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 $5 \times 10^{-3}$ $M$ 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 $0.54 \times 10^{-2}$ 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.

$$RX \rightleftarrows [R^+X^-] \rightleftarrows [R^+||X^-] \longrightarrow \text{products}$$
$$\phantom{RX \rightleftarrows} I \phantom{\rightleftarrows [R^+X^-]} II$$

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 ± 0.6% retention of configuration and 81.9 ± 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.

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(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.

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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).

halomethyl)mercurials with olefins[2] suggested to us that $Hg(CH_2X)_2$ compounds should, under proper conditions, transfer $CH_2$ to olefins.

Initial experiments with bromomethylmercury compounds[3] confirmed this expectation. The reaction of 0.03 mole of $Hg(CH_2Br)_2$ in 30 ml. of benzene with 0.3 mole of cyclohexene at reflux under nitrogen during 8 days produced bicyclo[4.1.0]heptane (norcarane), identified by the identity of its infrared spectrum and of its retention time with those of an authentic sample in 74% yield, based on the equation

$$Hg(CH_2Br)_2 \; + \; \bigcirc \hspace{-0.3em}| \;\; \longrightarrow \;\; \bigcirc\hspace{-0.3em}\triangleright \; + \; BrCH_2HgBr$$
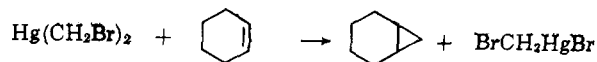
Bromomethylmercuric bromide was isolated in 83% yield. A separate experiment showed that the latter mercurial did not react with cyclohexene during an 8-day period under the identical conditions.

A search for conditions which might allow utilization of $BrCH_2HgBr$ as a $CH_2$-transfer agent (i.e., which also would allow use of both $CH_2$ groups in $Hg(CH_2Br)_2$) resulted in the finding that a mixed $BrCH_2HgBr$–$(C_6H_5)_2Hg$ system will react with cyclohexene. In

$$BrCH_2HgBr \; + \; (C_6H_5)_2Hg \; + \; \bigcirc \hspace{-0.3em}| \; \longrightarrow \; \bigcirc\hspace{-0.3em}\triangleright$$

$$+ \; 2 \; C_6H_5HgBr$$
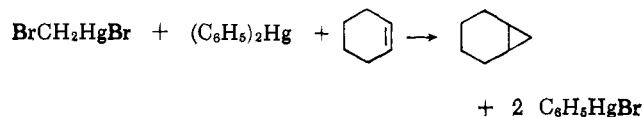
one such experiment (8-day reaction time, 0.014 mole of each mercury compound, 0.5 mole of cyclohexene, 10 ml. benzene, at reflux), norcarane was formed in 39% yield, phenylmercuric bromide in 74% yield. A possible explanation of this effect of diphenylmercury on this reaction involves the known facile ligand exchange which occurs in organomercury systems.[4] It is quite possible that such an exchange generates the more reactive bis(halomethyl)mercurial, $(C_6H_5)_2Hg + 2XCH_2HgX \rightarrow 2\ C_6H_5HgX + Hg(CH_2X)_2$.[5] Other explanations also are possible, and experiments designed to provide further information concerning this question are in progress.

This procedure, based on a starting material prepared by the reaction of diazomethane with mercuric bromide, is of very limited practicality. In the hope of developing a more useful procedure we investigated the reaction of iodomethylmercuric iodide with cyclohexene. This mercurial can be prepared in satisfactory yield by the reaction of methylene iodide with metallic

mercury.[6,7] The reaction of 0.02 mole each of iodomethylmercuric iodide and diphenylmercury in 15 ml. of benzene with 0.365 mole of cyclohexene during 8 days gave norcarane and phenylmercuric iodide in yields of 64 and 91%, respectively.[8] A similar reaction, but without diphenylmercury, also produced norcarane, but only in 24% yield.

The applicability of $ICH_2HgI$ establishes the synthetic utility of mercurials as $CH_2$ transfer reagents. This procedure, despite the long reaction times involved, may be preferable to methods based on diazomethane,[1,9] especially in larger scale reactions. It also may be preferable to the Simmons–Smith reaction[7] (based on $ICH_2ZnI$) in those cases where zinc iodide, a mild Lewis acid, is not compatible either with the olefin or the product.

It may be noted that norcarane is the only major product obtained in the reaction of halomethylmercurials with cyclohexene under these conditions. The gas chromatographic analysis of the reaction mixtures obtained in the case of bromomethylmercury compounds as described above showed essentially no other products in the region between the peaks due to cyclohexene–benzene and norcarane. Trace amounts of perhaps two compounds (insertion products?) were obtained when iodomethylmercuric iodide was used, but these have not been identified. In one experiment in which the effect of ultraviolet radiation was examined briefly (40 mmoles of $Hg(CH_2Br)_2$, 0.6 mole of cyclohexene in a quartz flask, at reflux for 20 hr.) two similar, barely perceptible peaks in the gas chromatogram were observed. (The yields of norcarane and bromomethylmercuric bromide in this experiment were 52 and 53.5%, respectively).[10]

(2) D. Seyferth, R. J. Minasz, A. J.-H. Treiber, J. M. Burlitch, and S. R. Dowd, *J. Org. Chem.*, **28**, 1163 (1963).

(3) R. Kh. Freidlina, A. N. Nesmeyanov, and F. A. Tokareva, *Ber.*, **69**, 2019 (1936).

(4) For a recent summary, see G. Köbrich, *Angew. Chem.*, **74**, 453 (1962).

(5) This equation only summarizes the net process. Stepwise reaction is more likely, $XCH_2HgX + (C_6H_5)_2Hg \rightarrow C_6H_5HgX + C_6H_5HgCH_2X$, followed by $2C_6H_5HgCH_2X \rightarrow (C_6H_5)_2Hg + Hg(CH_2X)_2$. Compounds of type $C_6H_5HgCH_2X$ are known to be unstable toward disproportionation [L. Hellerman and M. D. Newman, *J. Am. Chem. Soc.*, **54**, 2859 (1932)].

(6) J. Sakurai, *J. Chem. Soc.*, **37**, 658 (1880); **39**, 485 (1881); **41**, 360 (1882).

(7) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959), and a private communication from Dr. Simmons concerning improvements which make this procedure of practical value.

(8) A similar reaction was monitored by gas chromatography from time to time; the yields of norcarane determined were: 23 hr., 23%; 42 hr., 35%; 115 hr., 50%; 190 hr., 61%.

(9) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(10) It is our understanding that Dr. F. Wingler, University of Heidelberg, is studying the irradiation of iodomethylmercury reagents in the presence of olefins, and for this reason we have not pursued our irradiation studies further at this time.

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