

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_a^a	R_t^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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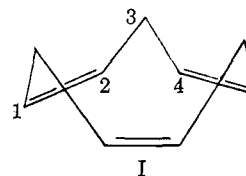
ARTHUR F. DIAZ
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On the Question of Homoconjugation in 1,4,7-Cyclononatriene

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

- (1) P. Radlick and S. Winstein, *J. Am. Chem. Soc.*, **85**, 344 (1963).
- (2) K. G. Untch, *ibid.*, **85**, 345 (1963).
- (3) W. R. Roth, *Ann.*, **671**, 10 (1964).
- (4) W. R. Roth, W. B. Bang, P. Goebel, R. L. Sass, R. B. Turner, and A. P. Yü, *J. Am. Chem. Soc.*, **86**, 3178 (1964).
- (5) (a) M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, **76**, 18 (1954); (b) C. F. Wilcox, S. Winstein, and W. G. McMillan, *ibid.*, **82**, 5450 (1960); (c) R. J. Piccolini and S. Winstein, *Tetrahedron. Suppl.*, **2**, 423 (1963).
- (6) K. G. Untch, *J. Am. Chem. Soc.*, **85**, 4061 (1963).

a *DE* 7.8% as large as in benzene, identical with the one mentioned earlier.

The situation as regards homoconjugative stabilization can be expected to be markedly different in the parent positive ion from ionization of I. Since ionization of an electron is from the $\alpha + 0.89\beta$ MO, one could expect the positive ion to be stabilized by 0.11β more than the ground state, the ionization potential (I.P.) being lowered by 0.11β compared to a corresponding monoolefin. Another factor which should lower the I.P. of I has to do with the neglect of electron repulsion in the simplest HMO treatment. With the so-called ω -technique,⁷ some electron repulsion can be introduced within the framework of the LCAO method. Thus, by setting the Coulomb integral α equal to $\alpha + \omega q\beta$, where q is the charge on the carbon atom, and using ω equal to 1.4, Streitwieser^{7a} and Ettinger^{7b} have successfully correlated ionization potentials of many hydrocarbons. For a monoolefin q is 0.5 and the positive ion has one π -electron, so the ω -calculation lowers I.P. by $0.5(1.4)\beta$ or 0.7β . In the positive ion from I, with five π -electrons and q equal to one-sixth, the ω -calculation lowers I.P. by five-sixths $(1.4)\beta$ or 1.17β , 0.47β more than in the case of the monoolefin. From the sum of the 0.47β and 0.11β terms and the existing correlations between I.P. values and MO calculations,⁷ we could expect the I.P. of I to be *ca.* 1 e.v. lower than a corresponding monoolefin.

The electron impact I.P. of 1,4,7-cyclononatriene does indeed turn out to be unusually low. The figure obtained, 8.72 e.v., is less than that for benzene^{8a} (9.50), toluene⁹ (9.23), or *p*-xylene⁹ (8.88). It is also less than that for propylene^{8b,9} (9.94, 9.84) or 1,2-disubstituted olefins such as *cis*-2-butene^{8c} (9.34) or cyclopentene^{8c} (9.27). In fact, it is as low as, or lower than, the values for typical conjugated 1,3-dienes such as cyclopentadiene^{8d,9} (9.00, 8.9), isoprene¹⁰ (9.08), and 1,3-pentadiene^{8c} (8.68).

In considering the I.P. of I, we must recognize that ionization potentials of olefins appear to be subject to strain and alkyl-substituent effects. As regards strain, any effect due to slight strain⁴ in I is probably very small.¹¹ Since the olefinic groups in the cyclononatriene are 1,2-dialkyl substituted, *cis*-2-butene represents one of the best available reference compounds for comparison with I. This choice may well involve an overly generous allowance for alkyl substituent effects since the geometry of the crown conformation of I is not especially favorable to hyperconjugative stabilization of the positive ion due to C-H electron delocalization. Thus, the *ca.* 0.6 e.v. (14 kcal./mole) by which the I.P. of I is lower than that of 2-butene may well be a conservative measure of the decrease in ionization potential of the cyclononatriene.

The lowering of ionization potential due to proper juxtaposition of nonadjacent olefinic groups may well be a general phenomenon. For example, the ionization

potential of bicyclo[2.2.1]heptadiene¹² is appreciably smaller than that of bicyclo[2.2.1]heptene.¹¹ This general phenomenon and semiempirical methods to calculate the effects are being explored further.

(12) S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Am. Chem. Soc.*, **83**, 1401 (1961).

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Racemization and Oxygen Exchange of Trisubstituted Phosphine Oxides¹

Sir:

The recent study of the racemization and oxygen exchange of aralkyl sulfoxides by hydrogen chloride under a variety of conditions has prompted a similar study with trisubstituted phosphine oxides.²

Phenylmethylpropylphosphine oxide, $[\alpha]_D^{26} + 18.5^\circ$, in dry dioxane saturated with hydrogen chloride was allowed to stand at room temperature for 9 days, at which time the specific rotation was $+0.3^\circ$. Periodic measurement of the rotation during the 9-day period gave the following results: after 20 hr., $+15.8^\circ$; 64 hr., $+10.8^\circ$; and 7 days $+3.4^\circ$. The phosphine oxide was recovered in 80% yield and shown to be racemic. In another experiment the phosphine oxide, 0.00148 mole, was dissolved in a hydrogen chloride saturated solution of 1 ml. of water, containing *ca.* 1.45 atom % excess ¹⁸O, and 4 ml. of dioxane. The solution rapidly became yellow and measurement of the rotation was extremely difficult. After 55 days at room temperature, the phosphine oxide was recovered and shown to be racemic. Oxygen-18 analysis showed it contained 0.87 atom % excess of ¹⁸O.³ In a similar experiment triphenylphosphine oxide containing 0.85 atom % excess ¹⁸O was treated for 80 days with hydrogen chloride dissolved in water-dioxane (1:4). The oxide was recovered and shown to contain 0.55 atom % excess ¹⁸O.

The results of these experiments clearly demonstrate that phosphine oxides are subject to racemization under the conditions specified. The process is certainly much slower than that found for the aralkyl sulfoxides. The diminution in rate in the presence of water is in accord with the sulfoxide experiments. Unfortunately, it was not possible to correlate oxygen exchange with rate of racemization; however, it is interesting to note that water is not required for racemization. Mislow, *et al.*,² have suggested that sulfoxide racemization occurs by formation of $R_1R_2SCl_2^4$; however, it is not necessary to form $R_1R_2R_3PCl_2$ to have racemization of the phosphine oxide. Undoubtedly the first step involves protonation of the oxide oxygen. This should be a rapid and reversible reaction, and also one highly dependent on the basicity of the medium. Addition of chloride ion yields II, the pentacovalent compound. Racemization can

(1) Research supported by the National Science Foundation under NSF GP-202.

(2) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, *J. Am. Chem. Soc.*, **86**, 1452 (1964).

(3) Result of one analysis only. Because of the extreme hygroscopicity of this material the value may be low.

(4) This could be an intermediate or transition state.

(7) (a) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960); (b) R. Ettinger, *Tetrahedron*, **20**, 1579 (1964).

(8) (a) I. P. Fisher, T. F. Palmer, and F. P. Lossing, *J. Am. Chem. Soc.*, **86**, 2741 (1964); (b) J. Collin and F. P. Lossing, *ibid.*, **79**, 5848 (1957); (c) J. Collin and F. P. Lossing, *ibid.*, **81**, 2064 (1959); (d) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *ibid.*, **82**, 5593 (1960).

(9) See ref. 7a for tabulated I.P. values and literature references.

(10) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

(11) For example, I.P. is 9.05 for the highly strained bicycloheptene (I. P. Fisher and F. P. Lossing, unpublished work).