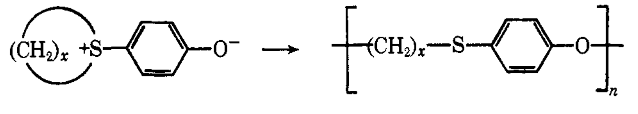
cyclic sulfonium and phenolate. They are noteworthy because when they are heated, polymerization occurs by phenolic anion attack upon the carbon adjacent to the sulfonium moiety. This polymerization proceeds with net loss of charge[1] and the formation of a nonionic polymer. The only by-products that have been successfully isolated are small amounts of cyclic dimer. Generally, the zwitterions are hydrated, crystalline solids that are highly soluble in water and in alcohols. By chlorination of the aromatic portion of the molecule, nonhydrated species are obtained.



$x = 4$ or 5

Five-membered cyclic sulfonium zwitterions were prepared by the reaction of a phenolic compound with tetrahydrothiophene 1-oxide and hydrogen chloride using the procedure reported for the synthesis of dimethylhydroxyarylsulfonium chlorides.[2] As a typical example, 1-(3,5-dichloro-4-hydroxyphenyl)tetrahydrothiophenium hydroxide inner salt I was prepared by the reaction of phenol with tetrahydrothiophene 1-oxide at 0–5° in absolute methanol solution saturated with hydrogen chloride. This hydrochloride salt was chlorinated at 35° in acetic acid with chlorine gas. The resulting hydrochloride salt of I was allowed to react with sodium methoxide in absolute methanol to a pH of 10.3, the solution was filtered, and the solvent was removed. After washing with small portions of water to remove NaCl, a colorless crystalline[3] solid I was obtained in 72% yield: nmr (CF$_3$COOH) δ 7.72 (s, 2, aromatic), 3.92 (m, broad, 4, $^+$S(CH_2)$_2$), and 2.62 ppm (m, broad, 4, CH_2CH_2); uv max (CH$_3$OH) 224 (ϵ 1720) and 294 mμ (ϵ 1470); ir (Fluorolube and Nujol, split mull) 1280 (aromatic CO$^-$) and 1571, 1518 cm^{-1} (aryl in-plane ring modes). *Anal.* Calcd for C$_{10}$H$_{10}$Cl$_2$OS: C, 48.21; H, 4.05; Cl, 28.46; S, 12.87. Found: C, 48.11; H, 4.35; Cl, 28.90; S, 12.50.

Heating I at 170° for 4 hr produced a tough, crystalline[3] polymer having a molecular weight[4] of 46,000 and a specific viscosity (η_{sp}) of 0.50.[5] The elemental analysis was identical with I. The polymer has infrared bands at 1030 and 2873 cm^{-1}, supporting ether functionality that is not present in the ir of I. The ir CH$_2$ stretching vibrations in the polymer are more intense than in I.

Attempts to react tetrahydrothiopyran 1-oxide with phenol were unsuccessful. The six-membered analog, 1-(3,5-dichloro-4-hydroxyphenyl)tetrahydro-2*H*-thiopyranium hydroxide inner salt II, was prepared *via* reaction of 1,5-dibromopentane with 4-(methylthio)phenol in refluxing chlorobenzene to yield the sulfonium salt and methyl bromide. The resulting hydrobromide salt was chlorinated and converted to the zwitterion by exchange with Dowex 1 resin (OH$^-$ form). The colorless crystalline solid was isolated (50%) by removal of solvent: nmr (CF$_3$COOH) δ 8.08 (s, 2, aromatic), 3.75 (br, 4, $^+$S(CH_2)$_2$), and 2.15 (m, broad, (CH$_2$)$_2$CH$_2$); uv max (CH$_3$OH) 227 (ϵ 1730) and 288 mμ (ϵ 1430); ir (Fluorolube and Nujol, split mull) 1277 (aromatic CO$^-$) and 1564, 1523 cm^{-1} (aryl in-plane ring modes). *Anal.* Calcd for C$_{11}$H$_{12}$Cl$_2$OS: C, 50.20; H, 4.60; S, 12.18. Found: C, 50.21; H, 4.70; S, 12.32. After heating II at 170° for 4 hr, a polymer with η_{sp} of 0.20[5] was obtained.

Five other examples of aryl cyclic sulfonium zwitterions and the η_{sp} of the resulting polymers are given in Table I.

Table I. Aryl Cyclic Sulfonium Zwitterions and Resulting Polymers

Zwitterion	Yield, %	Polymerization temp, °C	Polymer η_{sp}
1-(4-Hydroxyphenyl)tetrahydro-2*H*-thiopyranium hydroxide inner salt (monohydrate) (III)	51	160	0.04
1-(4-Hydroxyphenyl)tetrahydrothiophenium hydroxide inner salt (dihydrate) (IV)	93	160	0.16
1-(4-Hydroxy-3-methylphenyl)tetrahydrothiophenium hydroxide inner salt (dihydrate) (V)	95	100	0.20
1-(3,5-Dimethyl-4-hydroxyphenyl)-tetrahydrothiophenium hydroxide inner salt (dihydrate) (VI)	86	100	0.18
1-(3-Chloro-4-hydroxyphenyl)tetrahydrothiophenium hydroxide inner salt (monohydrate) (VII)	36	160	0.20

Polymerization of the solid zwitterionic salts I and II occurs within seconds at 200° but higher molecular weight polymers are obtained at lower temperatures and longer heating times. The lower molecular weights of the polymer formed from II are probably related to the stability and steric requirements of the six-membered sulfonium ring. Chlorination of the aromatic portion of the molecules increases the temperature needed for polymerization and also increases the molecular weights of the polymers formed.

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Received May 17, 1971

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(1) This has been called a "death charge" type polymerization.

(2) E. Goethals and P. de Radzitsky, *Bull. Soc. Chim. Belg.*, 73, 546 (1964).

(3) X-Ray powder patterns confirmed crystallinity.

(4) Molecular weight determinations were made with a Mechrolab membrane osmometer in chlorobenzene 70°. Reported values were obtained by extrapolation to infinite dilution.

(5) Measurements were made in chlorobenzene (1 wt %) at 105°.

The Acid-Catalyzed Decomposition of α-Diazospiro[cyclopropanenorbornanones]. Participation by the C-7′ Spirocyclopropyl Group

Sir:

The decomposition of 3-diazonorcamphor (I) in aqueous acid has been shown to give the α-ketol II, the β-ketol III, and the acid IV in comparable amounts.[1,2] The formation of these products has been interpreted[1] as involving initial exo protonation to give V followed by formation of the bridged ion VI. As part of a study of the effects of substituents on the reaction pathway, we have prepared the α-diazospiro-

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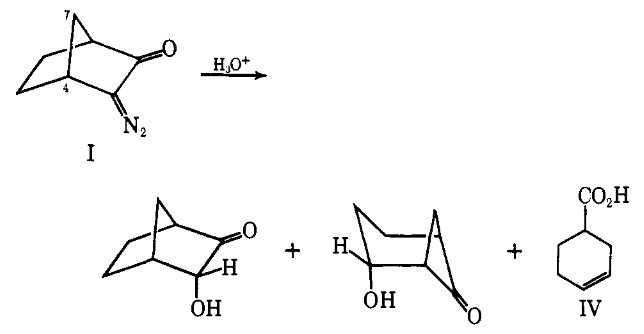
(1) P. Yates and R. J. Crawford, *J. Amer. Chem. Soc.*, **88**, 1561 (1966).

(2) P. Yates and C. Kashima, unpublished results.

[cyclopropanenorbornanones] VII and XVIII and examined their acid-catalyzed decomposition.

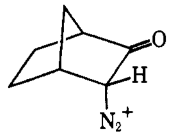


I

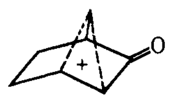
II

III

IV

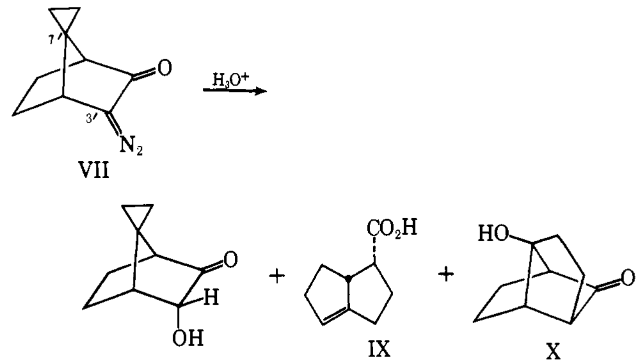


V



VI

3′-Diazospiro[cyclopropane-1,7′-norbornan-3′-one] (VII) on decomposition in aqueous tetrahydrofuran at pH 4–5 gave the α-ketol VIII (26%), mp 94–100°,[3] identified by comparison with an authentic sample prepared by hydrogenation of the α-dione XI in ethyl acetate over platinum. The major product (53%) from VII was a carboxylic acid, mp 75–77°, assigned structure IX on the basis of its hydrogenation in ethyl acetate over Pd/C to give XII,[4] and the oxidation of its methyl ester to XIII on treatment with osmium tetroxide followed by sodium periodate. A third product was obtained as an oil and is assigned structure X on the basis of its conversion to XIV[5] on treatment with base or acid.

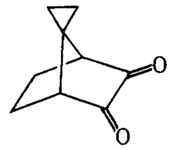


VII

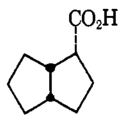
VIII

IX

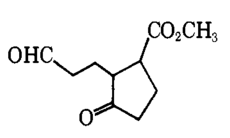
X



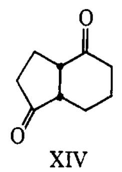
XI



XII

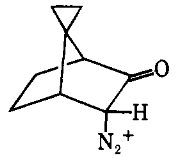


XIII

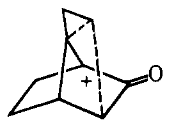


XIV

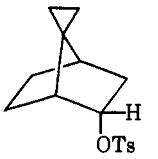
The formation of products VIII–X from VII can be interpreted in terms of exo protonation to give XV, the analog of V, and loss of nitrogen with participation of the syn C-7′ cyclopropyl bond to give the bridged ion XVI. The participation of the C-7′ cyclopropyl bond is of considerable interest in that it appears to be the first case in which such participation has been observed. Indeed, Wilcox and Jesaitis[6] have shown that the spirocyclopropane ring does not participate to any significant extent in the solvolysis of XVII. The occurrence of such participation in the case of the acid-catalyzed decomposition of VII can be attributed, at least in part, to the resulting amelioration of the unfavorable electrostatic interaction between a positive charge at C-3′ and the adjacent carbonyl group, a factor that has previously been invoked in the case of I to account for the unusual participation of the C-4–C-7 bond.[1]



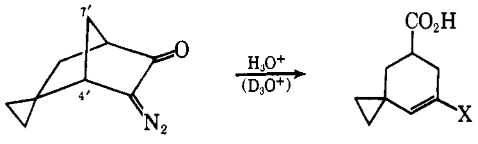
XV



XVI

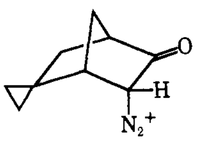


XVII

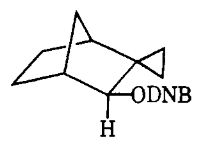


XVIII

XIX, X = H
XX, X = D



XXI



XXII

3′-Diazospiro[cyclopropane-1,5′-norbornan-2′-one] (XVIII) on decomposition in aqueous tetrahydrofuran at pH 4–5 gave the acid XIX as the sole product. That XIX arose by participation of the C-4′–C-7′ bond was demonstrated by the finding that decomposition of V in D_2O at "pH" 4–5 gave solely the acid XX. This result can again be interpreted in terms of exo protonation of the diazo ketone, giving XXI. The circumstance that no analogs of II and III are formed can be interpreted in terms of stabilization of a carbonium ion at C-4′ by the adjacent cyclopropyl group.[7] Although an intermediate of this type might have been expected to lead to products in which rearrangement of the cyclopropyl ring had occurred, there is excellent precedent for the absence of such rearrangement in the work of Wilcox and Jesaitis,[6] who have shown that while XXII solvolyzes in acetic acid *ca.* 10^3 times faster than the corresponding compound without the spiro-

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[3] The wide melting range is attributable to partial conversion to dimer.[1]

[4] A. C. Cope and M. Brown, *J. Amer. Chem. Soc.*, **80**, 2859 (1958).

[5] V. Hach and M. Protiva, *Collect. Czech. Chem. Commun.*, **23**, 1902 (1958); we thank Dr. Protiva for providing us with an authentic sample of the bis-2,4-dinitrophenylhydrazone of XIV.

[6] C. F. Wilcox, Jr., and R. G. Jesaitis, *Tetrahedron Lett.*, 2567 (1967).

[7] R. A. Blattel, D. G. B. Boocock, and P. Yates, unpublished results.

cyclopropyl ring, the product is very largely unrearranged.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Research Council of Canada for support of this research.

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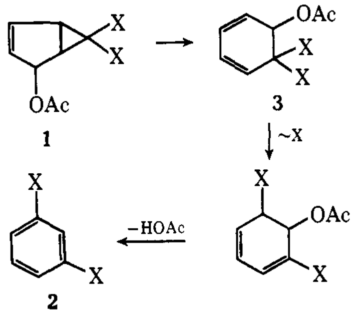
Thermal Sigmatropic Migration of the Carbomethoxyl Group

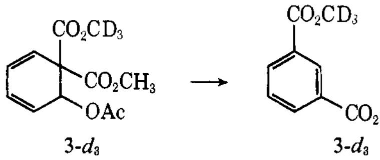
Sir:

Although there are scattered reports of photochemical[1] and thermal[2-4] carbomethoxyl group migrations, one of the few previous examples of a thermal process, the rearrangement of 5-carbomethoxy-1,5-dimethylbicyclo[2.1.0]pentane to 3-carbomethoxy-1,2-dimethylcyclopentene, has been interpreted[3] as a 1,2 shift in a diradical intermediate. Our observation that gas-phase pyrolysis at 295° of 6,6-dicarbomethoxybicyclo[3.1.0]hex-3-en-2-yl acetate (**1**, X = CO_2Me) gave a quantitative yield of acetic acid and *dimethyl isophthalate* (**2**, X = CO_2Me) therefore assumed special significance, because the 1,2-shift mechanism would have led to dimethyl phthalate instead. The present work elucidates the mechanism of the **1** → **2** rearrangement and establishes the occurrence of intramolecular thermal sigmatropic rearrangements of carbomethoxyl groups in this and related systems.

As a working hypothesis, we assumed that the rearrangement might occur by preliminary isomerization of **1** to the acetoxydiene diester **3**, which then might undergo [1,5] (or [1,3]) carbomethoxyl migration and elimination to **2**. A necessary condition for this mechanism was satisfied by the observation that pyrolysis of independently synthesized **3**[5,6] gave acetic acid and **2** quantitatively. Rough kinetic measurements indicated that the **3** → **2** rearrangement was not very much faster than the overall **1** → **2** process. Acetoxydiene **3** thus accumulated during incomplete pyrolysis of **1** and could be isolated (in addition to **2**) by thin-layer chromatography of the mixture obtained from pyrolysis of **1** to 38% conversion.

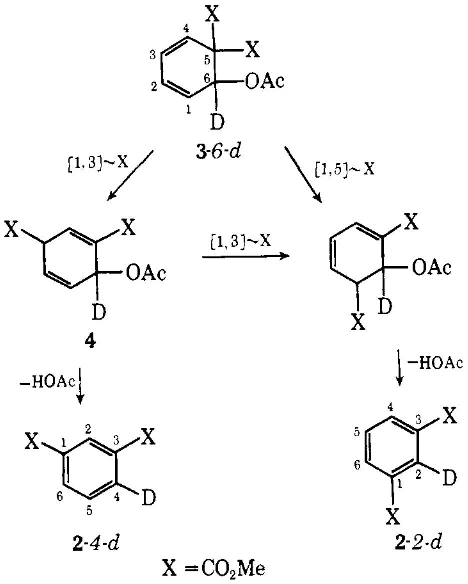


Pyrolysis of acetoxydiene **3**-d_3 (prepared by the synthesis already described[5] with the modification that the esterification was carried out with methyl-d_3 *p*-toluenesulfonate) gave **2**-d_3 containing no **2**-d_0 or **2**-d_6 (analysis by mass spectrometry). This excluded a radical-chain mechanism and demonstrated the complete intramolecularity of the **3** → **2** rearrangement.



Scheme I shows how examination of the dimethyl phthalate (**2**) obtained from pyrolysis of ring-labeled acetoxydiene (**3**-*6*-*d*) provides the basis for a distinction between two mechanistic categories: (i) direct [1,3]-carbomethoxyl migration and (ii) direct [1,5] or two successive [1,3] shifts. The 100-MHz nmr spectrum of ordinary dimethyl isophthalate (**2**) had absorptions at δ 7.5, H_5 (1 H, t, J = 8 Hz), 8.2, H_4, H_6 (2 H, d of d, J = 8, 2 Hz), and 8.7, H_2 (1 H, t, J = 2 Hz). The dimethyl isophthalate recovered from pyrolysis of **3**-*6*-*d*[7] to 15% conversion showed the complete absence of the absorption at δ 8.7 (H_2) and was therefore at least 95% **2**-*2*-*d*.[8] Mechanistic category i, involving a single

Scheme I



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(1) See, for example, D. M. Madigan and J. S. Swenton, *J. Amer. Chem. Soc.*, 92, 7513 (1970).

(2) M. J. Jorgenson and T. J. Clark, *ibid.*, 90, 2188 (1968).

(3) A thermal acetyl group migration has been observed (H. Monti and M. Bertrand, *Tetrahedron Lett.*, 1235 (1969)] and briefly discussed theoretically [N. Trong Anh, "Les Regles de Woodward-Hoffmann," Ediscience, Paris, 1970, p 50] although formal proof of its intramolecularity remains to be supplied.

(4) Thermal cyano group rearrangements also have been observed [E. Ciganek, *J. Amer. Chem.Soc.*, 89, 1458 (1967)].

(5) Sodium–ammonia–ethanol reduction of anisic acid followed by esterification (CH_2N_2) and carbomethoxylation [LiN(*i*-Pr)$_2$, $ClCO_2Me$] gave 1-methoxy-6,6-dicarbomethoxycyclohexa-1,4-diene, which upon hydrolysis to the ketone and $NaBH_4$ reduction was converted to 3,3-dicarbomethoxy-4-hydroxycyclohexene. Acetylation, allylic bromination (*N*-bromosuccinimide), and dehydrobromination (diazabicycloundecane) gave **3**.

(6) New substances were characterized by elemental analyses and spectroscopic properties.

(7) Prepared by the synthesis described in ref 5 with the exception that $NaBD_4$ was used in place of $NaBH_4$.

(8) The product isolated from higher conversion showed some absorption at δ 8.7, but this was ascribable to a competing degenerate rearrangement (of H or OAc?) of the starting material 3-*6*-*d* which mixed protium at C_4 and deuterium at C_6, as was demonstrated by the nmr spectra of trisdipivaloylmethanatoeuropium [(DPM)$_3$Eu] treated[9] samples of ring-labeled 3 isolated from partial pyrolyses.

(9) (a) C. C. Hinckley, *J. Amer. Chem. Soc.*, 91, 5160 (1969); (b) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).