ments that deuteration of 2-lithio-2-methyl-*cis*-4,6-dimethyl-1,3-dithiane involves a highly stereospecific equatorial attack of the deuteron, similar to the deuteration of the lithium salt of the parent 2-lithio-*cis*-4,6-dimethyl-1,3-dithiane (*vide supra*). One may also conclude that the lithium salt is formed appreciably more rapidly when the 2-methyl group is axial (as in **8**) than when it is equatorial (as in **9**), confirming Oae's postulate[2] that the lithium derivative is formed more readily by abstraction of an equatorial than by abstraction of an axial hydrogen at C-2.

Finally we record that methylation of 2-lithio-*cis*-4,6-dimethyldithiane (lithium salt of **4**) by methyl iodide leads exclusively to *r*-2-*cis*-4,*cis*-6-trimethyl-1,3-dithiane (**9**) ($\ll$1% **8**), as evidenced gas chromatographically. Once again equatorial attack on the lithio derivative is indicated.

While these observations do not settle the question of whether the equatorial orientation of the lithium derivative is occasioned by d-orbital overlap,[2] by preferential equatorial solvation,[2] by a preferred orientation of the carbanion partner of the ion pair (assuming that 2-lithio-1,3-dithiane in ether forms an ion pair) relative to the unshared electron pairs of the adjacent sulfur atoms,[8] or by preferential equatorial orientation of a covalent lithium compound, they provide a number of interesting features. Thus, the H–D exchange is nearly as stereospecific, in the selection between diastereotopic hydrogens,[9] as is the H–D exchange occasioned by enzymes such as liver alcohol dehydrogenase (in the presence of the coenzyme system NAD^+–NADH)[10] in the selection of enantiotopic hydrogens.[11,12] Also, the stereoselective protonation provides a viable method for synthesis of the otherwise poorly accessible[4] anancomeric 1,3-dithianes in which the 2 substituent is axial. It is interesting that this synthesis proceeds by what may well be an equatorially preferred carbanion or ion pair,[13] whereas a similar synthesis of 2-axially substituted anancomeric 1,3-dioxanes[14] involved an axially preferred carbonium ion.

We are presently engaged in exploring a number of unanswered ancillary problems, such as the stereoselectivity of the lithiation itself (as distinct from the stereoselectivity of the protonation of the lithium salt), the effect of solvents more ionizing than ether on the stereoselectivity, and—related to these two points—the possibility of carrying out a stereoselective H–D exchange under equilibrium conditions.

(8) S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *Chem. Commun.*, 96 (1970).

(9) For nomenclature, see K. Mislow and M. Raban, *Top. Stereochem.*, 1, 1 (1967).

(10) *E.g.*, in the classical work of F. A. Loewus, F. H. Westheimer, and B. Vennesland, *J. Amer. Chem. Soc.*, **75**, 5018 (1953).

(11) For general review, see D. Arigoni and E. L. Eliel, *Top. Stereochem.*, **4**, 127 (1969).

(12) Our findings suggest the remote possibility that enzyme stereoselectivity, rather than being caused by the topography of the enzyme as a whole, is due to a *local* effect converting enantiotopic ligands of the substrate to diastereotopic ligands of greatly different reactivity in the enzyme–substrate complex.

(13) A highly stereospecific exo protonation of a bridged annulene carbanion has previously been recorded by P. Radlick and W. Rosen, *J. Amer. Chem. Soc.*, **89**, 5308 (1967). A case somewhat analogous to the present one is the apparently stereospecific oxidation of cyclic phosphinates; *e.g.*, W. G. Bentrude, K. C. Yee, R. D. Bertrand, and D. M. Grant, *ibid.*, **93**, 797 (1971). A stereoselective H–D exchange in a sulfonium salt has been reported by G. Barbella, A. Garbesi, and A. Fava, *Helv. Chim. Acta*, **54**, 341 (1971).

(14) E. L. Eliel and F. W. Nader, *ibid.*, **92**, 584 (1970).

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(15) From the Ph.D. Dissertation of A. A. H., University of Notre Dame, 1971.

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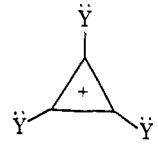
Aminocyclopropenium Ion

Sir:

The cyclopropenyl cation system is a "highly strained $2\pi3C$" ring system, and the electron-donating σ-inductive effect of an attached *n*-propyl group is more significant for the stabilization of this carbonium ion than the electron-donating π-conjugative effect of the phenyl group,[1] in contrast to most other carbonium ions. Also, the ^{13}C–H coupling constant of the parent cyclopropenyl cation indicates that the orbital used for bonding with hydrogen is sp hybrid.[2]

These features of this system led us to investigate the trisubstituted cyclopropenyl cation, **1**, in which Y is a



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conjugatively electron-donating and inductively electron-withdrawing substituent. The trihalocyclopropenium ion[3] is one such example, the σ-inductive effect of Y being greater than the electron-donating π-conjugative effect of Y. However, so far we have not encountered any case where the electron-donating π-conjugative effect of Y is larger than the electron-withdrawing σ-inductive effect of Y. The triaminocyclopropenyl cation might be a case. The results of HMO and INDO calculations[4] confirm that, in accord with intuitive expectation, the amino group has a much stronger electron-donating π-conjugative effect ($+R = -0.190$) than the electron-withdrawing σ-inductive effect ($-I = +0.050$) in the cyclopropenyl cation system. These calculations prompted us to synthesize the triaminocyclopropenyl cation system.

We succeeded in finding a novel synthetic method for this system. It has been established that alcohol or water as the protic nucleophile easily attacks the carbon–carbon double bond of tetrachlorocyclopropene to afford ring-opened products.[5] However, attempted reaction of tetrachloropropene with a secondary amine (YH) as the protic nucleophile afforded exclusively the triaminocyclopropenyl cation in almost quantitative yield. For instance, trisdimethylaminocyclopropenyl

(1) R. Breslow, H. Höver, and H. W. Chang, *J. Amer. Chem. Soc.*, **84**, 3168 (1962).

(2) R. Breslow and J. T. Groves, *ibid.*, **92**, 984 (1970).

(3) S. W. Tobey and R. West, *ibid.*, **88**, 2488 (1966); R. West, *Accounts Chem. Res.*, **3**, 130 (1970).

(4) To be published later.

(5) S. W. Tobey and R. West, *Tetrahedron Lett.*, 1179 (1963).

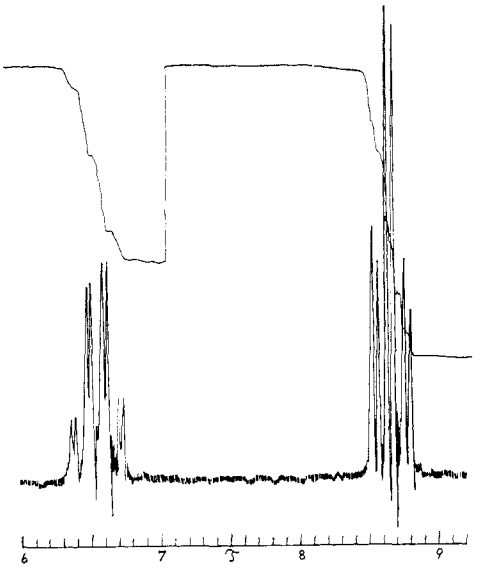
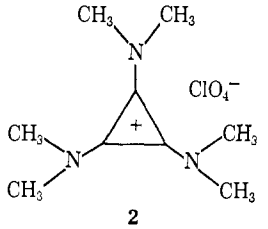


Figure 1. The 60-MHz spectrum of 1,2-bisdiethylamino-3-chlorocyclopropenyl perchlorate.

perchlorate was quantitatively obtained by the following procedures. Excess dimethylamine was added to tetrachlorocyclopropene in methylene chloride at 0° and stirred at this temperature for 5 hr and then at room temperature for 17 hr, and then refluxed for 3 hr. After cooling to room temperature, 70% perchloric acid was added to the solution followed by further stirring for several minutes. The organic layer was separated and dried over sodium sulfate. After removal of the solvent, trisdimethylaminocyclopropenyl perchlorate (**2**) was quantitatively obtained[6] [**2** ($C_9H_{18}N_3ClO_4$), τ^{CDCl_3} 6.84 (sharp singlet with half-line width 0.3 Hz); $\lambda_{max}^{CH_3OH}$ 233 mμ (log ε 4.22)]. Comparison of the ir spectrum with the results of a normal coordinate analysis[7] indicates the expected D_{3h} symmetry for the trisdimethylaminocyclopropenyl cation. The



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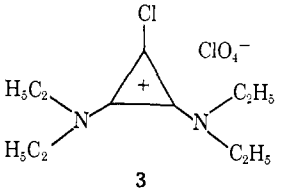
233-mμ band is assigned to an intramolecular charge-transfer band from the amino group to the cyclopropenyl ring by the modified Pariser–Parr–Pople type calculation (variable integrals method[8]) and solvent effect. Piperidine, morpholine, *N*-methylaniline, and *N*-ethylaniline have similarly been treated with tetrachlorocyclopropene to afford the corresponding triaminocyclopropenyl perchlorates (Ia, Ib, Ic, and Id, respectively) in quantitative yield [Ia [$C_{18}H_{30}N_3O_4Cl$], Y = $N(C_6H_5)$; mp 146° dec; $\tau^{CF_3CO_2D}$ 6.50 (m, 12 H), 8.25 (m, 18 H); $\lambda_{max}^{CH_3OH}$ 237 mμ (log ε 4.40); Ib [$C_{15}H_{24}N_3O_7Cl$], Y = $N(C_6H_4)O$; mp 270° dec; τ^{CDCl_3} 6.30 (m, 12 H), 5.90 (m, 12 H); $\lambda_{max}^{CH_3OH}$ 234 (4.37); Ic [$C_{24}H_{24}N_3O_4Cl$], Y = $N(CH_3)C_6H_5$; τ^{CDCl_3} 6.70 (s, 9 H), 2.80 (m, 15 H); $\lambda_{max}^{CH_3CN}$ 230 (4.18), 279 (4.45); Id [$C_{27}H_{30}N_3O_4Cl$], Y = $N(C_2H_5)C_6H_5$; τ^{CDCl_3} 9.00 (t, 9 H), 6.60 (q, 6 H), 2.70 (m, 15 H); $\lambda_{max}^{CH_3CN}$ 230 (4.18), 277 (4.30)]. Even in the reaction of diphenylamine, the triaminocyclopropenyl perchlorate was exclusively obtained. In contrast to the above cases, the reaction of diethylamine with tetrachlorocyclopropene afforded exclusively 1,2-bisdiethylamino-3-chlorocyclopropenyl perchlorate (**3**). As is seen in Figure 1, the nmr spectrum [τ^{CDCl_3}



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8.62 (a pair of triplets, 12 H), 6.50 (a pair of quartets, 8 H)] showed the existence of two kinds of ethyl groups whose magnetic environments are slightly different from each other, suggesting that the rotational barrier about the C–N bond is enhanced by the increased double bond character of the C–N linkage [$\lambda_{max}^{CH_3CN}$ 210 mμ (end absorption)]. Diisopropylamine has also afforded 1,2-bisdiisopropylamino-3-chlorocyclopropenyl perchlorate in 60–70% yield [τ^{CDCl_3} 8.55 (doublet, 4 H), 6.00 (sesquitet, 24 H); $\lambda_{max}^{CH_3OH}$ 235 (sh, log ε 3.20), 210 mμ (end absorption)].

All of these aminocyclopropenyl perchlorates are soluble in polar solvents stable in the atmosphere and not hygroscopic. Especially the triaminocyclopropenyl perchlorates are very stable to water (even in hot) in contrast to trichloro- and triphenylcyclopropenyl perchlorates. The chemical behavior of the aminocyclopropenyl cations will be published soon.

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Received February 1, 1971

(6) No aminocyclopropenyl perchlorates have been found in the aqueous layer.
(7) To be published later.
(8) Z. Yoshida and T. Kobayashi, *Theor. Chim. Acta*, **19**, 377 (1970); *J. Chem. Phys.*, in press.

X-Ray Analysis of 1-Phenyl-4-phosphorinanone. Evidence for a Chair Conformation with an Axial Substituent[1]

Sir:

The principles of conformational analysis are increasingly being applied to saturated, six-membered heterocycles.[2,3] The system containing trivalent phosphorus (phosphorinane) remains little studied, however, and no direct evidence has been reported for the shape of the ring. Phosphorus is pyramidal and a high barrier to inversion makes possible in certain cases the isolation of stable configurational isomers. In the phosphorinane family, this property leads to the existence of separable cis,trans forms of 1,4-dialkyl-4-phosphorinanols.[4] No direct determination of the position (axial or equatorial) adopted by a substituent on phosphorus in such systems has been reported. We have performed the first X-ray single-crystal analysis

(1) Supported in part by U. S. Public Health Service Research Grant No. CA-05507 from the National Cancer Institute.
(2) E. L. Eliel, *Accounts Chem. Res.*, 3, 1 (1970).
(3) C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.*, **4**, 39 (1969).
(4) H. E. Shook, Jr., and L. D. Quin, *J. Amer. Chem. Soc.*, **89**, 1841 (1967).