nm). The excitation spectrum followed the absorption spectrum and was independent of monitoring wavelength. The onsets of absorption and emission coincided; the 0–0 bands were hardly discernible as weak shoulders. No phosphorescence was detected. No triplet epr signal was present after completed irradiation under conditions which easily permitted observation of the half-field triplet signal of ground-state triplets (triphenylene dianion).

Upon strong irradiation (λ >345 nm, 200-W Hg arc) the 373-nm band of the photoproduct was replaced by the uv absorption spectrum[20] of **4**. Conversion was virtually complete after 24 hr. After warm-up, glc analysis confirmed the presence of **4** (two columns, authentic sample[10]).

Melting (*ca.* −150°) of the glassy solution containing the photoproduct from **6** rapidly destroyed the 373-nm uv absorption band and the spectrum[4] of **2** appeared.

Based upon these data the photoproduct from **6** was assigned structure **1**. Further support was obtained by use of additional precursors. Irradiated glassy solutions of **4**,[21] **7**, **8**, and **9** (EPA, −196°, 254-nm light) contained a common species with a uv absorption spectrum as above, except that additional absorbing materials were present. A convincing proof that the photoproduct was the same as obtained from **6** was provided by the identity of emission and excitation spectra in all cases.

Transition energies and intensities calculated in the SCF–CI–PPP approximation using singly excited configurations[22] agreed well with the experimental spectrum. The Franck–Condon forbidden shape of the first band is in accordance with a substantial change of calculated bond orders upon excitation (toward regular hexagon).

Results of additional PPP calculations using up to 150 configurations[23] were similar, except that one of the higher energy transitions acquired partial doubly excited character (*cf.* ref 2) and became approximately degenerate with the first transition. Similar states have been calculated for other polyolefins[24] and probably observed in one case.[25] An observation of a predominantly doubly excited state has also been claimed.[15b]

Energy of vertical excitation from the lowest singlet state S_0 into T_1 calculated using the method and parameters of ref 26 is 8000 cm^{-1} compatible with ref 2 and our epr results indicating that **1** does not have a triplet ground state.[27] The triplet has been predicted[3] to slightly prefer a geometry with one CH_2 group twisted.[28] On the other hand, spectral shape and intensity of fluorescence indicate that S_1 is planar. According to calculations, planar S_1 and T_1 have the same orbital occupancy (HOMO → LUMO excitation) and **1** thus may be an example of the sought type of S_1–T_1 geometry differences.

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(20) M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, 80, 2255 (1958).

(21) G. Quinkert, M. Finke, J. Palmowski, and W.-W. Wiersdorff (*Mol. Photochem.*, 1, 433 (1969)) report that matrix photolysis of **4** produced no reaction.

(22) Methods as in J. Koutecký, J. Paldus, and R. Zahradník, *J. Chem. Phys.*, **36**, 3129 (1962), and in P. Hochmann, R. Zahradník, and V. Kvasnička, *Collect. Czech. Chem. Commun.*, **33**, 3478 (1968).

(23) For selection of configurations see J. Downing and J. Michl, *Int. J. Quantum Chem.*, **6S**, 311 (1972); J. Michl and J. Downing in "Excited State Calculations on Large Molecules," Proceedings of the 1972 Summer Research Conference on Theoretical Chemistry, Boulder, Col., June 1972, in press; J. Downing, J. Michl, P. Jorgensen, and E. W. Thulstrup, *Theor. Chim. Acta*, submitted for publication.

(24) J. Koutecký, *J. Chem. Phys.*, **47**, 1501 (1967); K. Schulten and M. Karplus, *Chem. Phys. Lett.*, **14**, 305 (1972).

(25) B. S. Hudson and B. E. Kohler, *Chem. Phys. Lett.*, **14**, 299 (1972).

(26) J. Pancír and R. Zahradník, *J. Phys. Chem.*, **77**, 107 (1973).

(27) Planar **1** in the T_1 state is calculated to distort to an almost regular hexagon. At this geometry, T_1 is predicted to be 5000 cm^{-1} above S_0. The calculated $T_1 \rightarrow T_x$ spectrum of the planar species does not agree with that observed.

(28) The absorption spectrum of the twisted triplet should resemble somewhat the spectrum of the benzyl radical: T. O. Meiggs, L. I. Grossweiner, and S. I. Miller, *J. Amer. Chem. Soc.*, **94**, 7981, 7986 (1972), and references therein. The observed spectrum is dissimilar.

(29) Alfred P. Sloan Foundation Fellow, 1971–1973.

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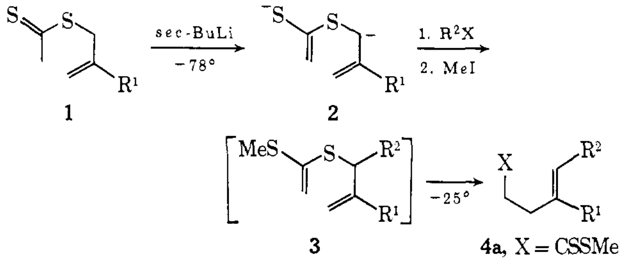
A Simple Stereoselective Version of the Dithio Ester Thio-Claisen Rearrangement Leading to *E*-Trisubstituted Olefinic Bonds

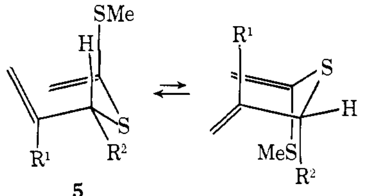
Sir:

We wish to disclose a version of the dithio ester thio-Claisen rearrangement which is highly stereoselective and can be applied to the synthesis of *E*-trisubstituted double bonds as they appear in many natural products. The method simply involves treatment of the dithio ester **1** with 2 equiv of *sec*-butyllithium followed by successive addition of an alkyl halide and methyl iodide. Evidently a dianion **2** was first formed, which, on stepwise alkylation followed by thio-Claisen rearrangement, affords the dithio ester **4a** *via* the ketene thioacetal **3**.



4a, X = CSSMe
b, X = COOEt

As compared with the current processes for the preparation of the γ,δ-unsaturated acids,[1] this route provides a convenient and versatile method for the introduction of a five-carbon chain terminating in a carboxyl function starting with a simple halide, and the stereoselectivity is also very high. The rigorous stereoselectivity is probably attributable to nonbonding interaction between the thiomethyl and R² groups (**5′**) that



5 **5′**

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(1) (a) Ortho ester process: W. S. Johnson, L. Werthemann, W. R. Bartlett, T. J. Brocksom, T. T. Li, D. J. Faulkner, and M. R. Petersen, *J. Amer. Chem. Soc.*, **92**, 741 (1970); (b) enol ester rearrangement: R. E. Ireland and R. H. Mueller, *ibid.*, **94**, 5897 (1972); see also J. E. Baldwin and J. A. Walker, *J. Chem. Soc., Chem. Commun.*, 117 (1973).

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 ($\epsilon_{220\,nm}$ 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 ($\epsilon_{220\,nm}$ 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).