similar mixture (<1% **3**, 34% **4**, and 66% **5**) was obtained upon quenching **2** in HMPA in the same manner. That these mixtures primarily represent a *kinetic quench* was established by the observation that a markedly different mixture of isomers (67% **3**, 31% **4**, and 2% **5**) was obtained on equilibration of either **3** or **4** in 0.5 *M* potassium *tert*-butoxide in dimethyl sulfoxide at 25°.[13]

The coupling constants in **2** are all relatively large (>10 Hz) and are indicative of a more or less planar delocalized structure.[14] Of particular interest is the observation that the chemical shifts of all protons in **2** move significantly upfield on changing the solvent from ammonia to hexamethylphosphoramide (see Table I). The nearly identical upfield shifts for H_1–H_7 (0.3 ppm) coupled with the somewhat larger shift for H_9 (0.46 ppm) can perhaps be explained by a change from contact to solvent-separated ion pairing and/or to free ions[15] The detection of this phenomenon by nmr spectroscopy seems to have been reported previously only in the case of simple "aromatic" anions.[16]

Interestingly, if one employs "model" chemical shifts of δ 6.1 and 5.0 for the ring[17] and exocyclic methylene[18] protons, respectively, and corrects for charge-induced chemical shifts ($\Delta\delta_q$) by us of the equation $\Delta\delta_q = kq_r$ where $k = \pm$ 10.7 ppm per ± charge,[19] then it is seen that the chemical shifts for H_2–H_6 in **2** in liquid ammonia[20] are in good agreement with calculated chemical shifts based on self-consistent HMO charge densities (see Table I).[21] The observed chemical shifts for H_1 and H_7 are, as expected, lower than the calculated value due to deshielding by the exocyclic double bond.

The above analysis points to several important conclusions. First, both the nmr data and the quenching data suggest that there is not a significant amount of negative charge at C_9 in **2** and that structure **2** is the major valence bond contributing structure.[22] Second, *there is no evidence for substantial diamagnetic or paramagnetic ring currents in this anion, thereby indicating that "4n + 1" π systems are atropic.*[3] Interestingly, this behavior is dramatically altered by the presence of donor and acceptor groups conjugated with the eight-membered ring, as will be reported in subsequent publications.

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[13] Uncertainties are <1%; material balances were >85%.

[14] For the (dilithium) isopropenylcyclooctatetraene dianion J_{23} = 11.5 Hz and $J_{34} = J_{45}$ = 9.9 Hz. We greatly appreciate the assistance of Dr. Jeffrey Seeman with these measurements.

[15] That this shift is real and is not due to a referencing problem is demonstrated by the observation of a similar shift for the ring protons of the 9-*tert*-butyl derivative of **2** but not for the *tert*-butyl protons, which are essentially unshifted. We thank Professor A. G. Anastassiou and Dr. R. C. Griffith for a sample of the *anti*-9-*tert*-butyl derivative of **1**.

[16] J. B. Grutzner, J. M. Lawlor, and L. M. Jackman, *J. Amer. Chem. Soc.*, **94**, 2306 (1972), and references cited therein.

[17] R. C. Haddon, *Tetrahedron*, **28**, 3613 (1972), and references cited therein.

[18] C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).

[19] T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

[20] Comparison is made with the liquid ammonia data since the value of *k* in this equation is based on chemical shifts obtained from what are probably contact ion pairs.[19]

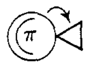
[21] The ω technique was employed with all $\beta = \beta_0$; A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 115–116. Calculated charge densities are −0.197 (C_1), −0.056 (C_2), −0.201 (C_3), −0.063 (C_4), and −0.013 (C_9).

[22] Calculations based on the CNDO/2 approximation (J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); P. A. Dobosh, Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Ind., Program 141) appear to overestimate the amount of negative charge on C_9.

Contrasting Reactivities of the Spiro[2.5]octadienyl and Spiro[2.7]decatrienyl Anions

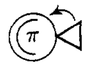
Sir:

The title anions exemplify classes of compounds in which cyclopropyl rings are spiro fused with cyclic π systems containing 4*n* + 2 and 4*n* π electrons (**1** and **2**,



4*n* + 2 π electrons

1



4*n* π electrons

2

respectively). The elucidation of the properties of such systems is of interest since, on the basis of simple perturbation theory, type **1** compounds are expected to experience electron donation from the π system into the cyclopropyl ring whereas type **2** compounds should display somewhat greater polarizations in the opposite direction.[1] The latter point has been verified for several compounds,[2] including the spiro[2.7]decatrienyl anion **3**,[3] but evidence concerning this point has yet to be obtained for type **1** compounds.[4] In addition, the spiro[2.5]octadienyl anion **4** has been of continuing interest as a possible intermediate or transition state in the 1,2 carbon to carbon migration of the phenyl group in carbanions.[5] In this paper we report data which demonstrate remarkably different reactivities for anions **3** and **4**.

Spirodienes **5**[6] and **6**[7] were obtained in 7 and 1% yields, respectively, by careful application of the alkyla-

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[1] This result obtains regardless of the charge in the π system and is a consequence of the fact that the highest occupied molecular orbitals (HOMO's) of the 4*n* π-electron systems are antisymmetric with respect to the plane of the cyclopropyl ring and therefore do not interact with the (Walsh) cyclopropyl orbitals, whereas the symmetric lowest unoccupied molecular orbitals do. The reverse situation (*i.e.*, symmetric HOMO's and antisymmetric LUMO's) is found in the 4*n* + 2 π-electron systems.

[2] (a) Spiro[2.5]octadienyl cation: G. A. Olah and R. D. Porter, *J. Amer. Chem. Soc.*, **93**, 6877 (1971); (b) spiro[2.4]hepta-4,6-diene: R. A. Clark and R. A. Fiato, *ibid.*, **92**, 4736 (1970).

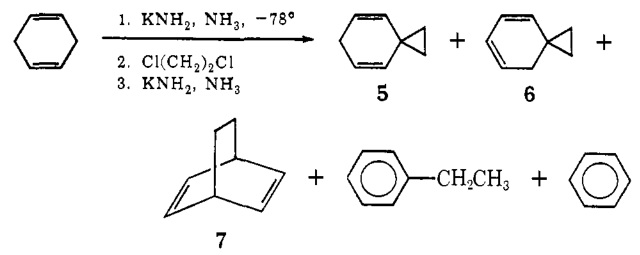
[3] S. W. Staley and W. G. Kingsley, *ibid.*, in press.

[4] Spiro[2.6]nona-4,6,8-triene is probably folded and shows no evidence of significant interaction; (a) C. J. Rostek and W. M. Jones, Jr., *Tetrahedron Lett.*, 3957 (1969); (b) see also M. Jones, Jr., and E. W. Petrillo, Jr., *ibid.*, 3953 (1969).

[5] (a) Review: H. E. Zimmerman in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 6; see also (b) E. Grovenstein, Jr., and Y.-M. Cheng, *J. Amer. Chem. Soc.*, **94**, 4971 (1972), and references cited therein; (c) G. Fraenkel and J. W. Cooper, *ibid.*, **93**, 7228 (1971), and references cited therein; (d) J. J. Eisch and C. A. Kovacs, *J. Organometal. Chem.*, **25**, C33 (1970).

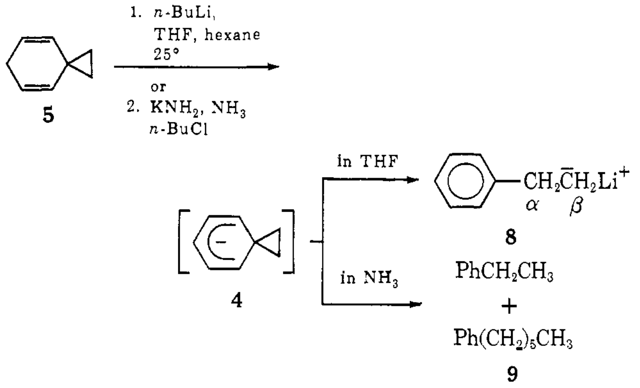
[6] Nmr (CCl_4): complex d of t at δ 5.55 (H_5 and H_7, J_{45} = 10.5 Hz, J_{56} = 3.4 Hz), d of t at 4.97 (H_4 and H_8, J_{46} = 1.9 Hz), a seven-line multiplet (t of t) at 2.77 (H_6), and a singlet at 0.62 (4 H, cyclopropyl); uv (hexane) end absorption only ($\epsilon_{220\ \mathrm{nm}}$ 3470).

[7] A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, **9**, 899 (1970). We thank Professor de Meijere for a copy of the nmr spectrum of this compound.



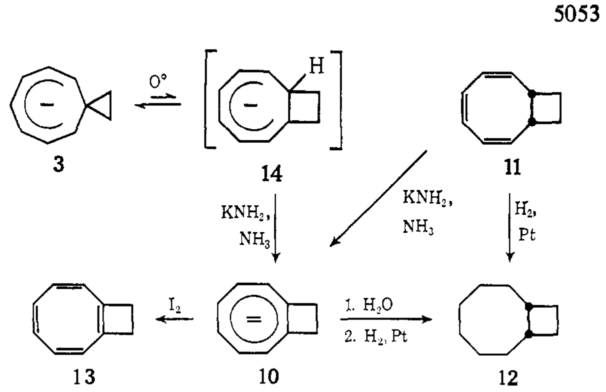
tion procedure given below.[8] Of particular interest is the fact that the major product is bicyclo[2.2.2]octa-2,5-diene (**7**), a useful compound formerly available only *via* multistep syntheses[9] but now obtainable in 30% yield in a single reaction sequence.

Anion **4** is clearly of limited kinetic stability since **5** suffers immediate cyclopropyl ring opening to afford ethylbenzene as the sole product upon treatment with potassium amide in liquid ammonia at temperatures as low as −65°. The initial product of opening, the β-phenethyl anion (**8**) could be observed by nmr spectroscopy [multiplet at δ 7.2 (5 H, aromatic), triplet at 2.84 (2 H, α methylene, J = 9.2 Hz), and triplet at −0.61 (2 H, β methylene)] upon treatment of **5** with butyllithium in THF–hexane at room temperature. Note that the relatively high-field position of the β-methylene protons of **8**[10] and the relatively narrow phenyl multiplet suggest that there is no significant bridging of the phenyl group in **8**.[11] Although **8** (or a precursor anion) is rapidly protonated in liquid ammonia, it can nevertheless be partially trapped with 1-chlorobutane in this medium to afford only **9** (in addition to ethylbenzene).

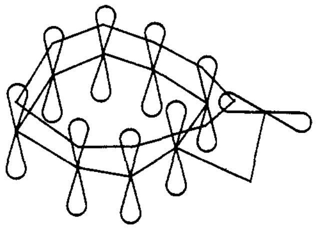


In contrast to the behavior of **4**, anion **3** is stable at −30°.[3] However, the nmr signals for **3** (in potassium amide–liquid ammonia) are slowly replaced by two sharp singlets at δ 5.58 and 3.30 (area ratio = 3:2) at *ca.* 0°; this process is complete within 5 min at 25°.

An anion (**10**) with an nmr spectrum identical with that of the new species is generated by treatment of *cis*-bicyclo[6.2.0]deca-2,4,6-triene[12] (**11**) with potassium amide in liquid ammonia. The fact that the bicyclic skeleton in **11** is retained in anion **10** is conclusively demonstrated by the further observations that (a) catalytic hydrogenation of the mixture of products obtained from quenching **10** with wet ether produced **12** as the major (92%) product, identical with a sample obtained by the catalytic hydrogenation of **11** and (b) **10** can be oxidized with iodine in pentane to afford **13**, identified by comparison of its nmr spectrum with published data.[13] We note in passing that the general sequence exemplified by the conversion of cyclooctatetraene to **13** *via* **11** represents a potentially useful synthesis of substituted cyclooctatetraenes.



The conversion of **3** to **10** is the first example of a 1,2 carbon to carbon migration of an alkyl group in a carbanion.[14] We suggest that this reaction occurs in two steps, an initial thermodynamically unfavorable isomerization to **14** followed by rapid deprotonation to the stable aromatic dianion **10**. Such 1,2 rearrangements are normally not expected to occur in a concerted manner with retention of configuration.[15] However, the conversion of **3** to **14**, if concerted, would be better described as a 1,8 migration *via* an "aromatic" array of nine orbitals containing ten electrons in the transition state (**15**).[16]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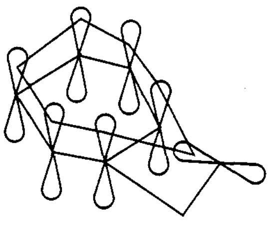
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The above mechanism provides a basis for understanding the contrasting reactivities of anions **3** and **4**. Thus, the analogous 1,2 (or 1,6) migration in **4** is topologically "forbidden" since it must occur *via* an "antiaromatic" array of eight π electrons (**16**). On the other hand, cleavage of the cyclopropyl ring in **4** generates an "aromatic" phenyl ring whereas the analogous cleavage in **3** would generate a potentially "antiaromatic" cyclooctatetraene ring.

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[8] Potassium amide in ammonia was added inversely (step 3) within 2 min and the reaction was quenched with water within an additional minute in order to minimize the isomerization of 5 to ethylbenzene. We have subsequently found that 5 can be more conveniently prepared by treatment of a mixture of the intermediate 2-chloroethylcyclohexadienes with excess lithium amide in liquid ammonia at *ca.* −65° for 0.5 hr.

[9] (a) C. A. Grob, H. Kny, and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957); (b) P. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelen, and T. Whitesides, *Tetrahedron Lett.*, 5117 (1968); (c) H. H. Westberg and H. J. Dauben, Jr., *ibid.*, 5123 (1968).

[10] The CH_2Li protons of n-butyllithium were observed at δ −0.97; *cf.* A. R. Lepley, *J. Amer. Chem. Soc.*, **91**, 1237 (1969).

[11] D. J. Cram, "Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 63–64. Also *cf.* ref 5c.

[12] S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **92**, 7612 (1970).

[13] J. A. Elix, M. V. Sargent, and F. Sondheimer, *ibid.*, **89**, 180 (1967).

[14] Benzyl migration has been observed in carbanions but this has been shown to be an intermolecular reaction; E. Grovenstein, Jr., and G. Wentworth, *ibid.*, **89**, 1852 (1967).

[15] See, *e.g.*, H. E. Zimmerman, *Accounts Chem. Res.*, **5**, 393 (1972), and references cited.

[16] Evidence for an isomerization of bicyclo[3.2.0]hepta-1,3-diene, which is topologically analogous to the reverse of our rearrangement, has recently been published; N. K. Hamer and M. E. Stubbs, *Tetrahedron Lett.*, 3531 (1972), and references cited therein. We consider a nonconcerted rearrangement of 3 to 14 *via* one of several conceivable ion pair transition states to be a somewhat less likely possibility.

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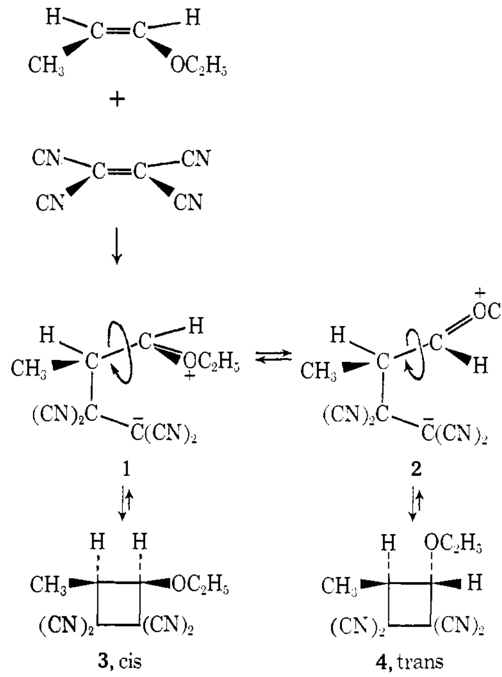
Nonstereospecificity in the [2 + 2] Cycloadditions of Tetracyanoethylene to Enol Ethers

Sir:

Concerted $[_{\pi}2_s + {}_{\pi}2_s]$ cycloadditions are forbidden by orbital symmetry.[1] This ban is bypassed by reactions occurring *via* biradicals[2] or zwitterions, as well as by the concerted process $[_{\pi}2_a + {}_{\pi}2_s]$.[1] Polycyanoolefin additions to electron-rich double bonds[3] are rated as a prototype of the mechanism with a zwitterionic intermediate,[4,5] though the evidence is still scant.

Proskow, *et al.*,[5] found the [2 + 2] cycloadditions of *cis*- and *trans*-1,2-bis(trifluoromethyl)-1,2-dicyanoethylene to ethyl vinyl ether highly stereospecific while those to *cis*- and *trans*-propenyl propyl ether were accompanied by loss of configuration at the dicyanoolefin component; allegedly, the stereochemistry of the propenyl ether bond was retained.[6] On reacting tetracyanoethylene (TCNE) with *cis*-anethole, Bartlett[7] observed a configuration loss which amounted to 10% in benzene and 49% in acetonitrile; *trans*-anethole reacted stereospecifically, and so did *cis*- and *trans*-3-ethylidene-1-methylcyclohexene.[7] The additions of fumaro- and maleonitrile to tetramethoxyethylene likewise proceed with retention, and stereospecificity was suggested as a criterion for distinguishing between the zwitterionic and the biradical paths.[8]

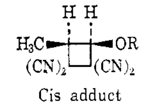
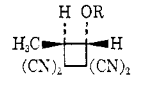
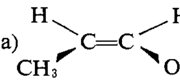
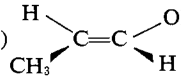


On treating *cis*-1-propenyl ethyl ether[9] (0.02 *M*) in benzene with 1.17 equiv of TCNE, adduct formation is quantitative in 8 hr; nmr analysis reveals 95% **3** and 5% **4**. Pure **3** and **4** were obtained by recrystallization of the products from the cis–trans isomeric enol ethers. Rotation of the assumed zwitterionic intermediate **1** starts to compete with the cyclization to give **3**. Though many zwitterion conformations are conceivable, discussing the steric course of cyclization requires only the cis and trans conformers **1** and **2**.

Table I shows more results for *cis*- and *trans*-propenyl alkyl ethers. All the adducts were characterized by elemental analysis and configurationally elucidated by nmr. The nonstereospecific portion of the cycloaddition increases with solvent polarity. In acetonitrile 14–16% trans adducts were obtained from *cis*-propenyl ethers, and 19–23% cis adducts from *trans*-propenyl ethers (in contrast to the results with *trans*-anethole[7]). The ratio of retention to inversion of olefin configuration corresponds to the ratio of cyclization to rotation in the assumed zwitterionic intermediate.[10]

Are the cis:trans adduct ratios kinetically controlled?

Table I. Steric Course of Cycloadditions of *cis*- and *trans*-Propenyl Alkyl Ethers (0.01–0.1 *M*) and TCNE (1.17 equiv) in Various Solvents at 20°; Percentages of Cis and Trans Adducts (±1%)

						
		Cis adduct			Trans adduct	
	R =					
Solvent	CH_3	C_2H_5	C_3H_7	CH_3	C_2H_5	C_3H_7
(a)  (cis) + $(CN)_2C{=}C(CN)_2$						
Benzene	95	95	96	5	5	4
Dichloromethane	94	95	95	6	5	5
Ethyl acetate	92	94	95	8	6	5
Acetone	91	92	91	9	8	9
Acetonitrile	84	85	86	16	15	14
(b)  (trans) + $(CN)_2C{=}C(CN)_2$						
Benzene	3	4	4	97	96	96
Dichloromethane	5	6	7	95	94	93
Ethyl acetate	9	10	9	91	90	91
Acetonitrile	20	23	19	80	77	81

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(1) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781, 847 (1969).

(2) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964); P. D. Bartlett and L. K. Montgomery, *ibid.*, **86**, 628 (1964).

(3) J. K. Williams, D. W. Wiley, and B. C. McKusick, *ibid.*, **84**, 2210 (1962).

(4) T. L. Cairns and B. C. McKusick, *Angew. Chem.*, **73**, 520 (1961); R. Huisgen, R. Grashey, and L. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, p 786; D. Seebach, "Methoden der Organischen Chemie," Vol. IV/4, Georg Thieme, Stuttgart, 1971, p 287.

(5) S. Proskow, H. E. Simmons, and T. L. Cairns, *J. Amer. Chem. Soc.*, **88**, 5254 (1966).

(6) The model is very demanding because the cycloadduct possesses four chiral centers which make eight racemates conceivable. The structural assignment[5] is not unequivocal in our opinion.

(7) P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970).

(8) R. W. Hoffmann, U. Bressel, J. Gehlhaus, and H. Häuser, *Chem. Ber.*, 104, 873 (1971).

(9) The cis and trans isomers were separated by preparative vpc (Apiezon L on siliceous earth) and used with >99% purity. They are thermostable under the experimental conditions.

(10) R. Huisgen and G. Steiner, *J. Amer. Chem. Soc.*, **95**, 5055 (1973).