

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 AcO^- partner. 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 $[(k_{\text{eq}} + k_e)/k_t]$, while for RCl, the polarimetric/titrimetric rate ratio, k_a/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^{2d} (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	T , °C.	$R\alpha^a$	Rt^b
ROPNB	80% acetone	100	1.6	2.5
RCl	AcOH	25	38	
ROAc	AcOH	75	1.0	1.38

^a (k_a/k_t) or (k_a/k_e) . ^b $[(k_{\text{eq}} + k_t)/k_t]$ or $[(k_{\text{eq}} + k_e)/k_e]$.

For the ROAc system in acetic acid solvent, k_a and k_e are equal within experimental error, so the k_a/k_e ratio, akin to the k_a/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 ¹⁸O-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_a , 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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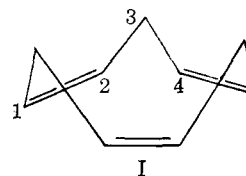
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On the Question of Homoconjugation in 1,4,7-Cyclononatriene

Sir:

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,¹ HMO calculations on this hydrocarbon indicate a non-zero delocalization energy. In a recent communication,⁴ 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,¹ 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 ± 2 , ± 1 , and ± 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 value⁵ for a , ca. 0.3, into the above-mentioned 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 0.16β , ca. 8% as large as in benzene. If β 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.*,⁴ are not at all surprising.

In their communication, Roth, Turner, *et al.*,⁴ refer to "more quantitative" MO calculations by Untch² which suggest a negligible DE for I. Actually, Untch² 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 corrected⁶ to give MO energy levels at $\alpha + 1.30\beta$ and a degenerate pair at $\alpha + 0.889\beta$. Thus, Untch⁶ predicts

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