period of 40 min. After a further 15 min, 25 ml (0.24 mol) of bromobenzene was added *via* the same dropping funnel, the reaction flask was placed in the photochemical reactor equipped with 350-nm lamps, and irradiation was started, the solution being constantly stirred and gently swept with nitrogen. Samples (*ca.* 1 ml) were taken by the procedure described above and analyzed by glpc; after 110 min, the bromobenzene had all reacted. To the reaction mixture, solid NH_4Cl was added until the orange-yellow solution became pale yellow, 350 ml of ether was added, and the ammonia was evaporated. Sufficient water was added to dissolve the inorganic salts and the ether layer was separated. The water layer was extracted with a further 150 ml of ether. The combined ether extracts were washed thrice with 100-ml portions of water saturated with NaCl and dried over anhydrous Na_2SO_4. One-tenth of the ether solution was separated from the rest; measured amounts of toluene and *p*-dichlorobenzene were added to it; glpc analysis of the resulting mixture indicated 86% of phenylacetone and 14% of 1,1-diphenyl-2-propanone to have been formed, but no significant amount of benzene. The remaining nine-tenths of the ether solution was concentrated and distilled under vacuum; 21.0 g (73%) of phenylacetone, bp 103–106° (19 Torr), of purity >98% as judged by glpc and nmr, was isolated.

Registry No.—Acetone enolate ion, 24262-31-5.

Acknowledgments.—We thank Dr. William J. Boyle, Jr., for a sample of di-*tert*-butyl nitroxide, and Professor Frederick D. Greene for suggesting its use.

Mechanisms of SNi Reactions. The Effect of Aralkyl Group Structure on Ion-Pair Return in the Decomposition of Aralkyl Thiocarbonates[1]

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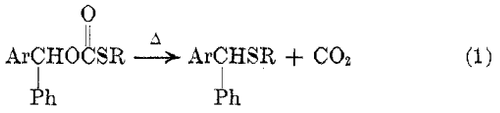
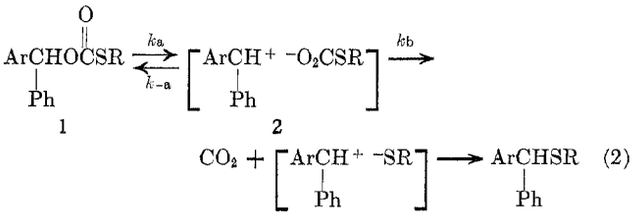
The effect of a change in the nature of Ar in $ArPhCH^+$ on the extent and stereochemistry of ion-pair return accompanying the decomposition of aralkyl *S*-methyl thiocarbonates (eq 2) has been examined by investigating the behavior of *p*-methylbenzhydryl and α-naphthylphenylcarbinyl *S*-methyl thiocarbonates (**1b** and **1c**) and comparison of the results with those obtained earlier with *p*-chlorobenzyhydryl *S*-methyl thiocarbonate. The change from Ar = *p*-ClC_6H_4 to *p*-$CH_3C_6H_4$ leads to a decrease in the percentage of ion pairs **2** undergoing return and to an increase in the fraction doing so with racemization, in accord with the effect expected of a structural change that leads to an increase in the stability of the carbonium ion portion of the ion pair, and, where appropriate, with the results of Goering and Hopf on a related system. In contrast the change from Ar = *p*-ClC_6H_4 to α-$C_{10}H_7$, while also leading to a carbonium ion of increased stability, leads to only very small changes in the extent and stereochemistry of ion pair return. The implications of this result are discussed.

Previous work[2] has shown that the thermal decomposition of aralkyl thiocarbonates (eq 1), which occurs



(1)

when these compounds are heated in a polar aprotic solvent at 130–170°, takes place *via* the two-step mechanism outlined in eq 2 and that extensive ion-pair



(2)

return from **2** to thiocarbonate (step k_{-a}) accompanies the decomposition.

In this earlier study[2] the variation in both the extent and stereochemistry of ion-pair return was investigated for a trio of *p*-chlorobenzhydryl (Ar = *p*-ClC_6H_4) thiocarbonates as a function of (1) changes in the structure of the thioalkyl (RS–) group and (2) a change from a relatively polar (benzonitrile) to a less polar solvent (bromobenzene). In the present investigation we have explored the effect of changes in the structure of Ar in the carbonium ion portion of **2** on ion-pair return by studying the decomposition of a pair of aralkyl *S*-methyl thiocarbonates in benzonitrile and comparing the results with those obtained earlier[2] for the decomposition of *p*-chlorobenzhydryl *S*-methyl thiocarbonate (**1a**, Ar = *p*-ClC_6H_4; R = CH_3) in this solvent. The two thiocarbonates chosen for study were *p*-methylbenzhydryl (**1b**, Ar = *p*-$CH_3C_6H_4$; R = CH_3) and the α-naphthylphenylcarbinyl (**1c**, Ar = α-$C_{10}H_7$; R = CH_3) *S*-methyl thiocarbonate.

The reasons for choosing these two particular thiocarbonates were as follows. As judged by the rates of solvolysis of the corresponding aralkyl chlorides in aqueous acetone,[3,4] both *p*-$CH_3C_6H_4CHPh^+$ and α-$C_{10}H_7CHPh^+$ are more stable carbonium ions than *p*-$ClC_6H_4CHPh^+$. However, while with Ar = *p*-$CH_3C_6H_4$ this increase in carbonium ion stability is achieved with no change in the steric requirements of the Ar group, this is not the case with Ar = α-$C_{10}H_7$, since α-naphthyl represents a significantly bulkier group than *p*-chlorophenyl. Our interest was first to compare the effect of the change from Ar = *p*-ClC_6H_4 to *p*-$CH_3C_6H_4$ on the extent and stereochemistry of ion-pair return in the thiocarbonate decomposition with the results of Goering and Hopf[5] on the effect of the same change on ion-pair return in the solvolysis of para-substituted benzhydryl *p*-nitrobenzoates. Second, we were interested in the extent to which the change in steric bulk of Ar on going to Ar = α-$C_{10}H_7$ would have any significant effect on ion-pair return.

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) J. L. Kice, R. L. Scriven, E. Koubek, and M. Barnes, *J. Amer. Chem. Soc.*, **92**, 5608 (1970).

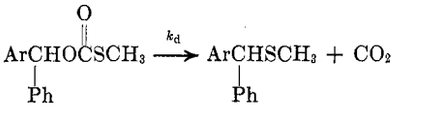
(3) L. Verbit and E. Berlinger, *ibid.*, **86**, 3307 (1964).

(4) J. R. Fox and G. Kohnstam, *Proc. Chem. Soc.*, 115 (1964).

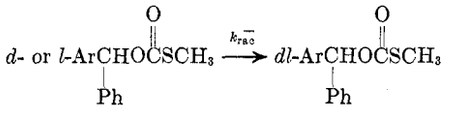
(5) H. L. Goering and H. Hopf, *J. Amer. Chem. Soc.*, **93**, 1224 (1971).

Results

Using optically active and ^{18}O-labeled thiocarbonates one can measure the rates associated with the following processes.



(3)



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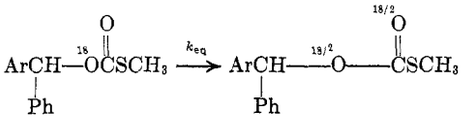


(5)

One can also determine the stereochemistry of the aralkyl methyl sulfide, ArPhCHSCH$_3$, produced by the decomposition of optically active thiocarbonate. It turns out, as was also true in earlier work,[2] that the sulfide is in each instance racemic. Because of this one can determine k_{rac} by measuring k_α, the first-order rate constant for the rate of loss of optical activity by the solution during the decomposition of optically active thiocarbonate, and then taking advantage of the fact that, since the sulfide product is racemic, $k_\alpha = k_{rac} + k_d$.

Rates of decomposition of the thiocarbonates, k_d, were determined, as before,[2] by following the disappearance of the absorption band due to the carbonyl group of the thiocarbonate in the infrared.

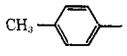
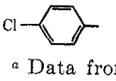
The rate constant for equilibration of the oxygen-18 label in the thiocarbonate, k_{eq}, was measured by partially decomposing samples of labeled thiocarbonate, recovering the undecomposed thiocarbonate, reducing it with lithium aluminum hydride, and then determining the ^{18}O content of the alcohol ArPhCHOH isolated from this reduction. Earlier work[2] has shown that the rate of equilibration of the label can be determined reliably by this procedure.

The necessary optically active and ^{18}O-labeled thiocarbonates were synthesized by reaction of the optically active or ^{18}O-labeled alcohol, as appropriate, with methyl chlorothiolformate, CH$_3$SCOCl.

Table I gives the values of k_{eq}, k_α, and k_d for **1b** and **1c** in benzonitrile at 135° as determined in the present work together with the previously measured[2] values of these rate constants for **1a** in this same solvent at 145°.

TABLE I

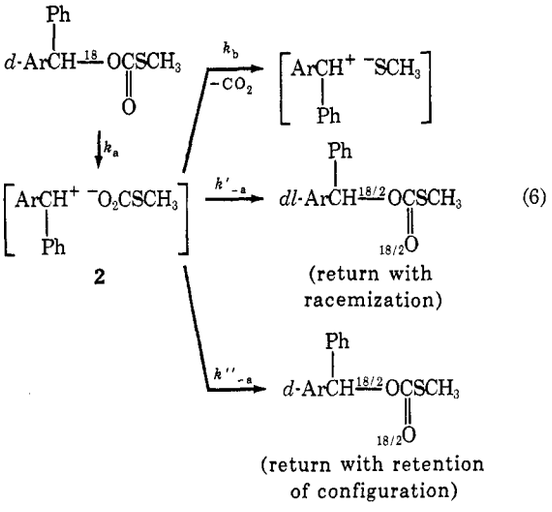
KINETICS OF THE DECOMPOSITION OF ARALKYL *S*-METHYL THIOCARBONATES IN BENZONITRILE

Ar in ArPhCHOC(O)SMe	Temp, °C	$k_{eq} \times 10^5$, sec^{-1}	$k_\alpha \times 10^5$, sec^{-1}	$k_d \times 10^5$, sec^{-1}
	135	44 ± 4	28.1 ± 0.2	9.1 ± 0.6
	135	38 ± 3	18.4 ± 0.8	4.9 ± 0.4
	145[a]	5.1 ± 0.4	2.6 ± 0.1	0.65 ± 0.01
	166[b]			6.0

[a] Data from ref 2. [b] Data from J. L. Kice, R. A. Bartsch, M. A. Dankleff, and S. L. Schwartz, *J. Amer. Chem. Soc.*, **87**, 1734 (1965).

Discussion

The ion pair **2** (eq 2) formed by dissociation of the aralkyl–oxygen bond in the thiocarbonate can either undergo loss of CO_2 (step k_b) or return to thiocarbonate (step k_{-a}). Goering and Linsay[6] have provided evidence that, for carbonium–carboxylate ion pairs involving strongly resonance-stabilized carbonium ions, such as ArPhCH$^+$$^-O_2$CSR, ion-pair return results in essentially complete equilibration of the oxygen-18 label between the ether and carbonyl oxygens, so that k_{eq} is a reliable indicator of total ion-pair return in such systems. As outlined in eq 6, return can take



(6)

place with either loss (step k'_{-a}) or retention (step k''_{-a}) of configuration.

The various rate constants in eq 6 can be related to k_{eq}, k_α, and k_d in the following manner.

$$(k_b/k'_{-a}) = \frac{k_d}{k_\alpha - k_d} \quad (7a)$$

$$(k_b/k''_{-a}) = \frac{k_d}{k_{eq} + k_d - k_\alpha} \quad (7b)$$

$$\left(\frac{k'_{-a}}{k'_{-a} + k''_{-a}}\right) = \frac{k'_{-a}}{k_{-a}} = \frac{k_\alpha - k_d}{k_{eq}} \quad (7c)$$

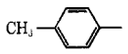
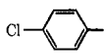
$$\left(\frac{k_b}{k'_{-a} + k''_{-a}}\right) = \frac{k_b}{k_{-a}} = \frac{k_d}{k_{eq}} \quad (7d)$$

It is also possible to analyze the data in Table I on the basis of a mechanism (eq 8) where one assumes that there are two types of ion-pair intermediates, one of which has lost its stereochemical memory and the other of which has not, and where one assigns rate constants, k_2 and k_4, to the rates at which "optically active" ion pairs *d*-**2** and *d*-**3** undergo loss of configuration. (A mechanism of this variety involving two ion pairs with different stereochemical behavior was felt by Goering and Levy[7] to be needed in order to explain certain aspects of their data on ion-pair return phenomena accompanying the solvolysis of *p*-chlorobenzhydryl *p*-nitrobenzoate in aqueous acetone.) Since the aralkyl sulfide formed is optically inactive, if we

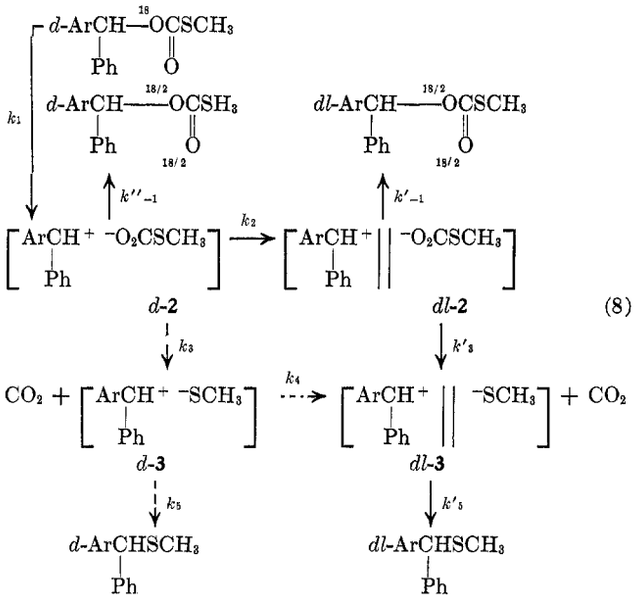
(6) H. L. Goering and E. C. Linsay, *J. Amer. Chem. Soc.*, **91**, 7435 (1969).
(7) H. L. Goering and J. F. Levy, *ibid.*, **86**, 120 (1964).

TABLE II

BEHAVIOR OF ION PAIRS IN THE DECOMPOSITION OR ARALKYL *S*-METHYL THIOCARBONATES IN BENZONITRILE

Ar in ArPhCHOC(O)SMe	Temp, °C	$\left(\frac{k_b}{k'_{-a}}\right)$	$\left(\frac{k_b}{k''_{-a}}\right)$	$\left(\frac{k'_{-a}}{k'_{-a}+k''_{-a}}\right)$	$\left(\frac{k_b}{k'_{-a}+k''_{-a}}\right)$	—% Return to thiocarbonate— total	With retention	With racemization	% Ion pairs losing CO_2
	135	0.48 ± 0.04	0.36 ± 0.06	0.43 ± 0.04	0.21 ± 0.02	83	47	37	17
	135	0.36 ± 0.03	0.20 ± 0.03	0.35 ± 0.03	0.13 ± 0.01	88	57	31	12
	145	0.33 ± 0.02	0.21 ± 0.03	0.38 ± 0.05	0.13 ± 0.01	89	55	34	11

are to assume a mechanism for the thiocarbonate decompositions as shown in eq 8, we must also assume



(8)

that reactions k_3 and k_5 play no role under our reaction conditions.[8] For this reason reactions k_3, k_4, and k_5 are shown with dashed arrows in eq 8.

The relationship of the experimentally measurable rate constants k_{eq}, k_α, and k_d to those in eq 8 is as follows.

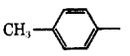
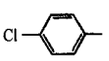
$$(k'_3/k'_{-1}) = \frac{k_d}{k_\alpha - k_d} \quad (9a)$$

$$(k_2/k''_{-1}) = \frac{k_\alpha}{k_{eq} + k_d - k_\alpha} \quad (9b)$$

Tables II and III give the values for the various rate-constant ratios (eq 7a–d and 9a–b) for the different thiocarbonates for the mechanisms shown in eq 6 and 8 as calculated from the data on k_{eq}, k_α, and k_d in Table I. One should recognize that because of the estimated experimental uncertainties in k_{eq}, k_α, and k_d (see Table I) the various rate-constant ratios in Tables II and III are only accurate to ±10% on the average. This should be kept in mind in the ensuing discussion.

TABLE III

VALUES OF (k'_3/k'_{-1}) AND (k_2/k''_{-1}) FOR DECOMPOSITION OF ARALKYL *S*-METHYL THIOCARBONATES IN BENZONITRILE

Ar in ArPhCHOC(O)SMe	Temp, °C	(k'_3/k'_{-1})	(k_2/k''_{-1})
	135	0.48 ± 0.04	1.12 ± 0.18
	135	0.36 ± 0.03	0.74 ± 0.10
	145	0.33 ± 0.02	0.85 ± 0.11

The data for the *p*-tolyl and α-naphthyl derivatives were obtained at 135° while the earlier data[2] for the slower reacting *p*-chlorobenzhydryl compound were for 145°. Since $k_b < k'_{-a}$ or k''_{-a}, it seems likely that $\Delta H^{\pm}$ for loss of CO_2 from $CH_3SCO_2^-$ is somewhat greater than $\Delta H^{\pm}$ for return. Therefore, in all probability the percentage of *p*-$ClC_6H_4PhCH^+$–$^-O_2CSCH_3$ ion pairs undergoing return at 135° would be slightly larger than the 89% found at 145° and k_b/k'_{-a}, k_b/k''_{-a}, and $k_b/(k'_{-a} + k''_{-a})$ would all be somewhat smaller for this thiocarbonate at 135° than they are at 145°. The same will be true for k_3'/k'_{-1}. For various para-substituted benzhydryl *p*-nitrobenzoates Goering and Hopf[5] have shown that the $\Delta H^{\pm}$ associated with ion-pair return occurring with racemization is several kilocalories/mole larger than $\Delta H^{\pm}$ for return with retention. From this we would also expect that both $k'_{-a}/(k'_{-a} + k''_{-a})$ and k_2/k''_{-1} for the *p*-chlorobenzhydryl thiocarbonate would be somewhat lower at 135° than the values given in Tables II and III for 145°.

With this effect of temperature in mind we can now examine the data for the *p*-methylbenzhydryl and *p*-chlorobenzhydryl compounds and see whether it is in accord with our *a priori* expectations of the effect which a change in carbonium ion stability from *p*-$ClC_6H_4CHPh^+$ to *p*-$CH_3C_6H_4CHPh^+$ should have. From its rate of decomposition at higher temperatures (Table I) k_d for **1a** at 135° is calculated to be 0.21×10^{-5} sec^{-1}; this is about 45 times smaller than k_d for the *p*-methylbenzhydryl thiocarbonate at this temperature, and not particularly different from either the 90-fold difference in solvolysis rates of *p*-chlorobenzhydryl and *p*-methylbenzhydryl chlorides in aque-

(8) Since the decomposition of aralkyl chlorocarbonates gives aralkyl chlorides with a high degree of retention of configuration,[9] we believe that the failure to obtain optically active sulfide in the present systems would have to be due, within the framework of eq 8, *not* to k_4 being much faster than k_5, but rather to k_3 being much slower relative to k_2 for $CH_3SCO_2^-$ than is the case for $ClCO_2^-$ in the chlorocarbonate decomposition. The fact[10] that there is no equilibration of oxygen-18 in the undecomposed chlorocarbonate recovered from the partial decomposition of $PhCH_3CH^{18}OC(O)Cl$, while for the thiocarbonates in Table I $k_{eq} > k_d$, is in accord with such a postulate.

(9) K. B. Wiberg and T. M. Shryne, *J. Amer. Chem. Soc.*, **77**, 2774 (1955).

(10) J. L. Kice and G. C. Hanson, *Tetrahedron Lett.*, 2927 (1970).

ous acetone observed by Fox and Kohnstam[4] or the 22-fold difference in solvolysis rates of the *p*-nitrobenzoates observed by Goering and Hopf.[5] These facts clearly indicate that *p*-$CH_3C_6H_4CHPh^+$ is a somewhat more stable carbonium ion than *p*-$ClC_6H_4CHPh^+$. Since step k_b in eq 6 simply involves the loss of CO_2 from $CH_3SCO_2^-$, its rate should presumably be independent of the nature of the carbonium ion $ArCHPh^+$. On the other hand, one would expect that the rate of ion-pair return to thiocarbonate, steps k'_{-a} and k''_{-a}, in eq 6, should be faster the less stable the $ArPhCH^+$ carbonium ion. Thus one would expect that $k_b/(k'_{-a} + k''_{-a})$ should be larger for the *p*-methylbenzhydryl compound than for the *p*-chlorobenzhydryl, and this is indeed what is observed. As already noted, the actual value of $k_b/(k'_{-a} + k''_{-a})$ for **1a** at 135° is almost certainly smaller than the value of 0.13 found at 145°, and so the actual change in this ratio is undoubtedly slightly larger than from 0.13 to 0.21.

Goering and Hopf[5] have studied the stereochemistry of ion-pair return accompanying the solvolysis of *p*-methylbenzhydryl and *p*-chlorobenzhydryl *p*-nitrobenzoates. At a given temperature more of the return from the *p*-methylbenzhydryl ion pair occurs with racemization than with the *p*-chlorobenzhydryl ion pair. The same thing is true in the thiocarbonate decomposition, $k'_{-a}/(k'_{-a} + k''_{-a})$ being smaller for **1a** than for **1b** (particularly when one remembers that at 135° the value for the *p*-chlorobenzhydryl compound will be somewhat less than the value of 0.38 found at 145°). However, the effect is not as large in the present case as in the one studied by Goering and Hopf.[5] They report values of 0.60 and 0.35 for the *p*-methylbenzhydryl and *p*-chlorobenzhydryl *p*-nitrobenzoates, respectively, at 99.6°, a considerably larger change with substituent than the one from 0.43 to something somewhat less than 0.38 found in the thiocarbonate decomposition.

Nonetheless, the data for the change in both the extent and stereochemistry of ion-pair return in the thiocarbonate decomposition (eq 1) on going from Ar = *p*-ClC_6H_4 to Ar = *p*-$CH_3C_6H_4$ are generally in accord with one's expectations of what would be observed, based on (1) intuitive considerations of how the change in carbonium ion stability should influence ($k'_{-a} + k''_{-a}$) and k_b and (2) the results of Goering and Hopf[5] on the stereochemistry of ion-pair return involving the same pair of benzhydryl cations in another reaction. Satisfying though this situation may be, we should realize that this agreement of experiment with expectations occurs in a system in which the change in the stability of the carbonium ion partner in the ion pair is achieved without any significant change in the shape and steric requirements of the carbonium ion. We have only to turn from this case to the one involving the α-naphthylphenylcarbonium ion to see that when the steric requirements of the cation are significantly altered the picture is apparently no longer such a simple one.

Both the relative rates of decomposition of **1b** and **1c** (Table I) and the relative rates of solvolysis of *p*-methylbenzhydryl and α-naphthylcarbinyl chlorides[3] suggest that α-$C_{10}H_7CHPh^+$ and *p*-$CH_3C_6H_4CHPh^+$ do not differ much in stability as carbonium ions, both being more stable than *p*-$ClC_6H_4CHPh^+$. On that basis one might therefore have thought *a priori* that both $k_b/(k'_{-a} + k''_{-a})$ and $k'_{-a}/(k'_{-a} + k''_{-a})$ for **1c** would turn out to be very similar to those for the *p*-methylbenzhydryl thiocarbonate. In actual fact they turn out to be much closer to the values for the *p*-chlorobenzhydryl compound than to those for **1b**.

What is the explanation for this? Frankly, we don't know. Since we doubt that k_b should be sensitive in any way to the nature of the carbonium ion, we assume that it must be due to the fact that k'_{-a} and, to a greater extent, k''_{-a} are somewhat larger for **1c** than for **1b**. However, we do not have any really satisfying explanation for why this might be the case. Verbit and Berliner[3] have suggested that in the α-$C_{10}H_7CHPh^+$ ion there is about a 15° greater angle of twist between the two aryl groups than in the more coplanar Ph_2CH^+ or *p*-$CH_3C_6H_4CHPh^+$. While this could conceivably lead to return with retention being more strongly favored than in the case with a *p*-methylbenzhydryl cation and could therefore explain the smaller value of $k'_{-a}/(k'_{-a} + k''_{-a})$ for **1c** as compared to **1b**, it does not explain why $k_b/(k'_{-a} + k''_{-a})$ is less for the α-naphthyl compound; for, while one can see how the difference in geometry of the two carbonium ions could alter the stereochemistry associated with ion-pair return, there is no readily apparent reason why it should increase the total rate of return relative to the rate of loss of CO_2 from $CH_3SCO_2^-$ in the ion pair.

However, at the same time it is important to stress that the magnitude of the change in $k_b/(k'_{-a} + k''_{-a})$ from **1b** to **1c** is only a factor of 1.6, so that, if we assume that k_b remains the same, $\Delta F^{\pm}$ for k_{-a} would need only to decrease by 0.4 kcal/mol to account for the change. Ion-pair return to thiocarbonate is in each instance undoubtedly a highly exothermic reaction of relatively low $\Delta F^{\pm}$. From Hammond's principle[11] it would therefore be expected that the transition state for return would be *much closer* in structure to the ion pair than to the thiocarbonate. That being the case, it is certainly possible that it might be harder to predict accurately just what effect changes in carbonium ion structure would have on k'_{-a} and k''_{-a} than if the transition state for return were closer to the thiocarbonate in structure.

Our principal conclusion, therefore, is that, while the changes in ion-pair return with carbonium ion stability apparently follow predictable patterns when the change in carbonium ion stability is achieved without a significant change in the geometry of the carbonium ion, this is no longer necessarily true when the change in stability also involves a change in the geometry or steric requirements of the cation. In such cases the behavior of ion-pair return phenomena need not follow any readily predictable course. This suggests that one must exercise great caution in interpreting any variations in return behavior when comparing systems of this type.

Experimental Section

***p*-Methylbenzhydrol-^{18}O.**—*p*-Methylbenzophenone (69 g, 0.35 mol) was dissolved in a mixture of 350 ml of dioxane, 35 ml (1.7 mol) of oxygen-18 enriched water (1.59 atom % ^{18}O), and 0.1 ml of concentrated sulfuric acid, and the solution was heated to re-

(11) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 34 (1955).

flux for 24 hr. The majority of the solvent was then distilled off and the residue was taken up in 100 ml of ether and dried over magnesium sulfate. The dried ether solution was added dropwise with stirring to a flask containing 7.5 g (0.2 mol) of lithium aluminum hydride and 100 ml of anhydrous ether. The mixture was stirred overnight at room temperature and then hydrolyzed by the addition of saturated ammonium chloride solution. The organic layer was separated and washed twice with water and then once with saturated sodium chloride; it was then dried over magnesium sulfate. The solvent was removed under reduced pressure and the *p*-methylbenzhydrol-^{18}O was recrystallized from hexane, yielding 65 g (94%) of ^{18}O-labeled alcohol, mp 51–53° (lit.[12] mp 51–53°), 1.42 atom % ^{18}O.

Unlabeled *p*-methylbenzhydrol was prepared from unlabeled *p*-methylbenzophenone by an analogous reduction with lithium aluminum hydride.

α-Naphthylphenylcarbinol.—This was prepared in 45% yield by reaction of phenylmagnesium bromide with α-naphthylaldehyde. After recrystallization from benzene–hexane it melted at 86° (lit.[13] mp 86.5°).

α-Naphthylphenylcarbinol-^{18}O.—α-Naphthylphenylcarbinol was oxidized to α-naphthyl phenyl ketone with Jones reagent using the procedure of Meinwald, Crandall, and Hymans.[14] The ketone was purified by chromatography on Florisil using benzene as eluent, followed by recrystallization from benzene–hexane, mp 74–75° (lit.[13] mp 75–76°), yield 75%.

The ketone was converted to α-naphthyl phenyl ketone-^{18}O using the same type of procedure as employed to label *p*-methylbenzophenone. The labeled ketone was then reduced to α-naphthylphenylcarbinol-^{18}O with lithium aluminum hydride. The labeled alcohol (1.56 atom % ^{18}O) was obtained in 80% yield, mp 85°.

Resolution of *p*-Methylbenzhydrol.—Racemic *p*-methylbenzhydrol acid phthalate (20 g) was resolved by the procedure outlined by Goering and Hopf.[5] However, instead of using the (−) enantiomer we employed partially resolved (+) enantioner, which was obtained by taking the mother liquor from the first crop of crystals of the quinidine salt of the half-phthalate and proceeding as follows. About 30 ml of solvent was evaporated from the 400 ml of mother liquor and the solution was set aside to allow material to crystallize. The crystals which formed were filtered off and discarded and the procedure was repeated until the volume of the solution had been reduced to only 150 ml. At this point the solvent was completely evaporated and the residual quinidine salt was decomposed in the manner described by Goering Hopf[5] to give 6.95 g of the partially resolved (+) acid phthalate, $[\alpha]_{589}^{25}$ +4.3° (chloroform). The acid phthalate was then converted to partially resolved (+)-*p*-methylbenzhydrol, $[\alpha]_{589}^{25}$ +2.5° (chloroform).

Resolution of α-Naphthylphenylcarbinol.—This was resolved using the procedure outlined by Smetana[13] involving successive recrystallizations of the brucine salt of the acid succinate of α-naphthylphenylcarbinol. The resolved alcohol was crystallized from carbon tetrachloride, yielding (−)-α-naphthylphenylcarbinol, mp 73–74°, $[\alpha]_{579}^{25}$ −38.2° (95% ethanol) [lit.[13] mp 74–75°, $[\alpha]_D$ −35.8° (95% ethanol)].

***p*-Methylbenzhydryl *S*-Methyl Thiocarbonate.**—*p*-Methylbenzhydrol, 2.00 g (0.01 mol), and 1.5 ml of dry pyridine were dissolved in 10 ml of benzene. Methyl chlorothioformate,[15] 2 ml in 10 ml of benzene, was then added dropwise to this solution at room temperature with stirring. After the addition was complete the reaction was stirred for 4 hr more. Then 20 ml of ether was added; the solution was washed with three portions of water and then dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column using benzene as eluent. Recrystallization from hexane afforded 1.9 g (72%) of *p*-methylbenzhydryl *S*-methyl thiocarbonate, mp 36–38°. *Anal.* Calcd for $C_{16}H_{16}O_2S$: C, 70.59; H, 5.93. Found: C, 70.66; H, 5.84.

α-Naphthylphenylcarbinyl *S*-Methyl Thiocarbonate.—This was synthesized using the same general procedure as for the *p*-methylbenzhydryl thiocarbonate. From 2.5 g (0.01 mol) of α-naphthylphenylcarbinol there was obtained, after recrystallization from benzene–hexane, 1.2 g (40%) of α-naphthylphenylcarbinyl *S*-methyl thiocarbonate, mp 91–92°. *Anal.* Calcd for $C_{19}H_{16}O_2S$: C, 73.99; H, 5.23. Found: C, 74.28; H, 5.01.

Preparation of Optically Active and ^{18}O Thiocarbonates.—These were prepared from the appropriate optically active or ^{18}O-labeled alcohols using the same synthetic procedures used for the normal thiocarbonates.

In the case of the ^{18}O-labeled thiocarbonates a sample of the thiocarbonate was then reduced with lithium aluminum hydride back to the alcohol, using a previously described procedure,[2] and the oxygen-18 content of the alcohol was determined in the same manner as in the kinetic studies of ^{18}O equilibration (*vide infra*). For both ^{18}O-labeled thiocarbonates the ^{18}O content of the alcohol isolated from the reduction agreed within experimental error with that of the labeled alcohol used for the synthesis, showing that no equilibration of oxygen-18 between the alkyl and acyl oxygens occurs during the synthesis and purification of the thiocarbonate.

(+)-*p*-Methylbenzhydryl *S*-methyl thiocarbonate prepared from (+)-*p*-methylbenzhydrol of $[\alpha]_{589}$ +2.5° had $[\alpha]_{579}^{25}$ +8.2° and $[\alpha]_{334}^{25}$ +44.5° (benzonitrile). When optically active α-naphthylphenylcarbinyl *S*-methyl thiocarbonate obtained from (−)-α-naphthylphenylcarbinol was allowed to crystallize slowly from benzene–hexane the first material which crystallized out was optically inactive. After this was removed, the solvent was removed from the filtrate and the residue was allowed to stand for 4 days in the refrigerator until crystals formed. This crystalline material, mp 75–79°, was optically active and had an infrared spectrum identical in all respects with the spectrum of a sample of racemic thiocarbonate of mp 91–92°. A difference between the melting point of the racemic and partially resolved thiocarbonate was also observed earlier[2] in the case of *p*-chlorobenzhydryl *S*-methyl thiocarbonate. The specific rotation of the 75–79°-melting thiocarbonate in benzonitrile at various wavelengths was as follows: $[\alpha]_{579}^{25}$ +17.3, $[\alpha]_{404}^{25}$ +28.6°, $[\alpha]_{366}^{25}$ +20.0°, $[\alpha]_{334}^{25}$ −24.4°.

Kinetic Studies of the Thermal Decomposition of Thiocarbonates.—The rates of decomposition of **1b** and **1c** were measured using the infrared method described in an earlier publication.[15]

Kinetic Studies of the Rate of Loss of Optical Activity.—A solution of optically active **1b** or **1c** in benzonitrile was placed in the same type apparatus used for the kinetic studies of the rate of decomposition, and the apparatus was heated in a constant-temperature bath. At appropriate time intervals aliquots were removed and their rotation measured at 25° in a water-jacketed polarimeter cell in a Perkin-Elmer Model 141 spectropolarimeter. The loss of optical activity was followed at 404 mμ for the α-naphthylphenylcarbinyl thiocarbonate and at 334 mμ for the *p*-methylbenzhydryl compound. The final rotation of the solution in each case was zero.

The rate of loss of optical activity, k_α, was determined from the slope of a plot of log α *vs.* time. Rates were reproducible within 5%.

Kinetic Studies of the Equilibrium of Alkyl and Acyl Oxygens.—Except for the method used to determine the oxygen-18 content of the alcohol obtained on reduction of samples of thiocarbonate recovered after partial decomposition, the procedure was the same as that used earlier[2] to study oxygen-18 equilibration accompanying the decomposition of *p*-chlorobenzhydryl thiocarbonates. Rather than the procedure of Doering and Dorfman,[16] which was used in the earlier work to detremine the ^{18}O content of the alcohol, the following alternate procedure was employed. Mass spectra were taken of purified samples of alcohol on a Hitachi RMU-6 mass spectrometer. Each sample was scanned several times at different intensities. The ratio (M + 2)/(M + 1), where M is the main molecular peak, was determined by measuring peak heights accurately.

From this, *P*, the atom per cent oxygen-18 in the alcohol, was calculated using eq 10a for the *p*-methylbenzhydrol and eq 10b for the α-naphthylcarbinol data. These equations are obtained by taking the normal values of (M + 1)/(M + 2) for $C_{14}H_{14}O$

$$P = 15.392\left(\frac{M+2}{M+1}\right) - 1.099 \quad \text{for } C_{14}H_{14}{}^{18}O \quad (10a)$$

$$P = 18.633\left(\frac{M+2}{M+1}\right) - 1.633 \quad \text{for } C_{17}H_{14}{}^{18}O \quad (10b)$$

(12) A. G. Davis, J. Kenyon, B. J. Lyons, and T. A. Rohan, *J. Chem. Soc.*, 3474 (1954).

(13) R. D. Smetana, Ph.D. Thesis, Pennsylvania State University, 1964.

(14) J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Syn.*, **45**, 77 (1965).

(15) J. L. Kice, R. A. Bartsch, M. A. Dankleff, and S. L. Schwartz, *J. Amer. Chem. Soc.*, **87**, 1734 (1965).

(16) W. von E. Doering and E. Dorfman, *ibid.*, **75**, 5595 (1953).

and $C_{17}H_{14}O$, respectively, tabulated by Benyon[17] and then making provision for the fact that the oxygen-18 content is going to be variable in this case, rather than having the normal isotopic abundance used in calculating the tables in Benyon's book. The reliability of this method of determining P for the alcohol samples was verified by comparing the value of P for a sample of *p*-methylbenzhydrol determined in this way with the value determined by the method of Doering and Dorfman.[16] Within experimental error the results were the same.

The rate of ^{18}O equilibration between alkyl and acyl oxygens in the thiocarbonate was determined by plotting log $(P - P_\infty)/(P_0 - P_\infty)$ *vs.* time, where P_0 is the atom per cent oxygen-18 for a sample at $t = 0$, and $P_\infty = (P_0 + 0.204)/2$.

(17) J. H. Benyon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier, Amsterdam, 1960, pp 521, 537.

Registry No.—**1a**, 3326-54-3; (±)-**1b**, 38379-31-6; (+)-**1b**, 38379-32-7; **1b**-^{18}O, 38379-33-8; (±)-**1c**, 38379-34-9; (+)-**1c**, 38379-35-0; **1c**-^{18}O, 38379-36-1; *p*-methylbenzhydrol-^{18}O, 38379-37-2; *p*-methylbenzophenone, 134-84-9; α-naphthylphenylcarbinol-^{18}O, 38379-39-4; α-naphthyl phenyl ketone, 642-29-5; α-naphthyl phenyl ketone-^{18}O, 38379-41-8; (+)-*p*-methylbenzhydrol acid phthalate, 38379-42-9; (+)-*p*-methylbenzhydrol, 75832-67-4; (−)-α-naphthylphenylcarbinol, 1517-61-9; (±)-*p*-methylbenzhydrol, 38379-45-2; (±)-α-naphthylphenylcarbinol, 38379-46-3.

Protonation of Fumaric and Maleic Acids and Their Diethyl Derivatives

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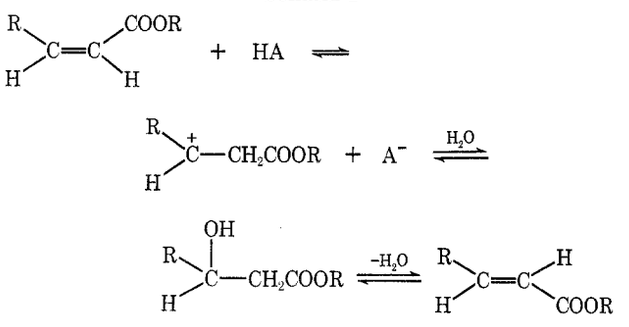
Strong acid media were employed to protonate maleic and fumaric acid and their diethyl ester derivatives. Nuclear magnetic resonance (nmr) showed that preferential oxygen protonation was occurring. In none of the compounds studied could protonation of the carbon–carbon double bond be observed.

As part of our continuing studies[1] of carbocations in strongly acidic solvents, we have investigated the thermodynamics of diprotonation of a series of diacids, diesters, and diketones. In light of the long-standing controversy regarding the site of protonation of the isomeric maleic and fumaric acids,[2] it was necessary to verify the structure of the protonated species in strong acid systems. That structure is the subject of this paper.

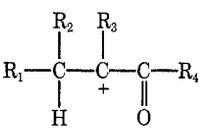
Many cis–trans isomerizations of α,β-unsaturated carboxylic acids are acid catalyzed. The mechanism of these reactions has been thoroughly studied. From their results Noyce and coworkers[3] detailed the mechanism as an addition–elimination in which the first step was protonation of the ethylenic linkage followed by the hydration of the resulting carbocation (Scheme I).

Richards, *et al.*,[2] recently concluded from secondary kinetic isotope effects and isotopic exchange experiments on the fumarase-catalyzed isomerization of *l*-malate to fumarate that the same type of carbocation intermediate is involved. This mechanism is quite different from that proposed by Fahey and Schneider[4] for the addition of HCl to diethyl maleate and fumarate in acetic acid. In compounds like XCH=CHY where X has positive character and is itself a base (*e.g.* O=COEt), protonation on carbon may not be the most favorable process. Fahey and Schneider have proposed that the interconversion of malate to fumarate might proceed *via* a modification of the 1,4-addition mechanism originally proposed by Ogg and Nozaki.[5] As they point out, formation of a carbocation adjacent to a carbonyl group is surprising. However, the data of Hansen, *et al.*,[2] seem to require this intermediate in the enzyme-catalyzed reaction.

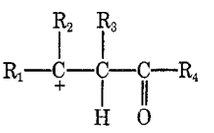
SCHEME I



Observation of the carbocation from malate or fumarate in strong acid, in conjunction with deuterium incorporation, would present strong evidence in favor of protonation of the –C=C– bond. α,β-Unsaturated carboxylic acids and carbonyl compounds have previously been shown to protonate on oxygen in superacid media.[6] However, no studies of maleic and fumaric acids or their derivatives appear to have been published. Previous attempts to prepare cations of the type **1** and **2**



1



2

by treating α- or β-halo ketones or aldehydes in strong acid have proven unsuccessful.[7] However, Kuta and

(1) J. W. Larsen, *J. Amer. Chem. Soc.*, **93**, 5107 (1971); J. W. Larsen, P. A. Bouis, M. W. Grant, and C. A. Lane, *ibid.*, **93**, 2067 (1971); J. W. Larsen, *ibid.*, **92**, 5136 (1970); J. W. Larsen, S. Ewing, and M. Wynn, *Tetrahedron Lett.*, 539 (1970).

(2) R. A. Alberty, W. G. Miller, and H. F. Fisher, *J. Amer. Chem. Soc.*, **79**, 3973 (1957); D. E. Schmidt, Jr., W. G. Nigh, C. Tanzer, and J. H. Richards, *ibid.*, **91**, 5849 (1969); R. C. Fahey and H. Schneider, *ibid.*, **92**, 6885 (1970); J. N. Hansen, E. L. Dinova, and P. D. Boyer, *J. Biol. Chem.*, **244**, 6270 (1969).

(3) D. S. Noyce, H. S. Avarbock, and W. L. Reed, *J. Amer. Chem. Soc.*, **84**, 1647 (1962); D. S. Noyce, P. A. King, F. B. Kirby, and W. L. Reed, *ibid.*, **84**, 1632 (1962).

(4) R. C. Fahey and H. Schneider, *ibid.*, **92**, 6885 (1970).

(5) K. Nozaki and R. Ogg, Jr., *ibid.*, **63**, 2583 (1941).

(6) For a general review see G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, **70**, 561 (1970).

(7) G. A. Olah, Y. Halpern, Y. K. Mo, and G. Liang, *J. Amer. Chem. Soc.*, **94**, 3554 (1972).