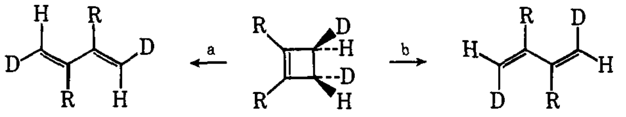
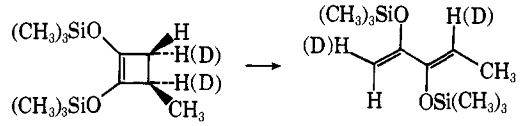
modes,[5] pathways a and b, respectively, distinguishable by the stereochemistry of the deuterium in the resultant 1,3-butadienes, **2a** and **2b**. Should these processes be kinetically differentiated, then a ratio of products (**2a**/**2b**) different from unity might be anticipated. In this communication we report observations bearing on this expectation.



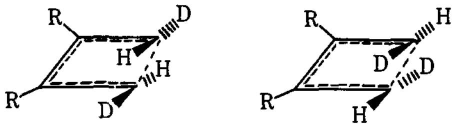
2a **1** **2b**

trans-3,4-Dideuterio-1,2-bis(trimethylsiloxy)cyclobutene (**1**) [R = $OSi(CH_3)_3$] and *cis*-3,4-dideuterio-1,2-bis(trimethylsiloxy)cyclobutene (**3**), stereospecifically deuterated derivatives of 1,2-bis(trimethylsiloxy)cyclobutene (**4**), were prepared from *dl*-dimethylsuccinate-d_2 and *meso*-dimethylsuccinate-d_2, respectively.[6,7] Isomerization of **1**, **3**, and **4** proceeded smoothly at *ca.* 180° ($t_{1/2}$ *ca.* 90 min)[8] and the product in each case was easily characterized as 2,3-bis(trimethylsiloxy)-1,3-butadiene by the nmr spectra; these exhibited besides a singlet at τ 9.90 (CH_3Si), two other well-separated and only slightly broadened singlets at 5.28 and 5.80 corresponding to the two different vinyl protons of the butadiene. Integration of these for products derived from **3** and **4** indicated a ratio indistinguishable from unity. In contrast, careful integration of the low-field singlets for the product obtained on isomerization of **1** gave an upfield-downfield ratio of 52.3:47.7,[9,10] revealing thereby an unequal proportion of **2a** and **2b** in this product.

To establish the identity of the predominant isomer in the mixture **2a** + **2b**, 3-methyl-1,2-bis(trimethylsiloxy)cyclobutene (**5**) and its cis 3,4-dideuterio derivative **6** were prepared starting with dimethyl pyrotartarate and *erythro*-dimethyl pyrotartarate-d_2, respectively.[6,7] It was expected that the direction of conrotatory ring opening of these cyclobutenes would be controlled by the C_3 methyl substituent[11] and that *trans*-2,3-bis(trimethylsiloxy)-1,3-pentadienes, **7** and **8**, would be formed stereospecifically. The stereochemistry of deuterium in diene **8** would thus be defined and nmr assignments could be made unambiguously. In fact, the vinyl proton region in the nmr of diene **7** consisted of singlets at τ 5.73 and 5.34 and a quartet ($J \sim 7.0$ Hz) at 4.60, whereas the nmr of diene **8** exhibited a singlet at 5.34.[12] Hence the high-field vinyl singlet in the nmr spectrum of **7** and **8** and by analogy the high-field singlet in the nmr spectrum of **2** [R = $OSi(CH_3)_3$] represents a proton cis to the trimethylsiloxy substituent, allowing therefore the conclusion that the predominant isomer formed on thermolysis of **1** [R = $OSi(CH_3)_3$] is the trans,trans d_2 isomer **2b** [R = $OSi(CH_3)_3$]. This conclusion is taken as evidence for selection between the two competitive conrotatory cyclobutene ring openings.[10] Considering further the importance of steric effects in such isomerizations,[4] our observations might best be explained in terms of the so-called "steric" deuterium isotope effect,[3,13] that is, as a consequence of the smaller effective size of carbon-bound deuterium compared with hydrogen. According to this view, the data thus reveal a preference for transition states involving deuterium–deuterium interaction over those involving hydrogen–hydrogen interaction (B *vs.* A). Simplified models of such processes suggest further that severe crowding will occur in nearly planar transition states *only* if the extent of C_3–C_4 bond cleavage is small and such transition states could thus be characterized as "closed." Evaluation of the kinetic secondary deuterium isotope effect for cyclobutene has led to a similar view,[14] although our study also shows a considerable variation in isotope effect (as might be expected) with C_3–C_4 disubstitution. A complete report of these results will be forthcoming.



5(**6**) **7**(**8**)



A B

Acknowledgment. Partial support of this research by the Research Corporation is gratefully acknowledged. We also recognize the generous support of the Department of Chemistry, Polytechnic Institute of Brooklyn.

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[5] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1960.

[6] Acyloin cyclization in the presence of trimethylchlorosilane according to J. J. Bloomfield, *Tetrahedron Lett.*, 587 (1968).

[7] Appropriate d_2 esters prepared by catalytic reduction under deuterium and/or diimide reduction in the presence of deuterium oxide.

[8] J. J. Bloomfield, H. M. Frey, and J. Metcalfe have reported a study of the gas-phase thermal isomerization of **3** (*Int. J. Chem. Kinet.*, **3**, 85 (1971)). We wish to thank the authors for making their manuscript available to us prior to publication.

[9] Integration by planimetry; standard deviation less than ±0.5%. Similar ratios were evident after *ca.* 30% isomerization of **1** as well as after prolonged heating of the diene mixture (**2a** + **2b**).

[10] Although appropriate rate data for the formation of **2a** + **2b** were not obtained, a kinetic effect appears most probable.

[11] For instance, 3-methylcyclobutene gives only *trans*-1,3-pentadiene on isomerization: E. Gil-Av and J. Shabtai, *J. Org. Chem.*, **29**, 257 (1964).

[12] Actually, the intensity of the quartet at τ 4.60 and singlet at 5.73 was 30–70% of that expected, depending on the extent of deuterium incorporation.

[13] K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *J. Amer. Chem. Soc.*, **86**, 1733 (1964); L. Melander and R. E. Carter, *ibid.*, **86**, 295 (1964); *Acta Chem. Scand.*, **18**, 1138 (1964); H. C. Drown and G. J. McDonald, *J. Amer. Chem. Soc.*, **88**, 2514 (1966).

[14] M. L. Honig, Ph.D. Thesis, Polytechnic Institute of Brooklyn, Brooklyn, N. Y., June 1970.

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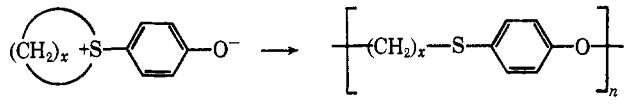
Novel Aryl Cyclic Sulfonium Zwitterions that Polymerize when Heated

Sir:

We wish to report a new class of zwitterion compounds in which the positive and negative sites are 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



$x = 4$ or 5

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.

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_3COOH) 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_3OH) 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 $C_{10}H_{10}Cl_2OS$: 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_3COOH) δ 8.08 (s, 2, aromatic), 3.75 (br, 4, $^+S(CH_2)_2$), and 2.15 (m, broad, $(CH_2)_2CH_2$); uv max (CH_3OH) 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 $C_{11}H_{12}Cl_2OS$: 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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[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.