common to these processes and solvolysis. According to this interpretation all rates depend on the rate of production of II and thus should be sensitive to the ioniz-

(14) In work to be published elsewhere it has been observed that solvolysis of *cis*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate-ether- ^{18}O in 80% acetone results in isotopic enrichment in the unsolvolyzed ester. The rate of this increase corresponds to a significant isotope effect; *e.g.*, $k_{^{18}\text{O}}/k_{^{16}\text{O}} \approx 1.08$.

ing power of the solvent. That the relative rates of the competitive reactions of II should be rather insensitive toward ionizing power of the medium is a corollary of the Hammond activity postulate.¹⁵ The intermediate II is a relatively high energy species and the various transition states presumably resemble it in structure and polarity. Thus solvent effects should be rather similar for the competing reactions.

The k_s/k_{rac} ratios for the two solvents show the effect of solvent polarity on the fate of that portion of the intermediate that returns. This ratio for 60% aqueous acetone at 60° is 0.42 as compared to a value of 0.34 for 90% acetone at 100°. It should be noted that this ratio probably has a small positive temperature coefficient and thus the observed difference represents a lower limit of the dependence of k_s/k_{rac} on solvent polarity. The value of 0.42 for this ratio means that the oxygen atoms in II react with the nearest carbon atom 3.8 times more rapidly than with the more remote one—for 90% acetone the ratio of the rates at which an oxygen atom in II reacts with the two carbon atoms is 4.9.

The increase in k_s/k_{rac} with increase in ionizing power of the solvent is in the expected direction.³ However, the difference for the two solvents is remarkably small considering the fact that the constants themselves vary by factors of over 30. This indicates that the tightness of the ion pair II, as reflected in the k_s/k_{rac} ratio, is quite insensitive to changes in the ionizing power of the solvent. This may be rationalized in terms of the Hammond activity postulate (*vide supra*). Alternatively, the similar behavior of II in the two solvents may be considered in terms of the local environment (inner solvation shell) of II. If solvation involves solvent sorting¹⁶ the local environment may be quite similar if not identical in the two solvents. In this case the k_s/k_{rac} ratios would be expected to be similar.

The fact that (k_s/k_{rac}) is less than 1 shows that the structure of the intermediate corresponds to II rather than III—the equivalent oxygen atoms are not equivalent with respect to each allylic carbon atom. In this connection it is extremely interesting that different behavior has been observed with two other allylic systems. For internal return involved in the solvolysis of *trans*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate in aqueous acetone $k_{\text{eq}}/k_{\text{rac}}$ (and thus also k_s/k_{rac}) is larger than unity.⁶ This means that oxygen equilibration occurs without interconversion of enantiomers. For the solvolysis of *cis*-5-methyl-2-cyclohexenyl *p*-nitrobenzoate in aqueous acetone $k_s/k_{\text{rac}} = k_{\text{eq}}/k_{\text{rac}} = 1$; *i.e.*, in the ion-pair intermediate the carboxyl oxygen atoms are equivalent with respect to both allylic carbon atoms (as in III).¹⁷ The reason for the strikingly different behavior between the *trans*- α,γ -dimethylallyl system I and the cyclic systems may be due to the fact that the arrangement represented by IIc is possible for the acyclic system but not for the cyclic systems. In the latter systems the conformation of the cyclic cation¹⁸ is such that a parallel *exo* arrangement for the ion-pair intermediate is sterically precluded. Thus, there is an indication that the parallel *exo* arrangement (IIc) is the favored one for the α,γ -dimethylallyl system and presumably for other systems in which this arrangement is sterically permissible. It is interesting that this arrangement corresponds to that recently found to be the favored one for the transition state of the Cope rearrangement.¹⁹

(15) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955); see also A. Streitwieser, Jr., and W. D. Shaeffer, *ibid.*, **79**, 2888 (1957).

(16) J. B. Hyne, R. Wills and R. E. Wonkka, *ibid.*, **84**, 2914 (1962).

(17) K. D. McMichael, unpublished work.

(18) H. L. Goering and R. R. Josephson, *J. Am. Chem. Soc.*, **84**, 2779 (1962).

(19) W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

Experimental

Materials.¹²—(+)-*trans*- α,γ -Dimethylallyl-*p*-nitrobenzoate carbonyl-¹⁸O, 3.70% ¹⁸O, m.p. 46.2–47.4°, [α]_D²⁵ 41.6° (CHCl₃) (lit.³ m.p. 45.7–46.7°, [α]_D²⁵ 42.5°) was prepared as described earlier³ from (+)-*trans*- α,γ -dimethylallyl acid phthalate, m.p. 80.5–82.8°, [α]_D²⁵ 38.0° (*l* 4, *c* 1.25, CHCl₃).

(+)-*trans*- α,γ -Dimethylallyl *p*-nitrobenzoate-ether-¹⁸O, 2.51% ¹⁸O, m.p. 45.0–46.0°, [α]_D²⁵ 41.9° (CHCl₃) was prepared as follows. Crotonaldehyde-carbonyl-¹⁸O, 2.90% ¹⁸O, b.p. 98–102°, *n*_D²⁵ 1.4337, was obtained by equilibration of freshly distilled crotonaldehyde with ¹⁸O-water, ca. 5% ¹⁸O, according to a general procedure.²⁰ This was converted⁴ to *trans*- α,γ -dimethylallyl alcohol-¹⁸O which in turn was converted to the acid phthalate derivative, 2.89% ¹⁸O, m.p. 88.0–89.5°. Resolution⁴ gave optically pure *trans*- α,γ -dimethylallyl acid phthalate-ether-¹⁸O, 2.82% ¹⁸O, m.p. 76.6–78.1°, [α]_D²⁵ 38.0°. This was converted to ¹⁸O-labeled (+)-*trans*- α,γ -dimethylallyl alcohol by reduction with lithium aluminum hydride.³ Reaction of the alcohol with *p*-nitrobenzoyl chloride gave ether-¹⁸O-(+)-I. That this material was discretely labeled in the ether oxygen position was shown as follows. A small portion of the labeled ester, 2.51% ¹⁸O, was reduced³ to *trans*- α,γ -dimethylallyl alcohol which was reconverted to the *p*-nitrobenzoate I and acid phthalate derivatives. The *p*-nitrobenzoate derivative I contained 2.52% ¹⁸O; the acid phthalate contained 2.49% ¹⁸O. These experiments prove that the *p*-nitrobenzoate derivative is labeled exclusively in the ether position and that the transformations used to determine the ¹⁸O-distribution in the unsolvolyzed *p*-nitrobenzoate do not lead to loss or scrambling of the ¹⁸O-label.

The aqueous acetone¹⁰ was prepared from purified²¹ acetone and conductivity water.

(20) H. L. Goering and R. E. Dilgren, *J. Am. Chem. Soc.*, **82**, 5744 (1960).

(21) J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953).

Kinetic Experiments.—All concentrations are given for 25°. The polarimetric and titrimetric rates were determined by methods described earlier.^{3,4} In the polarimetric experiments the total change in rotation was over 2° and individual measurements were reproducible to within 0.01°. For the titrimetric experiments reactions were followed by titrating 5-ml. aliquots with 0.0485 *N* aqueous sodium hydroxide to the brom thymol blue end-point. The change in titer for a typical experiment was about 5 ml. and titrations were reproducible to within 0.005 ml.

Determination of ¹⁸O-Equilibration and Scrambling.—All ¹⁸O-contents were determined³ in triplicate and the average deviation from the mean was less than 1%. Samples used for ¹⁸O-determinations were shown to be pure by their physical properties including infrared spectra.

The rate of ¹⁸O-equilibration (eq. 2) was determined by the method described earlier.⁶ The data are summarized in Table II.

Rates of ¹⁸O-scrambling in the enantiomers (eq. 3) were also determined by a method described earlier.³ Pertinent data are given in Tables III and IV.

Determination of Optical Purity of (+)-*trans*- α,γ -Dimethylallyl Acid Phthalate.—The optical purity was established by a modification of an isotope dilution method described earlier.^{6,22} Equal weights of (+)-*trans*- α,γ -dimethylallyl acid phthalate, [α]_D²⁵ 38.0° (*l* 4, *c* 1.25, CHCl₃), and *dl-trans*- α,γ -dimethylallyl acid phthalate, 5.90 ± 0.01% ¹⁸O, were mixed and the resulting mixture resolved⁴ to a constant rotation of [α]_D²⁵ 38.0° (*l* 4, *c* 1.25, CHCl₃). The latter had an ¹⁸O-content of 1.98 ± 0.02%. From these data it can be shown⁶ that acid phthalate, [α]_D²⁵ 38.0°, is 100 ± 5% optically pure.

(22) J. S. Berson and D. A. Ben-Efraim, *ibid.*, **81**, 4083 (1959).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

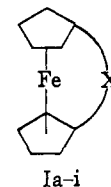
Organic Chemistry of Ferrocene. VI.¹ Acetylation of Mono-, Di- and Tri-bridged Ferrocenes²

BY KENNETH L. RINEHART, JR.,³ DONALD E. BUBLITZ AND DAVID H. GUSTAFSON

RECEIVED AUGUST 29, 1962

Synthesis of the isomeric bis- and tris-(trimethylene)-ferrocenes has been achieved. These compounds and the mono-bridged analog have been acetylated and the ratios of the isomeric acetyl products have been determined. Cyclization of certain bridged ferrocene-propionic acids has been shown to give homoannular ketonic products, as well as the expected heteroannular compounds. Nuclear magnetic resonance spectra of the compounds prepared are discussed.

Since the original reports^{4,5} of the preparation of a bridged ferrocene, 1,1'-(α -ketotrimethylene)-ferrocene (Ia), considerable interest has been displayed in compounds of this type and a number of other mono-bridged compounds have been prepared, as Ib,¹ Ic,^{1,6–8} Id,⁶ Ie,⁹ If,¹⁰ Ig,⁷ Ih,¹⁰ Ii.^{11,12} Recently, too, the di-bridged ferrocene XI and its α -keto derivative X have been reported by Schlögl and Seiler.¹³ The ketone X was prepared by them by cyclization of 1,1'-trimethyleneferrocene-3-propionic acid (IX),¹⁴ which



Ia-i

- a, X = -CH₂CH₂CO-
 b, X = -CH₂CH₂CHOH-
 c, X = -(CH₂)₃-
 d, X = -(CH₂)_n-; n = 4, 5
 e, X = -Si(CH₃)₂-O-Si(CH₃)₂-
 f, X = -CH₂-O-CH₂-
 g, X = -(CH₂)_nCOCHOH(CH₂)_m-; n = m = 1, 2, 3, 4; n = 3, m = 4
 h, X = -C(CH₃)₂C(CH₃)₂-
 i, X = -CH(CH₃)-O-CH(CH₃)-

in turn had been obtained by three routes: (1) formylation of 1,1'-trimethyleneferrocene (Ic) to an aldehyde (presumably 1,1'-trimethyleneferrocene-3-carboxaldehyde), which was converted *via* condensation with malonic acid in the Doebner reaction and subsequent hydrogenation to IX; (2) cyclization in trifluoroacetic anhydride of 1,1'-ferrocenedipropionic acid XII and

(3) Nomenclature employed throughout the present paper accords pre-eminence to the ring positions substituted by the hydrocarbon bridges; other groups are considered substituents of these basic skeletons. This system has the considerable advantage of consistency and is somewhat similar to that employed for bicyclic hydrocarbons.

(1) Paper V, K. L. Rinehart, Jr., R. J. Curby, Jr., D. H. Gustafson, K. G. Harbison, R. E. Bozak and D. E. Bublitz, *J. Am. Chem. Soc.*, **84**, 3263 (1962).

(2) Presented in part at the 141st National A.C.S. Meeting, Washington, D. C., March 20–29, 1962; *cf.* Abstracts, p. 19-O.

(3) Alfred P. Sloan Foundation Fellow.

(4) K. L. Rinehart, Jr., and R. J. Curby, Jr., *J. Am. Chem. Soc.*, **79**, 3290 (1957).

(5) In the Ph.D. Thesis of M. Rosenblum (Harvard University, August, 1953) it is noted that R. B. Woodward and E. Csendes obtained compound Ia, a m.p. is given, and a tentative structure is assigned.

(6) A. Lüttringhaus and W. Kullick, *Angew. Chem.*, **70**, 438 (1958).

(7) K. Schlögl and H. Seiler, *Monatsh.*, **91**, 79 (1960).

(8) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 4216 (1961).

(9) R. L. Schaaf, P. T. Kan and C. T. Lenk, *J. Org. Chem.*, **26**, 1790 (1961).

(10) K. L. Rinehart, Jr., A. K. Frerichs, P. A. Kittle, L. F. Westman, D. H. Gustafson, R. L. Pruett and J. E. McMahon, *J. Am. Chem. Soc.*, **82**, 4111 (1960).

(11) T. A. Mashburn, Jr., and C. R. Hauser, *J. Org. Chem.*, **26**, 1671 (1961).

(12) E. C. Winslow and E. W. Brewster, *ibid.*, **26**, 2982 (1961).

(13) K. Schlögl and H. Seiler, *Tetrahedron Letters*, No. 7, 4 (1960).