



Fig. 2.—N.m.r. spectrum of methyl acrylate- $\alpha$ , $\beta$ - $d_2$  monomer used in the present experiment. Signals are assigned as follows:  $\tau$  6.28 signal to the ester methyl group;  $\tau$  3.69 and 4.20 triplets to the  $\beta$ -protons of the *cis*- and *trans*- $\alpha$ , $\beta$ - $d_2$  isomers, respectively; signals near  $\tau$  3.84 to the  $\alpha$ -protons of the - $d_1$  and the - $d_2$  isomers; small signals at  $\tau$  3.56 and 3.73 to the  $\beta$ -protons of the *trans*- $\beta$ -disomer.

the intensity ratio of the  $\beta$ -proton signals at  $\tau$  3.69 and 4.20 to be 3:1. After every run of polymerization the unreacted monomer was recovered by distillation from the polymerization medium. The *cis/trans* molar ratio in the recovered monomer was found to be just the same as the ratio in the initial monomer. The ratio of  $\alpha$ -protons to  $\beta$ -protons was found to be approximately the same for the initial and the recovered monomer and the polymer, showing that deuterium exchange scarcely took place in the course of polymerization.

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## Ion Pairs in Acetolysis of *p*-Chlorobenzhydryl Acetate<sup>1</sup>

Sir:

Acetolysis of p-chlorobenzhydryl chloride (RCl) involves carbonium chloride ion pairs which lose configuration and return to racemic starting material much more rapidly than they dissociate, solvolyze, or exchange their chloride counterion with added radiolabeled common ion salt.<sup>2a,b</sup> The rate of ionization is substantially higher than that of solvolysis or exchange. Analogously, substantial gaps are observed between ionization and exchange or solvolysis rates for RCl<sup>2e</sup> and the corresponding p-nitrobenzoate<sup>2d</sup> (ROPNB) in 80% acetone.

It is instructive to consider the case of a substrate molecule whose negative counterion in the  $R^+X^-$  ion pair is the lyate ion of the solvent being employed. Such a situation is especially favorable for the leaving anion to merge into the solvent structure and be replaced by a new solvent molecule or anion.

It is interesting to measure the extent to which the  $R^+$  carbonium ion species under such circumstances can still discriminate between the original  $X^-$  partner and the rest of the solvent. In this connection, we have ex-

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IABLE I
RACEMIZATION, EXCHANGE, AND <sup>18</sup> O-EQUILIBRATION OF
$p$ -Chlorobenzhydryl Acetate in Acetic Acid at $75.0^{\circ}$

<i></i>		
$k_{\alpha}$	ke	keq
$1.30 \pm 0.08^{a}$	$1.00 \pm 0.02^{b}$	$0.284 \pm 0.027$
(1.04)	(0.99)	(0.39)
$1.04 \pm 0.05$	$0.99 \pm 0.02$	
	$0.995 \pm 0.05$	$0.400 \pm 0.008$
	$1.05 \pm 0.035$	$0.378 \pm 0.006$
$1.12 \pm 0.06$		
	$1.11 \pm 0.03$	$0.404 \pm 0.011$
$1.18 \pm 0.05$		
31.5	32.6	
	$ \frac{k_{\alpha}}{1.30 \pm 0.08^{a}} $ $ \frac{1.30 \pm 0.08^{a}}{1.04} $ $ 1.04 \pm 0.05 $ $ 1.12 \pm 0.06 $ $ 1.18 \pm 0.05 $ $ 31.5 $	$\begin{array}{c c} \hline & 10^{6}k, (\text{sec.}^{-1}) \hline \\ \hline k_{\alpha} & k_{e} \\ \hline 1.30 \pm 0.08^{a} & 1.00 \pm 0.02^{b} \\ (1.04) & (0.99) \\ \hline 1.04 \pm 0.05 & 0.99 \pm 0.02 \\ & 0.995 \pm 0.05 \\ \hline 1.05 \pm 0.035 \\ \hline 1.12 \pm 0.06 \\ \hline 1.11 \pm 0.03 \\ \hline 1.18 \pm 0.05 \\ \hline 31.5 & 32.6 \end{array}$

<sup>*a*</sup> First 30% reaction; some upward drift. <sup>*b*</sup> 1.25 from rate of <sup>18</sup>O-loss starting with Ic. <sup>*c*</sup>  $k^0$  values extrapolated to zero salt concentration from data with added LiOAc. <sup>*d*</sup> 1.79  $\times$  10<sup>-4</sup> *M* HClO<sub>4</sub> at 50.0°; first 30% reaction; slight downward drift.

amined the behavior of optically active ROAc (Ia),<sup>14</sup>Ccarboxylate-labeled ROAc (Ib), and <sup>18</sup>O-carbonyllabeled ROAc (Ic) in ordinary glacial acetic acid with and without added LiOAc. For comparison, the behavior of Ia-c was examined under HClO<sub>4</sub> catalyzed conditions where the conjugate acid of ROAc undergoes heterolysis and a R<sup>+</sup>O<sup>-</sup>Ac ion pair is not involved. Summarized in Table I are the first-order polarimetric  $(k_{\alpha})$ , exchange  $(k_{e})$ , and <sup>18</sup>O-equilibration  $(k_{eq})$  rate constants at 75.0°.

$$(-)-R^* - OCOCH_3 (Ia) R - OCOCH_3 (Ib) R - OCOCH_3 (Ic)$$

$$\downarrow^{k_{\alpha}} \qquad \downarrow^{k_{e}} \qquad \downarrow^{k_{eq}}$$

$$dl - ROCOCH_3 R - OCOCH_3 R - OCOCH_3 R - OCOCH_3$$

$$p - ClC_6H_4 \qquad p - ClC_6H_4$$

$$\downarrow \qquad p - ClC_6H_4 \qquad p - ClC_6H_4$$

$$\downarrow \qquad HOAc \qquad OAc$$

$$C_6H_5 H \qquad C_6H_5 H$$

With added  $1.79 \times 10^{-4} M$  HClO<sub>4</sub> at 50°,  $k_{\alpha}$  and  $k_{e}$  for Ia and Ib, respectively, are equal<sup>3</sup> within experimental error. Furthermore, starting with Ic, no <sup>18</sup>O-scrambling could be detected in the residual unexchanged ROAc under these conditions. Evidently, the original acetic acid molecule produced in the heterolysis of the ROAc conjugate acid is lost from the solvation shell of the carbonium ion before the latter collapses to covalent material.

With 0.01 M and higher concentrations of LiOAc in the acetic acid solvent,  $k_{\alpha}$  and  $k_{e}$  are again equal within experimental error and also quite insensitive to salt concentration. However, under these conditions <sup>18</sup>Oequilibration in the ester is a definite competing phenomenon. Without added LiOAc, there appears to be some indication that  $k_{\alpha}$  is slightly larger than  $k_{e}$ and therefore also slightly larger than the  $k_{\alpha}^{0}$  value extrapolated to zero salt concentration from the data with added LiOAc. Correspondingly,  $k_{eq}$  appears slightly low. The discrepancies are small, however, and may well be due to generation of acid catalyst from the Ia and Ic samples which were not distilled and as highly purified as Ib. Consistently,  $k_{e}$  estimated from <sup>18</sup>O-loss starting with Ic also tended to be slightly high.

It is quite evident that the carbonium ion from ionization of ROAc in acetic acid solvent shows only a

<sup>(2) (</sup>a) S. Winstein, J. S. Gall, M. Hojo, and S. Smith, J. Am. Chem. Soc.,
82, 1010 (1960); (b) A. F. Diaz, A. Ledwith, and M. Hojo, unpublished work;
(c) S. Winstein, M. Hojo, and S. Smith, Tetrahedron Letters, No. 22, 12 (1960);
(d) H. L. Goering and J. F. Levy, J. Am. Chem. Soc., 86, 120 (1964).

<sup>(3)</sup> A similar equality of  $k_{\alpha}$  and  $k_{e}$  has been reported by Pocker for acetolysis of p-methylbenzhydryl acetate: Y. Pocker, Proc. Chem. Soc., 226 (1959); Y. Pocker in "Progress in Reaction Kinetics," Pergamon Press, Vol. 1, 1961, pp. 227–228; Y. Pocker, private communication.

relatively small preference for its original AcO- partner. Assuming every ionization results in equivalence of the two ester oxygen atoms, one estimates that only 27% of recombination is with the original AcOpartner. In Table II the behavior of ROAc in acetic acid solvent is directly contrasted with that of the corresponding RCl by means of the ratio, R, between rate of ionization and rate of chemical reaction incorporating a component of the solvent. For ROAc, this ratio is approximated by  $[(k_{eq} + k_e)/k_e]$ , while for RCl, the polarimetric/titrimetric rate ratio,  $k_{\alpha}/k_{t}$ , is a lower limit. On this basis the ratio is greater than 38 with RCl and only 1.38 with ROAc. The latter is also much smaller than the corresponding figure of 2.5 for the p-nitrobenzoate<sup>2d</sup> (ROPNB) even in 80% acetone. Thus the case of ROAc in the corresponding acetic acid solvent shows a uniquely small R value. While this was rather, anticipated, it will be necessary to examine other examples before a clear picture emerges regarding the importance of ion-pair return in cases of ionization where the leaving anion is the solvent lyate ion.

## TABLE II

## RATIO (R) BETWEEN IONIZATION AND CHEMICAL CAPTURE RATES FOR p-CHLOROBENZHYDRYL DERIVATIVES (RX)

RX	Solvent	<i>T</i> , °C.	$R_{\alpha}{}^{a}$	$R_{t}^{b}$
ROPNB	80% acetone	100	1.6	2.5
RCI	AcOH	25	38	
ROAc	AcOH	75	1.0	1.38
- (1 /1 )			5/3 ( T	× /7 1

<sup>a</sup>  $(k_{\alpha}/k_{t})$  or  $(k_{\alpha}/k_{e})$ . <sup>b</sup>  $[(k_{eq} + k_{t})/k_{t}]$  or  $[(k_{eq} + k_{e})/k_{e}]$ .

For the ROAc system in acetic acid solvent,  $k_{\alpha}$  and  $k_{\rm e}$  are equal within experimental error, so the  $k_{\alpha}/k_{\rm e}$ ratio, akin to the  $k_{\alpha}/k_t$  ratio for RCl, gives no indication of a gap between rate of ionization and rate of chemical capture incorporating a solvent component. It is the occurrence of <sup>18</sup>O-equilibration in the unexchanged ester which discloses the existence of the small gap. It seems attractive to give a carbonium biacetate description (IIb), rather than a carbonium acetate one (IIa), to the ion pair which results from ionization of ROAc and which gives ROAc back again by ion-pair collapse. The IIb ion pair can be visualized to arise from an AcOH-promoted ionization of ROAc. The relationships between  $k_{\alpha}$ ,  $k_{e}$ , and  $k_{eq}$  then depend on the extent to which IIb loses configuration and/or loses its original acetate component before collapsing to product.4 On this basis only 27% of ion-pair collapse is with retention of configuration, racemization of IIb being 2.6 times as fast as collapse. Assuming equivalence of the two oxygen atoms in the original acetate component of IIb and also equivalence of both acetate groups in IIb, one calculates that exchange of the original acetate component of IIb for a solvent-derived acetate occurs 0.82 times as rapidly as ion-pair collapse. On this basis, 55% of ion-pair collapse occurs before the ion pair exchanges and 45% after such exchange.

(4) More separated ion pair species or dissociated carbonium ions may, in principle, occur between formation and collapse of some of the IIb type ion pairs.

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## On the Question of Homoconjugation in 1,4,7-Cyclononatriene

$\alpha$	
114	•
500	•

cis, cis, cis-1, 4, 7-Cyclononatriene (I), recently reported from three different laboratories, 1-3 is of interest not only as a synthetic intermediate but from the point of view of homoconjugation. As pointed out previously,<sup>1</sup> HMO calculations on this hydrocarbon indicate a nonzero delocalization energy. In a recent communication.<sup>4</sup> Roth and co-workers have referred to these calculations and have reported a heat of hydrogenation and molecular structure parameters from an X-ray diffraction study which give no indication of appreciable homoconjugative stabilization of the cyclononatriene ground state. We are prompted to comment further on the question of homoconjugation in the cyclononatriene ground state and to report the much larger effect in the cyclononatriene positive ion as indicated by the observed ionization potential.



As reported earlier,<sup>1</sup> a simple HMO treatment with  $a = (\beta_{24}/\beta_{12})$  leads to molecular orbital energy levels  $[(E - \alpha)/\beta]$  of  $\pm (a + 1)$ ,  $\pm \sqrt{a^2 - a + 1}$ , and  $\pm \sqrt{a^2 - a + 1}$ , as compared to  $\pm 2$ ,  $\pm 1$ , and  $\pm 1$  for benzene. These lead to a nonzero delocalization energy (DE), in contrast to the situation in bicycloheptadiene and barrelene where DE is identically zero for symmetry reasons. The extent of homoconjugative stabilization predicted for I can be assessed by substituting a reasonable value<sup>5</sup> for a, ca. 0.3, into the abovementioned bonding MO energy levels. The latter then consist of one level at  $\alpha + 1.30\beta$  and a degenerate pair at  $\alpha$  + 0.89 $\beta$ . The energy of the six-electron system in I is then  $6\alpha + 6.16\beta$ , the predicted DE being 0.16 $\beta$ , ca. 8% as large as in benzene. If  $\beta$  is taken as 20 kcal./mole, DE in I is predicted to be ca. 3 kcal./mole. This is quite small and can easily be obscured by steric factors. In any case, it is too small to be disclosed by heats of hydrogenation because of the well-known difficulties in choosing model compounds for reference. Thus the results of Roth, Turner, et al.,<sup>4</sup> are not at all surprising,

In their communication, Roth, Turner, et al.,<sup>4</sup> refer to "more quantitative" MO calculations by Untch<sup>2</sup> which suggest a negligible *DE* for I. Actually, Untch<sup>2</sup> reported MO energy levels at  $\alpha$  + 1.03 $\beta$  and  $\alpha$  + 0.985 $\beta$  (degenerate pair), leading to a *DE* 0.02% as large as in benzene. However, Untch's published results contained an arithmetic error which he has corrected<sup>6</sup> to give MO energy levels at  $\alpha$  + 1.30 $\beta$  and a degenerate pair at  $\alpha$  + 0.889 $\beta$ . Thus, Untch<sup>6</sup> predicts

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- (b) C. F. Wilcox, S. Winstein, and W. G. McMillan, *ibid.*, **82**, 5450 (1960).
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<sup>(1)</sup> P. Radlick and S. Winstein, J. Am. Chem. Soc., 85, 344 (1963).

<sup>(2)</sup> K. G. Untch, *ibid.*, **85**, 345 (1963).