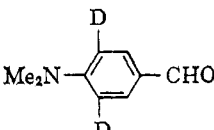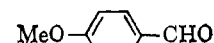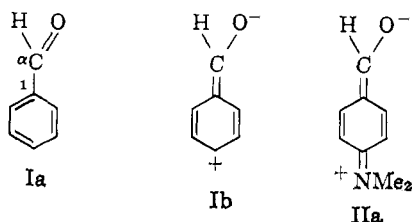of the barrier is not known. We have now found that low temperature n.m.r. spectra (60 Mc./sec.) of p-N,N-dimethylaminobenzaldehyde (II), p-methoxybenzaldehyde (anisaldehyde, III), and of I provide information on this point.

The aromatic protons of II and III gave rise to A_2B_2 (approximately A_2X_2) systems at room temperature,[3] but to much more complex spectra at low temperatures (e.g., below about $-85°$ for II and $-115°$ for III). The main change was a splitting of the resonance signal of the protons *ortho* to the aldehyde group; little change was observed in the bands of other protons. Thus, at the low temperatures the *ortho* protons become nonequivalent, as is expected[4] if the rate constant for internal rotation becomes[5] much less than $\pi\nu\sqrt{2}$, where ν (in c.p.s.) is the relative chemical shift between the nonequivalent protons.

With II, the situation was simplified by the use of 4-N,N-dimethylaminobenzaldehyde-3,5-d_2 (IIA) together with strong double-irradiation at the deuterium resonance frequency. The aromatic protons then gave a single sharp line at room temperature and an AB quartet (ν_{AB} = 8.4 c.p.s., J = 2.5 c.p.s.) below about $-85°$.

TABLE I

Compound	Solvent	Coalescence temperature, °C.	ΔF^*, kcal./mole
Ph CHO (I)	Vinyl chloride	-123	7.9
Me$_2$N—⟨⟩—CHO (IIA)	CH$_2$Cl$_2$	-71	10.8
MeO—⟨⟩—CHO (III)	Vinyl chloride	-99	9.2

Changes very similar to those occurring in the spectra of II and III took place below about $-120°$ in the spectrum of I. Measurements of the spectra of I, IIa, and III at intermediate temperatures gave apparent coalescence temperatures[4,5] (Table I) from which the free energies of activation (ΔF^*) for internal rotations were calculated[6] (Table I).

The increase ($\Delta\Delta F^*$) in ΔF^* of II over I may be ascribed to a direct resonance interaction of the aldehyde and dimethylamino groups (i.e., to a contribution of IIa to the resonance hybrid of II). The energy of this interaction (2.8 kcal./mole) is a little greater, as expected, than that (2.5 kcal./mole) calculated by

(3) The room temperature spectra of I, II, and III are well known; see' for example, N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "N.M.R. Spectra Catalog," Varian Associates, Palo Alto, Calif., 1961. The protons *ortho* to the aldehyde group in each case occur at lower field than the other aromatic protons.

(4) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw–Hill Co., Inc., New York, N. Y., 1959.

(5) Because of the presence of coupling, this expression[4] is not strictly correct, but the error involved should be small.

(6) The values of ΔF^* were calculated from the absolute rate theory for internal rotation over only one of the two possible barriers to rotation.

Taft[7] for the resonance interaction of a dimethylamino group and a p-carbethoxy group.

It is planned to investigate the low temperature spectra of other aromatic aldehydes, and particularly of suitably deuterated derivatives, so as to obtain values of ΔH^* and ΔS^*. The present results, as far as they go, are in agreement with the finding. from ultrasonic measurements[8] of appreciable barriers (ca. 5 kcal./mole) in $\alpha\beta$-unsaturated aldehydes.

(7) R. W. Taft, Jr., in M. S. Newman "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 583.

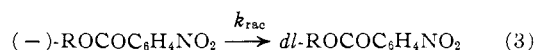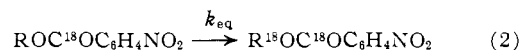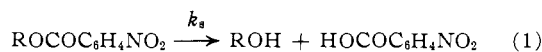(8) M. S. de Groot and J. Lamb, Proc. Roy. Soc. (London), **A242**, 36 (1957).

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On the Nature of Ion-Pair Intermediates Involved in the Solvolysis of p-Chlorobenzhydryl p-Nitrobenzoate

Sir:

We recently reported[1] that ion-pair return associated with solvolysis (alkyl–oxygen cleavage) of p-chlorobenzhydryl p-nitrobenzoate in aqueous acetone (reaction 1) results in randomization of the carboxyl oxygen atoms of ^{18}O-labeled ester (reaction 2) and racemization of optically active substrate (reaction 3). These transformations are first order and the last two are intramolecular.[1] This shows that ion-pair return is cleanly isolated from external ion return[2] and thus the two transformations of the unsolvolyzed ester (reactions 2 and 3) result from ion-pair return.[3]

$$\text{ROCOC}_6\text{H}_4\text{NO}_2 \xrightarrow{k_s} \text{ROH} + \text{HOCOC}_6\text{H}_4\text{NO}_2 \quad (1)$$

$$\text{ROC}^{18}\text{OC}_6\text{H}_4\text{NO}_2 \xrightarrow{k_{eq}} \text{R}^{18}\text{OC}^{18}\text{OC}_6\text{H}_4\text{NO}_2 \quad (2)$$

$$(-)\text{-ROCOC}_6\text{H}_4\text{NO}_2 \xrightarrow{k_{rac}} dl\text{-ROCOC}_6\text{H}_4\text{NO}_2 \quad (3)$$

Assuming that ionization gives rise to an ion pair in which the carboxyl oxygen atoms are equivalent,[1,4,5] oxygen equilibration (k_{eq}) measures total ion-pair return and k_{rac} measures racemization associated with this return. At 100° the k_{eq}/k_{rac} ratios for 80 and 90% acetone are 2.3 and 2.6, respectively. This shows that return involves predominating retention of configuration.

At the time of our earlier report[1] an important question concerning the stereochemical behavior of ion-pair species was left unanswered. This is whether the observed return is exclusively internal return (i.e., one intermediate which returns with partial loss of configuration) or if external ion-pair return[2] is also involved (two intermediates). We now wish to report evidence that at least two distinct ion-pair species are involved. The evidence is as follows. In the presence of 0.14 M sodium azide, ion-pair return also occurs (the carboxyl oxygen atoms mix), however, in this case, the optical configuration of the unsolvolyzed ester is preserved fully, i.e., k_{rac} = 0. Clearly, the nucleophilic azide ion is intercepting an intermediate that otherwise

(1) H. L. Goering, R. G. Briody, and J. F. Levy, J. Am. Chem. Soc., **85**, 3059 (1963).

(2) S. Winstein, P. E. Klinedinst, Jr., and G. C. Robinson, ibid., **83**, 885 (1961).

(3) The effects of varying structure and solvent on the rates and relative rates of reactions 1–3 are consistent with this interpretation (ref. 1 and 4).

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

(5) H. L. Goering and M. M. Pombo, ibid., **82**, 2515 (1960); H. L. Goering and J. T. Doi, ibid., **82**, 5850 (1960); H. L. Goering, M. M. Pombo, and K. D. McMichael. ibid., **85**, 965 (1963).

would return with loss of configuration, but is not intercepting an intermediate that returns with retention of configuration. The pertinent data are presented in Table I.

TABLE I

RATE CONSTANTS FOR SOLVOLYSIS (k_s), OXYGEN EQUILIBRATION (k_{eq}), AND RACEMIZATION (k_{rac}) ASSOCIATED WITH THE SOLVOLYSIS OF p-CHLOROBENZHYDRYL p-NITROBENZOATE IN 80% AQUEOUS ACETONE AT 99.6°[a]

[Ester], $10^2 M$	[Solute], $10^2 M$	Constant	k, 10^3 hr.$^{-1}$
2.78	None	k_s	4.41 ± 0.06[b]
2.76	14.11 NaN$_3$	k_s	30.0 ± 0.4
2.43	None	k_{eq}	6.5 ± 0.2[b]
2.80	14.11 NaN$_3$[c]	k_{eq}	5.9 ± 0.3
2.9	None	k_{rac}	2.76 ± 0.02[d]
2.79	14.11 NaN$_3$	k_{rac}	0.0
2.86	14.11 NaN$_3$	k_{rac}	0.0

[a] Solvent composition based on volumes of pure components at 25° prior to mixing. [b] Taken from ref. 1. [c] In this experiment 5×10^{-3} M radioactive p-nitrobenzoic acid was added at the outset and the second-order rate constant for exchange ($5.4 \pm 0.1 \times 10^{-3}$ l. mole^{-1} hr.$^{-1}$) was also obtained using this reaction mixture. [d] Average value of two experiments in which different methods were used to follow the reaction.

In the presence of 0.14 M sodium azide the first-order solvolysis results in the formation of 0.63 equivalent of titratable acid. This shows that 37% of the ester is converted to p-chlorobenzhydryl azide (no acid produced) and the rest to p-chlorobenzhydrol. The 6.8-fold increase in rate of solvolysis (k_s) is due in part to an azide-ion-promoted hydrolysis (with acyl–oxygen cleavage[6]) which is superimposed on the carbonium ion reaction. In the presence of azide ion, 82% of the p-chlorobenzhydrol (52% of the total product) is produced by acyl–oxygen cleavage; solvolysis in the absence of azide ion involves exclusive alkyl–oxygen cleavage.[1] Thus the ester undergoes the two simultaneous reactions at about equal rates and the rate constant for solvolysis with alkyl–oxygen cleavage is $^1/_2$ k_s (3.4 times that in the absence of azide ion).

The only complication resulting from the azide-ion-promoted hydrolysis is that this side reaction consumes half of the substrate and thus changes in the unsolvolyzed ester can only be observed for half as long as would otherwise be possible. Nonetheless, oxygen equilibration (reaction 2) was followed to 27% completion (82% solvolysis). The value of k_{eq} is the average of two first-order constants calculated for 20 and 27% reaction. Under these conditions the second-order rate constant for exchange between unsolvolyzed ester and the sodium p-nitrobenzoate produced by the solvolysis is 0.54×10^{-2} l. mole^{-1} hr.$^{-1}$.[7] With this constant it can be shown[4] that <1% of the remaining ester has undergone exchange at a point corresponding to 27% oxygen equilibration.

The last two experiments in Table I are the crucial ones. In the first of these, ester having $[\alpha]^{25}_{435}$ $-13.79°$ (CHCl$_3$) was solvolyzed and the remaining ester isolated after 62.5 hr. (85% solvolysis; 31% oxygen equilibration) had $[\alpha]^{25}_{435}$ $-13.93°$. In the last experiment the starting ester had $[\alpha]^{25}_{435}$ $-26.66°$ (CHCl$_3$) and after 72 hr. (88% solvolysis; 35% oxygen equilibration) the remaining ester had $[\alpha]^{25}_{435}$ $-26.57°$. In the absence of azide ion the unsolvolyzed ester

(6) Evidently this reaction involves attack by azide ion on the carbonyl carbon atom to give p-nitrobenzoyl azide which hydrolyzes rapidly. That the azide does not undergo a Curtius rearrangement to give p-nitroaniline was indicated by the ultraviolet spectrum of the reaction product.

(7) The exchange constant was determined as described previously (ref. 4). Since hydrazoic acid is weaker than p-nitrobenzoic acid and since in the solvolysis and exchange experiments sodium azide was present in large excess, the p-nitrobenzoic acid is present as the sodium salt.

racemizes to the extent of 16–18% during these periods.[8] Control experiments showed that isolation and purification of active unsolvolyzed ester does not affect the rotation and, in fact, when racemization occurs (e.g., as in the absence of azide ion), k_{rac} can be determined with good precision from the specific rotations of samples of isolated ester.[1] Thus it is clear that racemization would have been detected had it occurred.

This then shows that azide ion eliminates racemization but not carboxyl oxygen equilibration. We feel this is compelling evidence that two intermediates are involved; one which returns with preservation of configuration and one which returns with racemization. It is the latter that is intercepted by azide ion.

The observation that two intermediates are involved parallels the recent findings of Winstein and co-workers[2,9] that so-called intimate (I) and solvent-separated (II) ion pairs are involved in the ionization of certain alkyl arenesulfonates in acetic acid. The present results are nicely accommodated by the Winstein scheme for ionization. According to this interpretation internal return is completely stereospecific (retention) and external ion-pair return results in partial or complete racemization.[10] Azide ion acts as a scavenger for the solvent-separated ion pair II and thus eliminates racemization.

$$RX \rightleftarrows [R^+X^-] \rightleftarrows [R^+||X^-] \longrightarrow products$$
$$\qquad\qquad I \qquad\qquad\quad II$$
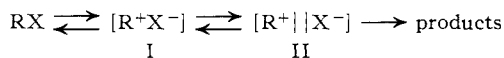
The stereochemistry of solvolysis was also investigated. Solvolysis of optically active carboxyl-^{18}O ester in 80% acetone containing 0.14 M sodium azide gives p-chlorobenzhydrol with $85.2 \pm 0.6\%$ retention of configuration and $81.9 \pm 1\%$ acyl–oxygen cleavage. These values are averages for two samples isolated at different times and the difference is considered to be real. This means that the carbonium ion portion of the solvolysis proceeds with excess retention of configuration. This parallels the observation that in the absence of azide ion, where solvolysis involves alkyl–oxygen cleavage exclusively, p-chlorobenzhydrol is formed with 10% retention of configuration.[1] The p-chlorobenzhydryl azide derived from active ester is also active. However, the relative configurations of substrate and azide have not been established.

(8) If azide ion were not intercepting an intermediate, the recovered ester would be expected to be substantially more than 18% racemized because of the positive salt effect on the rate of ionization.

(9) S. Winstein, P. E. Klinedinst, Jr., and E. Clippinger, J. Am. Chem. Soc., **83**, 4986 (1961), and previous papers in the series.

(10) The fact that the solvolysis product, p-chlorobenzhydrol, is not completely racemic (ref. 1) suggests that external ion pair return results in partial rather than complete racemization.

(11) National Science Foundation Fellow, 1959–1962; Minnesota Mining and Manufacturing Co. Fellow, 1962–1963.

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CH$_2$ Transfer from Halomethylmercury Compounds to Olefins

Sir:

It has been reported[1] that halomethylmercury compounds, such as Hg(CH$_2$I)$_2$, do not react with olefins. However, the observed high reactivity of phenyl(tri-

(1) G. Wittig and K. Schwarzenbach, *Ann.*, **650**, 1 (1961).