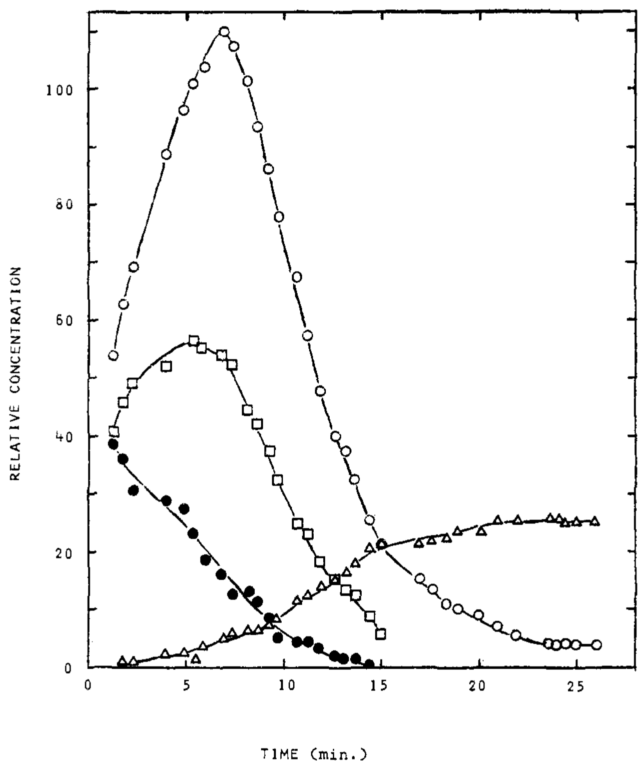

Figure 3. Relative variation with time for the polarized (*) and normal forms of 2-iodopropane (PrI, ●; Pr*I, □) and 1-iodobutane (BuI, △; Bu*I, ○) from the reaction of 150 μl of 2-iodopropane with 0.6 ml of 1.5 *M n*-butyllithium in hexane. These values were calculated from the statistical integral intensities for normal spectra and the optimum emission–absorption spectra of the individual species.

and

$$d + e = {}^{3}/_{4}(\mathrm{BuI}) - {}^{1}/_{2}(\mathrm{Bu^{*}I})$$

where *c*, *d*, and *e* are the measured integrals of the peaks so labeled. The relative concentrations are then

$$(\mathrm{BuI}) = c + d + e$$

$$(\mathrm{Bu^{*}I}) = [3c - (d + e)]/2$$

A similar evaluation of the iodomethine septet gives

$$(\mathrm{PrI}) = a + b$$

$$(\mathrm{Pr^{*}I}) = (11b - 21a)/16$$

Applying the first set or both sets of these equations in Figures 2 and 3, we see that the relative concentrations of polarized species initially increase while the starting iodide is consumed.[5] The 1-iodobutane formed slowly by the halogen–metal interchange between 2-iodopropane and *n*-butyllithium is extensively polarized, but absorption–emission activity in the triplet drops off after 7 min, even though the amount of this material contributing to the normal absorption component continues to increase. These equilibrium steps in reactions terminated by radical coupling and disproportionation give curves for relative changes in polarization or normal contributions of an individual compound which are in good agreement with standard concepts of reaction dynamics.

Since the current method is empirically based, complex multiplets with comparable emission–absorption combination signals[5] may be treated. In addition, the method provides a direct means of comparing rates for radical dissociation–recombination processes with those from optical racemization studies[12] or from other related reactions[13] involving one-electron intermediates if fast reactions[14] can be achieved.

Acknowledgment. The author is indebted to Mr. R. L. Landau for technical assistance and to Marshall University for the opportunity to carry out this work in the absence of financial support.

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[12] *E. g.*, K. Mislow, *et al.*, *J. Amer. Chem. Soc.*, **90**, 4854, 4861 4869 (1968).

[13] U. Schöllkopf and U. Ludwig, *Chem. Ber.*, **101**, 2224 (1968), and references cited therein.

[14] R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5519 (1967).

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Evidence for Homoallylic Stabilization of Carbanions. Reactions of Phosphines with 4-Trihalomethylcyclohexa-2,5-dien-1-ones[1]

Sir:

Although it is well established that carbonium ions can be stabilized by homoallylic conjugation with double bonds,[2] evidence for similar homoallylic stabilization of carbanions by interaction with distant π bonds is scarce. Enchanced acidity of the hydrogens at C-4 in bicyclo[3.2.1]octa-2,6-diene has been ascribed to homoaromatic stabilization of the π-electron system of the anion.[3] Acidity of otherwise unactivated C–H bonds in camphenilone due to formation of homoenolate anions has been demonstrated,[4] but no quantitative estimate of the amount of stabilization afforded the anion by homoallylic resonance has been made.[5]

This communication offers evidence that phosphine derivatives abstract positive halogen ions from 4-trihalomethylcyclohexa-2,5-dienones to give carbanions which are markedly stabilized by homoallylic resonance.

Reaction of the 4-trichloromethylcyclohexadienone **1** with tris(dibutylamino)phosphine in ethanol solution

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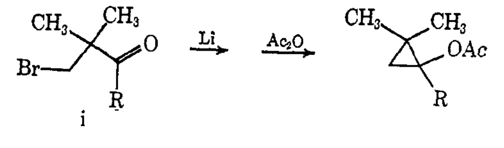
[1] Reactions of Cyclohexadienones. XXI. Part XX: *Chem. Commun.*, 1435 (1968).

[2] For recent reviews, see H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968); P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

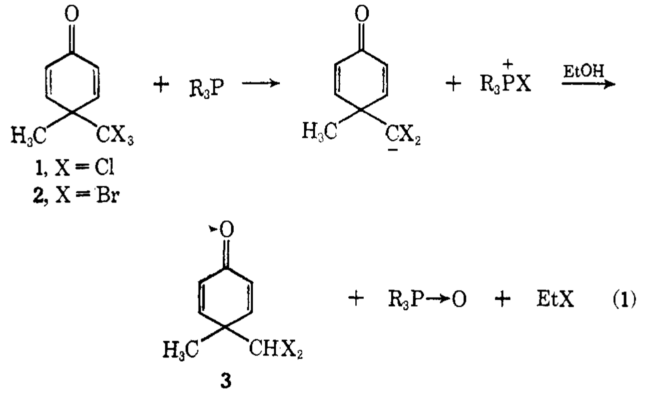
[3] J. M. Brown and J. L. Occolowitz, *Chem. Commun.*, 376 (1965).

[4] A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **88**, 1905 (1966); A. Nickon, J. L. Lambert, and J. E. Oliver, *ibid.*, **88**, 2787 (1966).

[5] The formation of derivatives of cyclopropanol by the reaction of i with lithium has been described as proceeding *via* a "homoenolate anion" [D. P. G. Hamon and R. W. Sinclair, *Chem. Commun.*, 890 (1968)]. In the absence of any rate data, however, there seems no reason to consider the intermediate lithium reagent to have homoenolate character.



gives quantitative yields of 4-dichloromethyl-4-methylcyclohexa-2,5-dien-1-one and tris(dibutylamino)phosphine oxide. Similarly, reaction of the 4-tribromomethylcyclohexadienone **2**[6] with tris(dibutylamino)phosphine or tributylphosphine gives the corresponding phosphine oxide and the 4-dibromomethylcyclohexadienone.[7] In dimethoxyethane solution containing deuterium oxide reduction to the 4-deuteriodihalomethylcyclohexadienones takes place. The rate of reaction of **1** with tris(dibutylamino)phosphine is first order in **1** and in the phosphine, with $k_2 = 3.2 \times 10^{-2}$ l. mol^{-1} sec^{-1}. The rate is not significantly affected by the presence of thiophenol or of traces of air. The phosphines, therefore, react with **1** and **2** by abstracting positive halogen atoms to give carbanions and phosphonium cations, which then react with hydroxylic solvents to give the products shown in eq 1.



1, X = Cl
2, X = Br
3

To assess the influence of the cyclohexadienone ring upon reaction 1, the reactions of other compounds bearing trichloromethyl groups with tris(dibutylamino)phosphine in ethanol were examined. Chloroform does not react at all at room temperature, its rate of reaction being conservatively estimated as less than one-millionth that of **1**. Methylchloroform is similarly unreactive. Bromoform and 1,1,1-tribromopropane each react with phosphines at least four to five powers of ten less rapidly than does **2**. On the other hand, tris(dibutylamino)phosphine reduces benzotrichloride and carbon tetrachloride to benzal chloride and chloroform, respectively, at rates which are too fast to be measured. Competitive reactions of tris(dibutylamino)phosphine with mixtures of 1 and benzotrichloride and with benzotrichloride and carbon tetrachloride were carried out, and the products were analyzed by vpc. Relative rate constants were obtained from the equation $k_A/k_B = (\log [A] - \log [A_0])/(\log [B] - \log [B_0])$, on the assumption that the reactions of benzotrichloride and carbon tetrachloride, like that of **1**, are first order in phosphine and in substrate. The validity of this assumption was confirmed by the observation that large variations in the concentrations of the reagents did not materially change the relative rate constants. The results of these studies are shown in Table I. The very large spread in reaction rates shown in Table I may reasonably be attributed to differences in the stabilities of the anions produced from each of the substrates. It may be noted that the actual difference in thermodynamic stabilities of the carbanions should be even greater than the "kinetic stabilities" measured in this work.[8]

Table I. Relative Rates of Reaction with $(Bu_2N)_3P$ in C_2H_5OH at 28°.

	k/k_1
CH_3CCl_3	$<10^{-6}$
$CHCl_3$	$<10^{-6}$
1	1
$C_6H_5CCl_3$	8
CCl_4	400

The cyclohexadienone ring obviously has a great influence upon the reaction rate of **1**, coming close to equaling a phenyl group in its activating effect. Part of this influence is undoubtedly due to the inductive effect of the carbonyl group. A rough idea of the magnitude of the inductive effect of a carbonyl group separated by three carbon atoms (including a double bond) from a free pair of electrons, as compared to a phenyl group in conjugation with the electron pair, can be gained by consideration of the relative effects of *meta*-carbonyl groups and N-phenyl groups in anilines. Substitution of an acetyl group into the *meta* position of aniline decreases its basicity about twelvefold.[9] (An acetyl group in the *ortho* position, which should exert large inductive and resonance effects, decreases the basicity by a factor of 300.[9]) In contrast, substitution of a second phenyl ring on the nitrogen atom of aniline decreases its basicity by a factor of *ca.* 10^4.[9,10] It is clear that if the inductive effect of the carbonyl group in **1** were the only factor operating to increase its reactivity compared to that of chloroform, **1** should be several powers of ten less reactive than benzotrichloride. The actual small difference between the reaction rates of **1** and of benzotrichloride suggests the existence of a large degree of resonance stabilization of the carbanion adjacent to the cyclohexadienone ring.

A reasonable explanation for the stability of the anion from **1** is resonance with the homodienolate anion structure **4**. In a normal boat conformation of the cyclohexadienone ring the free pair of electrons on an axial dichloromethyl group would be held in close proximity to the end of the double bond at C-3.[11] The alternative possibility exists that the anionic center may interact directly with the carbonyl group, as in structure **5**. This seems a less likely possibility, both because the strain energy of norbornadiene appears to be 5–8 kcal/mol greater than that of cyclopropane[12,13] and because

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[6] J. R. Merchant and V. B. Desai, *J. Chem. Soc.*, 2258 (1964).

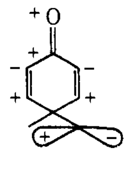
[7] J. R. Merchant and V. B. Desai, *ibid.*, *C*, 449 (1968).

[8] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 9.

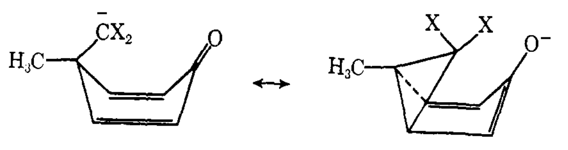
[9] J. M. Vandenbelt, C. Henrich, and S. G. Vanden Berg, *Anal. Chem.*, 26, 726 (1954).

[10] M. A. Paul, *J. Am. Chem. Soc.*, 76, 3236 (1954).

[11] Interaction of the anion center with the carbonyl group through *both* double bonds is forbidden by symmetry relationships in the lowest unoccupied molecular orbital (ii).



ii



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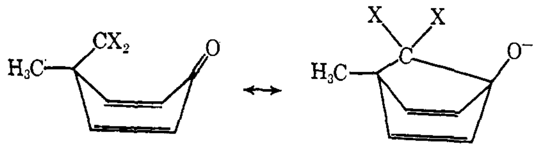

5

a resonance structure resembling a t-alkoxide anion should be less stable than one resembling an enolate anion. A clear choice cannot yet be made, however, between these two types of "nonclassical" resonance interaction.

Acknowledgment. This work was begun at The Chemical and Development Laboratories, Agricultural Division, American Cyanamid Co., Princeton, N. J., and was partially supported by Grant GP8998 from the National Science Foundation.

(12) See R. Turner, W. R. Meador, and R. E. Wenkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957); A. F. Bedford, A. E. Beezer, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3823 (1963).

(13) R. A. Nelson and R. S. Jessup, *J. Res. Natl. Bur. Std.*, **48**, 206 (1952); S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.*, **71**, 261 (1952).

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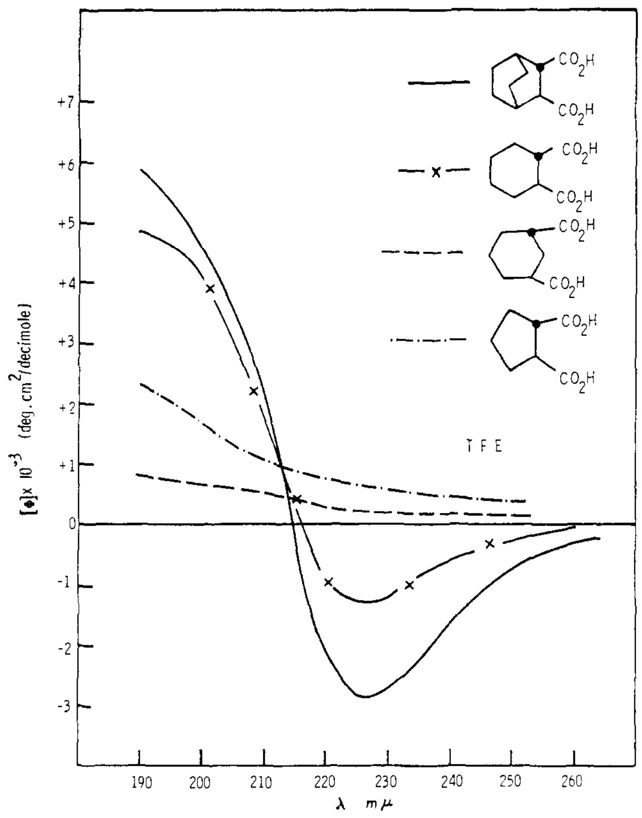


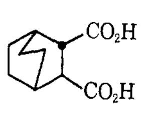
Figure 1. ORD spectra in 2,2,2-trifluoroethanol (TFE) of some cyclic dicarboxylic acids.

Optical Rotatory Properties and Conformational Rigidity of Cyclic Dicarboxylic Acids

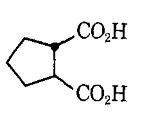
Sir:

We wish to report a case in which the analysis of optical rotatory properties of some cyclic dicarboxylic acids has allowed us to suggest whether these molecules are fixed in a rigid conformation or if they are flexible systems. Some nmr data supporting the optical data are also reported.

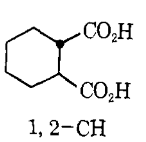
We have investigated the optical properties (uv, ORD, and CD spectra) of four optically active *trans*-dicarboxylic acids. The 2,2,2-bicyclooctane-2,3-dicarboxylic acid (2,3-BCO) is structurally rigid, and 1,3-cyclohexanedicarboxylic acid (1,3-CH) is, presumably, a flexible molecule undergoing chair interconversion.[1] Cyclopentanedicarboxylic acid (1,2-CP) and 1,2-cyclohexanedicarboxylic acid (1,2-CH) are less defined cases.



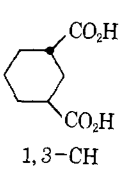
2, 3-BCO



1, 2-CP



1, 2-CH



1, 3-CH

In Figure 1 are reported the ORD curves for the four acids in trifluoroethanol (TFE). The curves of 2,3-BCO and 1,2-CH are quite similar and show a trough at 225–227 mμ, a crossover point at about 215 mμ, and a positive lobe which continues to increase beyond the limit of measurement. The curves of 1,2-CP and 1,3-CH, on the contrary, are much weaker and do not show any definite features, being almost plain curves. This is taken as an indication that 1,2-CH exists in a somewhat rigid, fixed conformation and that 1,2-CP is a flexible molecule.

Looking at the marked asymmetry of the curves of 1,2-CH and 2,3-BCO, it becomes apparent that this is due to the interaction of the two neighboring carboxyl groups (exciton splitting). This interaction, or coupling, is lost when the molecule becomes flexible.[2]

CD spectra confirm this interpretation and allow assignment of the transitions responsible for the Cotton effects. Data and relative assignments are collected in Table I. It is interesting to note that although the uv spectra show only the n–π^* transition at 280–210 mμ, ORD and CD spectra are dominated by the π–π^* transition. The latter appears at 200–203 mμ in the flexible systems 1,2-CP and 1,3-CH, but is shifted to 209–210 mμ in 1,2-CH and 2,3-BCO. This red shift supports strongly the hypothesis that the carboxyl groups are coupled in the latter molecules since this behavior is predicted by theory and has been observed in other, similar cases.[2]

Reported data on the question of which conformation (diaxial or diequatorial) is preferred in the 1,2-CH acid are conflicting. Measurements of ΔpK_a were at first interpreted as indicating that the diaxial confor-

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[1] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 211.

[2] For a review of exciton theory and its applications to organic molecules, see M. Kasha, *J. Radiation Res.*, **20**, 55 (1963).