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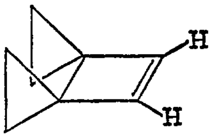
Dispiro[2.0.2.2]oct-7-ene

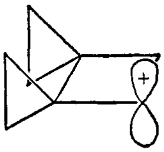
Sir:

There have been reported in the literature no examples of the highly interesting dispiro[2.0.2.2]oct-7-ene system (**1**). This molecule is ideally conducive to various studies of the interaction of cyclopropyl groups with conjugated π systems since it possesses the minimum-energy bisected geometry[1] in which the planes of both cyclopropane rings are normal to the nodal plane of the adjacent double bond. This should allow maximum delocalization between the π system and the p-character bonds of the cyclopropane rings.



1

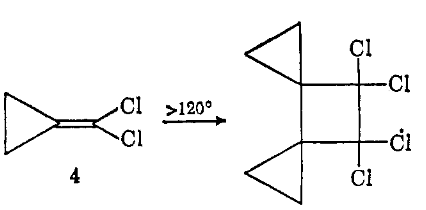
Among various possible probes into the chemical nature of this system, the thermal and photochemical reorganizational reactions as well as the study of the carbonium ion chemistry of the dispiro[2.0.2.2]oct-7-ene system should prove of significant theoretical value to organic chemists. The molecule should prove rather resistant to thermal rearrangement since all of the modes of decomposition that have previous analogy are unfavorable here. Indeed the cyclobutene → butadiene, vinylcyclopropane → cyclopentene, and bicyclopropyl → cyclohexene conversions each have obvious drawbacks when applied to this system. Generation of the carbonium ion **2** should also bring about intriguing results, since **2** has the ideal geometry for maximum overlap between the vacant p orbital and the π-like orbitals of the cyclopropane ring.[2] A symmetrical homoallylic structure would be predicted for the species, and one would expect a great resistance to skeletal rearrangement such as that observed by Winstein in a similar system.[3]



2

The first synthesis of this system was accomplished *via* our observation of the heretofore unknown thermal dimerization reaction of dichloromethylenecyclopropane (**4**).

Decomposition of sodium trichloroacetate in the presence of allene provided 2,2-dichloromethylenecyclopropane (**3**), in ~20% yield.[4] **3**, on heating in the gas phase at 215° for 1 hr, was converted quantitatively to dichloromethylenecyclopropane (**4**);[5] the nmr spectrum showed a singlet at 1.51 ppm and the mass spectrum, a parent peak at m/e 122. Longer heating or direct heating of **3** in the liquid phase results in quantitative conversion to 7,7,8,8-tetrachlorodispiro[2.0.2.2]octane (**5**) which had two symmetrical multiplets in the nmr centered at 0.64 and 1.13 ppm and a mass spectrum with a parent peak at m/e 244. Treatment of **5** with zinc in ethanol leads, in 85% yield, to 7,8-dichlorodispiro[2.0.2.2]oct-7-ene (**6**), which showed two symmetrical multiplets in the nmr centered at 0.50 and 0.85 ppm; a mass spectrum with a parent peak at m/e 174; $\lambda_{\max}$ (hexane) 203 mμ (ϵ 1.0 × 10^3). Reduction of **6** with sodium–tetrahydrofuran–*t*-butyl alcohol results in the formation, in 80% yield, of the desired dispiro[2.0.2.2]oct-7-ene, which showed two symmetrical multiplets in the nmr centered at 0.47 (4 H) and 0.73 (4 H) ppm and a singlet at 6.13 (2 H) ppm; bands, *inter alia*, in the ir (12 mm, gas phase) at 3080, 3010, 1014, 933, 876, and 737 cm^{-1}; $\lambda_{\max}$ (ethanol) 203 mμ (ϵ 5.72 × 10^3); a mass spectrum with a parent peak at m/e 106. Ozonolysis of **1** followed by treatment with performic acid results in >80% yield of bicyclopropyl-1,1′-dicarboxylic acid,[6] displaying two symmetrical multiplets in the nmr at 0.62 (4 H) and 1.01 (4 H) ppm and a broad singlet at 12.7 (2 H) ppm.



4 **5**

As might be expected, dispiro[2.0.2.2]oct-7-ene is thermally stable at temperatures up to 300°. We will report results from our investigation of its thermal rearrangement and other aspects of its chemistry.

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(1) See S. W. Staley, *J. Am. Chem. Soc.*, **89**, 1532 (1967), and references therein.

(2) R. Hoffmann, *Tetrahedron Letters*, 3819 (1965); *J. Chem. Phys.*, 40, 2480 (1964).

(3) L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 2316 (1966).

(4) H. G. Peer and A. Schors, *Rec. Trav. Chim.*, 161, 86 (1967).

(5) All new compounds gave satisfactory elemental analyses.

(6) L. Eberson, *Acta Chem. Scand.*, 13, 40 (1959).

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Ion-Pair Return in Racemization and Isomerization of Sulfinate Esters

Sir:

Sulfinate esters of aliphatic alcohols are known to undergo isomerization to sulfones when the nature of the alkyl moiety is such as to give rise to a comparatively stable carbonium ion.[1,2] Structure and solvent effects indicate that the isomerization is likely to occur by an ionization process, which appears to involve an ion-pair intermediate.[2] Since the sulfinate anion is

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(1) A. H. Wragg, J. S. McFadyen, and T. S. Stevens, *J. Chem. Soc.*, 3603 (1958).

(2) D. Darwish and R. A. McLaren, *Tetrahedron Letters*, 1231 (1962).

polydentate, its use as a leaving group in ionization reactions can serve to detect and quantitatively evaluate covalent return phenomena.[3-5] Return to covalent state from ionic species may occur with sulfur or with either oxygen;[6] isomerization measures return with sulfur, while return with oxygen may be measured either by isotopic oxygen scrambling[4] or by taking advantage of the asymmetry of the sulfur of sulfinate esters. That the latter method may be successfully applied appears likely from the observation that the solvolysis of diastereomerically pure α-phenylethyl or α-(p-methoxyphenyl)ethyl 2,6-dimethylbenzenesulfinate is accompanied by isomerization to sulfone as well as by conversion of the unreacted ester to a mixture of diastereomers.[7,8]

We report here the observation that optically active sulfinate esters, whose only asymmetric center is the sulfur atom, lose optical activity during isomerization in acetic acid, and the rate of loss of optical activity, k_α, considerably exceeds the isomerization rate, k_{isom}.

A sulfinate ester whose alkyl moiety may give rise to a moderately stable carbonium ion, benzhydryl p-toluenesulfinate (I), was prepared in an optically active form by the asymmetric oxidation of the corresponding sulfenate ester.[9] The sample of I which was used for the racemization studies had mp 70.5–74°; $[\alpha]^{25}{}_{436}$ +6.5° (c 5.2, acetic acid). At 51° in acetic acid the following first-order rate constants were measured: $k_\alpha{}^{10} = 2.1 \times 10^{-4}$ sec^{-1}, [I] = 0.15 M; $k_{\text{isom}}{}^{11} = 0.8 \times 10^{-4}$ sec^{-1}, [I] = 1.5×10^{-4} M. Since sulfone is recovered in almost quantitative amount, solvolysis cannot be very important and the difference $k_\alpha - k_{\text{isom}}$ can only be accounted for in terms of racemization of the unreacted starting material, $k_\alpha - k_{\text{isom}} = k_{\text{rac}}$. From the data above $k_{\text{rac}} = 1.3 \times 10^{-4}$ sec^{-1}.

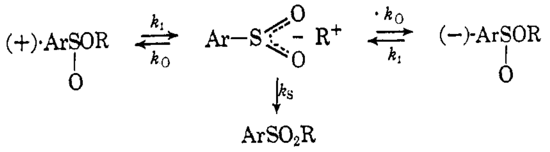
$$(+)\text{-Ar(SO)OR} \xrightarrow{k_{\text{rac}}} (\pm)\text{-Ar(SO)OR}$$

$$\text{Ar(SO)OR} \xrightarrow{k_{\text{isom}}} \text{ArSO}_2\text{R}$$

Assuming that isomerization occurs *via* ionization,[2] the question arises of whether racemization is an independent process or whether it also is formed *via* ionization. An independent process could involve a pyramidal inversion at sulfur. This, however, seems most unlikely for the following reasons. (i) The values of k_{rac} and k_{isom} are comparable, which would be a remarkable coincidence if racemization occurred *via* pyramidal inversion; moreover, $k_{\text{rac}}/k_{\text{isom}}$ appears to be almost independent of temperature. (ii) Activation parameters are: $\Delta H^{\ddagger} = 23$ kcal/mol, $\Delta S^{\ddagger} = -4$ eu for k_α; $\Delta H^{\ddagger} = 22.5$ kcal/mol, $\Delta S^{\ddagger} = -9$ eu for k_{isom}. These values, while not inconsistent with an ionization mechanism,[12] appear to be definitely different from those found for pyramidal inversion at sulfur in neutral substrates.[13] (iii) Substrate structure affects k_{rac} and k_{isom} in the same direction and to nearly the same extent, an increase by a factor of about 6 in going from 4,4′-dichlorobenzhydryl[14] to unsubstituted benzhydryl ester. The increase in rate with electron-releasing power of the alkyl moiety is consistent with an ionization mechanism. On the other hand, pyramidal inversion is known to be slightly affected by electronic effects in the opposite direction.[13]

We therefore conclude that both racemization and ionization arise from a common ionization process leading to carbonium and sulfinate ions which may return to covalent state with either the oxygen or the sulfur ends of the tridentate leaving group. The lack of solvolysis products in substantial amounts indicates that ionization past the intimate ion-pair stage is not greatly important. This agrees also with the isomerization mechanism proposed by Darwish.[6]

A simplified mechanistic scheme which involves only one ionic species is given by eq 1. Assuming that the



$$(+)\text{-ArS(=O)OR} \underset{k_O}{\overset{k_1}{\rightleftharpoons}} \text{Ar–S}{\overset{O}{\underset{O}{\lessdot}}}{}^{-}\ \text{R}^{+} \underset{k_1}{\overset{k_O}{\rightleftharpoons}} (-)\text{-ArS(=O)OR} \qquad \text{Ar–SO}_2^-\ \text{R}^+ \xrightarrow{k_S} \text{ArSO}_2\text{R} \tag{1}$$

oxygens of the sulfinate anion are equivalent,[15] the ionization rate, k_1, is equal to k_α. On the other hand, application of the steady-state approximation to eq 1 gives $k_{\text{isom}} = k_1[k_S/(2k_O + k_S)]$; $k_{\text{rac}} = k_1[2k_O/(2k_O + k_S)]$. From the experimental data reported above, it turns out that $k_O/k_S = 0.8$. Apparently the benzhydryl carbonium ion in acetic acid does not strongly discriminate between the available nucleophilic "teeth," and collapse to covalent state is nearly statistical.

The preliminary data above show that the use of optically active sulfinate esters in ionization reactions is particularly suitable for the detection and quantitative study of return phenomena.[17] We are currently applying this method to sulfinate esters of optically active alcohols with the aim of studying the stereochemistry of covalent return from ion pairs.[20]

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(3) S. Winstein, R. Appel, R. Baker, and A. Diaz, Special Publication No. 19, The Chemical Society, London, 1965, p 109.

(4) H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, 84, 3853 (1962).

(5) A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *ibid.*, 87, 1045 (1965).

(6) D. Darwish and E. A. Preston, *Tetrahedron Letters*, 113 (1964).

(7) D. Darwish and R. A. McLaren, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, p 44S.

(8) It may be observed that diastereomer interconversion can arise not only from stereomutation at sulfur but also from stereomutation at carbon as well. However, it is difficult to visualize a mechanism where stereomutation at carbon occurs independently from stereomutation at sulfur.

(9) L. Sagramora, P. Koch, A. Garbesi, and A. Fava, *Chem. Commun.* 985 (1967).

(10) The first-order plots for racemization are linear up to about 20% reaction, showing marked acceleration afterward. Addition of 1.25×10^{-2} M triethylamine, while not affecting the initial rate, effectively eliminates this phenomenon.

(11) Isomerization was followed by measuring the decrease in optical density with time at 260 mμ. The reaction followed good first-order kinetics.

(12) (a) J. B. Hyne, R. Wills, and R. E. Wonkka, *J. Am. Chem. Soc.*, 84, 2914 (1962); (b) A. K. Colter, F. F. Guzik, and S. H. Hui, *ibid.*, 88, 5754 (1966).

(13) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *ibid.*, 88, 3138 (1966).

(14) M. Isola, unpublished.

(15) This may be an approximation, however close. Recent data by Winstein and Diaz[16] seem to indicate that, in returning to the covalent state, the benzhydryl benzoate ion pair formed in the ionization of benzhydryl benzoate may return to the covalent state somewhat more frequently with the ether oxygen than with the carbonyl oxygen.

(16) A. F. Diaz and S. Winstein, *J. Am. Chem. Soc.*, 88, 1318 (1966).

(17) This method is formally similar to the detection of ion–molecule pair return which has been discussed by Darwish and coworkers for racemization of sulfonium salts.[18,19] No clear-cut example of the operation of the mechanism has as yet been reported, however.

(18) D. Darwish and G. Tourigny, *J. Am. Chem. Soc.*, 88, 4303 (1966).

(19) D. Darwish and S. H. Huy, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, No. S20.

(20) Supported by Consiglio Nazionale delle Ricerche, Rome, under Contracts 115-894-1204 and 115-894-399.

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