develop only in the transition state leading to the Z isomer.[2,3]

The transformation of dithio ester to ester has usually been effected under rather drastic conditions.[4] Seeking a milder exchange procedure, we investigated the use of cupric chloride–cupric oxide in ethanol[5] and found that this system afforded almost quantitative yield of the desired ester under extremely mild conditions.

Thus, the dithio ester **1** ($R^1 = CH_3$),[6–8] on treatment with *sec*-butyllithium (2 equiv) at −78° in tetrahydrofuran, was converted to a light yellow solution of the dianion **2** ($R^1 = CH_3$). Metalated dithio ester **2** is apparently quite stable in the indicated solvent system at least up to −25°. The success of metalation can be attributed in large measure to the use of *sec*-butyllithium, which among other factors confers favorable basicity for this system.[9] After 30 min at −78°, octyl bromide (1 equiv) was added at the same low temperature, and the solution was kept there for 45 min and at −25° for 1 hr to complete the first alkylation process.[10] The second alkylation was performed by the addition of methyl iodide (1 equiv) at −25° and the resulting solution was stirred at −25° for 3 hr, during which period the facile thio-Claisen rearrangement[11] took place to give the yellow dithio ester **4a** ($R^1 = CH_3$; $R^2 = n\text{-}C_8H_{17}$).[12] The crude dithio ester, after extractive work-up, was treated with a threefold excess of cupric chloride and cupric oxide (1:1) in ethanol and the suspension was stirred at 25° for 5 hr to produce the ester **4b** ($R^1 = CH_3$; $R^2 = n\text{-}C_8H_{17}$)[13] in 63% overall yield after preparative layer chromatography on silica gel.[14] The 100-MHz nmr spectrum (in CCl_4, TMS internal standard) showed a sharp singlet at 1.60 ppm (3 H) corresponding to the methyl group of E olefinic bond.[15] Analysis by glpc indicated that this product consisted of >98% E isomer. Similarly, benzyl bromide gave the ester **4b** ($R^1 = CH_3$; $R^2 = CH_2C_6H_5$)[16] in 70% overall yield.

This process is also applicable to the stereoselective production of E-disubstituted olefinic bonds. Thus, octyl bromide was converted by reaction with dithio ester **1** ($R^1 = H$) into (E)-ester **4b** ($R^1 = H$; $R^2 = n\text{-}C_8H_{17}$) in 70% overall yield; ir (neat) 975 cm^{-1}, homogeneous by tlc and glpc assay.

Further work is in progress on the extension of this reaction to other systems and application to the synthesis of certain natural products.

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[2] (a) D. J. Faulkner and M. R. Petersen, *Tetrahedron Lett.*, 3243 (1969); (b) *J. Amer. Chem. Soc.*, **95**, 553 (1973).

[3] Although the substitution of S for CH_2 in the six-membered ring transition state had been reported to cause a slight decrease in stereoselectivity of [3,3]-sigmatropic rearrangement,[2b] the present reaction was performed at a low temperature (−25°) which may overcome this disadvantage.

[4] J. J. Willand and E. Pacsu, *J. Amer. Chem. Soc.*, **82**, 4347 (1960).

[5] T. Mukaiyama, K. Narasaka, and M. Furusato, *ibid.*, **94**, 8641 (1972).

[6] Prepared simply from methallyl mercaptan and acetonitrile (>60% yield): E. Schmidt, *Chem. Ber.*, **47**, 2545 (1914).

[7] Bp 77° (18 mm); mass m/e 146 (M^+); ir (neat) 1650, 1195, 1100, 900, 860 cm^{-1}; nmr (CCl_4, TMS) δ 1.74 (d, 3 H, J = 1 Hz), 2.75 (s, 3 H), 3.75 (s, 2 H), 4.74 and 4.85 (two br s, 1 H each).

[8] All new compounds reported in this communication have been characterized spectrometrically and analytically.

[9] *sec*-Butyllithium was the most satisfactory base for the metalation of allyl sulfide; see K. Oshima, H. Takahashi, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, **95**, 2693 (1973).

[10] Most of the color was discharged after 10 min at −78°.

[11] The characteristic yellow color of dithio ester was developed during this period. For thio-Claisen rearrangement of ketene thioacetal see P. J. W. Schuijl and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **87**, 929 (1968).

[12] Mass m/e 272 (M^+); ir (neat) 1210 and 1140 cm^{-1}; nmr (CCl_4, TMS) δ 1.62 (s, 3 H), 2.57 (s, 3 H), 5.19 (t, 1 H, J = 7 Hz); homogeneous by tlc and glpc assay.

[13] Mass m/e 254 (M^+); ir (neat) 1730, 1160 cm^{-1}; nmr (CCl_4, TMS) δ 0.89 (t, 3 H, J = 7 Hz), 1.22 (t, 3 H, J = 7 Hz), 1.27 (br s), 1.60 (s, 3 H, E olefinic methyl), 1.85–2.35 (m, 6 H), 4.05 (q, 2 H, J = 7 Hz), 5.10 (t, 1 H, J = 7 Hz).

[14] Chromatographic removal of small amounts of many nonpolar by-products was easily achieved either by thin layer techniques (silica gel, benzene, R_f 0.63) or simple column chromatography (silica gel, benzene).

[15] W. S. Johnson, A. van der Gen, and J. J. Swoboda, *J. Amer. Chem. Soc.*, **89**, 170 (1967); see footnote 9.

[16] Mass m/e 232 (M^+); ir (neat) 1730, 1600, 1155, 1105, 1055 cm^{-1}; nmr (CCl_4, TMS) δ 1.71 (s, 3 H), 5.30 (t, 1 H, J = 7 Hz); homogeneous by tlc and glpc assay (>99% E isomer).

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The Spiro[2.7]decatrienyl Anion. An Experimental Evaluation of Criteria for Aromaticity

Sir:

The concept of aromaticity has been central to the development of chemical structural theory. In this paper we report the preparation and direct observation (by nmr spectroscopy) of the spiro[2.7]decatrienyl anion (**1**), the first example of a cyclic anion spiro fused with a cyclopropane ring,[1,2] and present data which show that the two most commonly employed criteria for "aromaticity,"[3] diamagnetic ring currents[4] and π resonance energies,[5] lead to opposite conclusions when **1** is compared with the closely related methylenecyclooctatrienyl anion (**2**).[6]

The synthesis of anion **1** is outlined in Scheme I.[7] The coupling constants for **1** ($J_{45} = 12.5 \pm 0.3$ Hz, $J_{56} = 10.0 \pm 0.2$ Hz, and $J_{67} = 10.9 \pm 0.2$ Hz), are almost identical with those for **2**[6] and suggest that both anions are more or less planar. Of particular interest is the large downfield shift of the cyclopropyl protons of **1** (δ 1.50) compared with the corresponding protons in

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[1] For recent studies of spiro fused anions as transition states or intermediates, see (a) E. Grovenstein, Jr., and Y.-M. Cheng, *J. Amer. Chem. Soc.*, **94**, 4971 (1972); (b) G. Fraenkel and J. W. Cooper, *ibid.*, **93**, 7228 (1971); (c) M. F. Semmelhack, R. J. DeFranco, Z. Margolin, and J. Stock, *ibid.*, **95**, 426 (1973).

[2] The interactions in 1 should not be confused with spiro conjugation; see (a) H. E. Simmons and T. Fukunaga, *ibid.*, **89**, 5208 (1967); (b) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967).

[3] For recent discussions of the definition of aromaticity, see (a) J.-F. Labarre and F. Crasnier, *Fortschr. Chem. Forsch.*, **24**, 33 (1971); (b) D. Lloyd and D. R. Marshall, *Angew. Chem., Int. Ed. Engl.*, 11, 404 (1972).

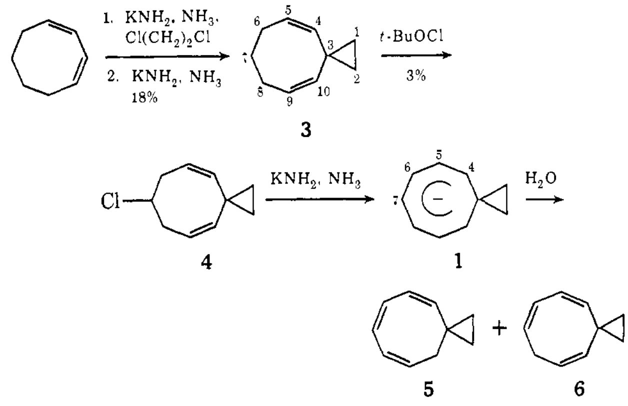
[4] L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, p 98, and references cited therein.

[5] M. J. S. Dewar, *Chem. Soc. Spec. Publ.*, **No. 21**, 207 (1967).

[6] S. W. Staley and G. M. Cramer, *J. Amer. Chem. Soc.*, **95**, 5051 (1973).

[7] Diene **3**: nmr (CCl_4) δ 5.5–4.2 (seven-line m, 4, olefinic), 2.37 (apparent q, 4, allylic), 1.33 (apparent t of t, 2, methylene), 0.73 (s, 4, cyclopropyl); uv (hexane) end absorption ($\epsilon_{220\,\text{nm}}$ 5510). Diene **4**: nmr (CCl_4) δ 5.6–5.0 (seven-line m, 4, olefinic), 4.05 (t of t, H_7, $J_{6a,7}$ = 5.2 Hz, $J_{6b,7}$ = 6.4 Hz), 2.78 (apparent d of d, 4, allylic), and 0.82 (s, 4, cyclopropyl); uv (hexane) end absorption ($\epsilon_{220\,\text{nm}}$ 6870). Triene **5**: nmr (CCl_4) δ 6.2–4.6 (m, 5, olefinic), 4.83 (AB d, H_4, J_{45} = 13.0 Hz), 2.27 (three-line m, 2, allylic), and 0.53 (s, 4, cyclopropyl); uv (hexane) λ_{max} 275 nm (ϵ 3040). Triene **6**: nmr (CCl_4) δ 6.1–5.3 (m, 4, olefinic), 5.15 (J = 12.6 Hz), and 4.99 (J = 10.8 Hz) (AB d, 2, H_4 and H_9), 2.85 (t, 2, methylene, J = 7.2 Hz), and 0.68 (s, 4, cyclopropyl); uv (hexane) λ_{max} 268 nm (ϵ 550).

Scheme I



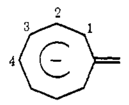
3, 4, 5, and 6 (δ 0.73, 0.82, 0.53, and 0.68, respectively). This indicates a substantial polarization of electron density out of the cyclopropyl ring and into the heptatrienyl anion portion of the molecule,[8] which is opposite to what would be expected on the basis of a greater dispersal of negative charge. Since the heptatrienyl anion portion of **1** has equal π donor and acceptor properties,[6] this polarization firmly establishes the cyclopropane ring as an intrinsically better donor than acceptor group.[9,10]

The chemical shifts for the eight-membered ring protons in **1**, and in the closely related anions **2** and **7**, are given in Table I. The remarkable point which emerges from the comparison of these data is that H_5–H_9 in **1** are shifted *ca.* 0.6–0.8 ppm *downfield* relative to the corresponding protons (H_2–H_6) in **2** and **7**, despite the fact that electron density is donated to the eight-membered ring from the cyclopropyl ring of **1**.[11] This is best explained on the basis of a substantial diamagnetic ring current in the π system of **1** (compared with the essentially atropic[6,12] system of **2**) and is the first case in which a ring current has been shown to result from spiro cyclopropyl conjugation. Thus, if aromaticity is defined on the basis of π-electron ring currents,[4] than **1** would be considered to be more "aromatic" than **2**.

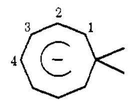
Table I. Chemical Shifts for the Olefinic Protons in the Potassium Salts of the Spiro[2.7]decatrienyl (**1**), Methylenecyclooctatrienyl (**2**), and 8,8-Dimethylcyclooctatrienyl (**7**) Anions in Liquid Ammonia

	Chemical shift, ppm^{a,b}			
Anion	H_1 (H_4)	H_2 (H_5)	H_3 (H_6)	H_4 (H_7)
1	4.13	5.97	4.41	5.84
2^c	4.40	5.35	3.76	5.17
7^d	4.52	5.42	3.54	5.20

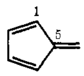
[a] Obtained at −40, −60, and −55° for **1**, **2**, and **7**, respectively; trimethylamine ($\delta_{\mathrm{TMS}}{}^{\mathrm{NH_3}}$ 2.135) was employed as an internal standard. [b] The numbering of the protons in anion **1** is different from that in **2** and **7** and is given in parentheses. [c] Reference 6. [d] S. W. Staley and N. J. Pearl, *J. Amer. Chem. Soc.*, **95**, 2731 (1973).



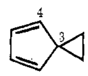
2



7



8



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On the other hand, aromaticity is often defined in terms of the resonance energy of a π system compared with that of some appropriate model.[5] Interestingly, analysis of the photoelectron spectra of fulvene (**8**) and spiro[2.4]hepta-4,6-diene (**9**) shows a significantly greater C_1–C_5 π-bond integral in **8** (β_{15} = −2.4 eV) compared with the corresponding integral in **9** (β_{34} = −1.9 eV).[13] This, in turn, leads to a greater π-delocalization energy (*cf.* the corresponding π-orbital energies) in **8** than in **9**.[13,14] If the same considerations apply in the case of anions **1** and **2**, the latter species would be considered to be more "aromatic."[15] Thus, the foregoing data provide, for the first time, evidence that the ring current and the resonance energy criteria for the concept of aromaticity may lead to different conclusions.[16]

Acknowledgment. We are pleased to acknowledge the support of this work by the National Science Foundation.

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[8] Evidence for similar polarizations has been reported by (a) R. A. Clark and R. A. Fiato, *J. Amer. Chem. Soc.*, **92**, 4736 (1970); (b) P. Rys, P. Skrabal, and H. Zollinger, *Tetrahedron Lett.*, 1797 (1971).

[9] This is a consequence of the Möbius array of p orbitals around the periphery of the cyclopropane ring in the Walsh model which (unlike a double bond) results in the lowest unoccupied (acceptor) orbital being displaced twice as far from the nonbonding level (in the HMO approximation) as are the highest occupied (donor) orbitals.

[10] For previous indications of the donor–acceptor properties of the cyclopropyl ring, see, *e.g.*, (a) R. H. Eastman and J. C. Selover, *J. Amer. Chem. Soc.*, **76**, 4118 (1954); (b) R. C. Hahn, T. F. Corbin, and H. Shechter, *ibid.*, **90**. 3404 (1968); (c) N. L. Bauld, J. D. McDermed, C. E. Hudson, Y. S. Rim, J. Zoeller, Jr., R. D. Gordon, and J. S. Hyde, *ibid.*, **91**, 6666 (1969).

[11] The signals for the protons at C_4 and C_{10} in 1 are shifted upfield relative to H_1 and H_7 in 2 and 7 primarily due to the shielding by the cyclopropyl ring in 1; *cf.* C. D. Poulter, R. S. Boikess, J. I. Brauman, and S. Winstein, *ibid.*, **94**, 2291 (1972), and references cited therein. See also ref 4, pp 98–101.

[12] We feel that the terms diatropic, paratropic, and atropic best designate the ability to sustain diamagnetic, paramagnetic, or no ring currents, respectively, in cyclic delocalized π systems; see ref 5 and P. J. Garratt and F. Sondheimer, cited by F. Sondheimer, *Accounts Chem. Res.*, **5**, 81 (1972).

[13] R. Gleiter, E. Heilbronner, and A. de Meijere, *Helv. Chim. Acta*, **54**, 1029 (1971).

[14] The nmr spectra for 8 and **9** have not been fully interpreted and ring currents have not been demonstrated for either compound (although these compounds may, in fact, possess ring currents).

[15] Anion 1 is nevertheless probably substantially stabilized by π delocalization between the spiro rings. A similar interaction undoubtedly also influences the results reported in ref 1c.

[16] The resonance energy is a function of the amount of overlap between the p orbitals at C_1 and C_5 in **8** and at C_3 and C_4 in **9**. It is important to note in this connection that the C_1–C_5 bond length in **8** is 1.470 Å (P. A. Baron, R. D. Brown, F. R. Burden, P. J. Domaille, and J. E. Kent, *J. Mol. Spectrosc.*, 43, 401 (1972)) compared with 1.509 Å for the C_3–C_4 bond length in **9** (J. F. Chiang and C. F. Wilcox, Jr., *J. Amer. Chem. Soc.*, **95**, 2885 (1973)). On the other hand the ring current is a function of the electron density in the cyclic π system. Since the cyclopropyl group is a poorer acceptor than a double bond,[9] 1 is closer to being a cyclic $4n + 2$ π-electron system than is **2**. Similar considerations apply to **8** and **9**.

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A Derivative of 3-Oxahomobiphenylene. A New Antiaromatic System

Sir:

Several stable heterocyclic analogs of biphenylene have been reported.[1,2] In these compounds, one of

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[1] P. J. Garratt and K. P. C. Vollhardt, *Chem. Commun.*, 109 (1970).

[2] P. J. Garratt, A. B. Holmes, F. Sondheimer, and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, **92**, 4492 (1970).