

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.

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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

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(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).

(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.

