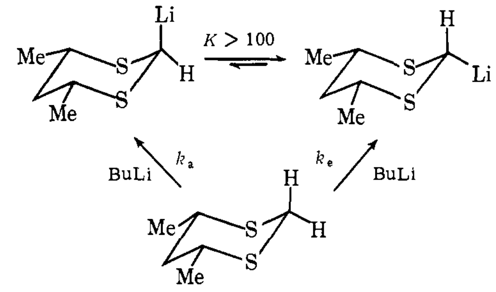
Kinetic Preference between Equatorial and Axial Hydrogens in the Lithiation of Conformationally Fixed 1,3-Dithianes

Sir:

In a previous communication[1] we have reported a *thermodynamic* preference by a factor of over 100 for the equatorial position in the lithium derivative of a conformationally fixed 1,3-dithiane (Scheme I, top line). While the original experiments were carried out in tetrahydrofuran solvent, we have since obtained the same result in 1,2-dimethoxyethane (DME); the thermodynamic preference for the equatorial position thus seems to be that of the carbanion partner of a (contact or solvent-separated) ion pair rather than of a covalent organometallic compound.[2,3] In view of other recent reports[4] on *kinetic* preferences in abstraction of diastereotopic hydrogens, we felt it desirable to establish the kinetic preference in the system shown in Scheme I.

Scheme I



To this end we have treated the stereospecifically deuterated compounds **1** and **2** (Scheme II) with butyllithium[5,6] in tetrahydrofuran followed by methyl iodide.[1] The *r*-2,*c*-4,*c*-6-trimethyl-1,3-dithianes (**3**) obtained thus were purified by gas chromatography and submitted to mass spectral analysis.

Scheme II

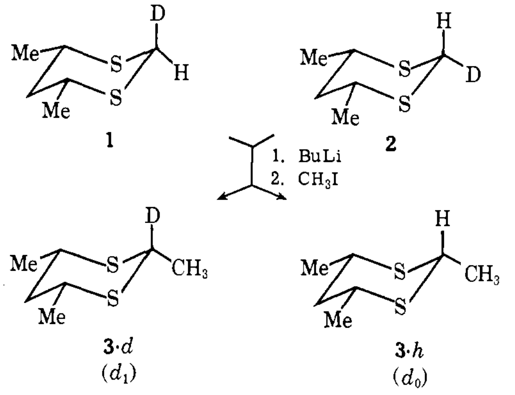


Table I shows the deuterium content of the trimethyl compounds from four different experiments using both **1** and **2** as starting material in each. Also indicated in Table I are the isotope effects[7] (IE) and the ratios k_e/k_a (*cf.* Scheme I) calculated from the mass spectrometric data assuming[8] that the observed ratio of equatorial to axial H or D abstraction (Table I) is equal to $k_e\text{IE}/k_a$ when the starting material is **1** and $k_e/k_a\text{IE}$ when the starting material is **2**.

Table I. Mass Spectrometric Results[a] and Conclusions

Run	Starting material[b]	Product **3** d_0, %	Product **3** d_1, %	k_e/k_a	IE
1	**1**	3.2	96.8		
	2	84.3	15.7	12.9	2.41
2	**1**	4.4	95.6		
	2	73.5	26.5	9.9	3.73
3	**1**	6.8	93.2		
	2	74.85	25.15	7.3	2.55
4	**1**	6.42	93.58		
	2	77.2	22.7	8.5	2.57

[a] Runs 2–4 were analyzed (on a MS-9 instrument) at 12 V; pure **3**-*h* showed no P − 1 peak under these conditions. Run 1 was analyzed at 30 V with a correction being made for the (small) P − 1. [b] The starting materials for runs 2 and 3 had the following isotopic purity: **1**, 98.2%, **2**, 97%; in run 4 the purities were **1**, 97.86%, **2**, 97.4%. (These percentage figures refer to d_1; balance is d_0.) In run 1, isotopic purity was monitored by nmr only and was 98% for **2** but only 71% for **1** which contained a considerable amount of d_2 contaminant. Cross contamination of **1** and **2** was less than 1% (by nmr).

If one rejects the extreme values for k_e/k_a and IE in Table I one obtains $k_e/k_a = 8.6 \pm 1.3$ and IE $= 2.5 \pm 0.1$.[9] The relatively small ratio of k_e/k_a shows that the kinetic stereoselectivity for the lithiation is considerably less than the thermodynamic stereoselectivity;[10] while this result is somewhat disappointing if one looks for chemical reactions of high kinetic stereoselectivity,[11] it cannot be considered surprising since in the reaction of a very strong base (BuLi) to give a less strong base (the 2-lithio-1,3-dithiane) one would expect relatively little proton transfer at the transition state, *i.e.*, the transition state resembles the starting materials rather than the products.[12] This is also emphasized by the relatively low isotope effect. Evidently the equatorial lithium

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(1) A. A. Hartmann and E. L. Eliel, *J. Amer. Chem. Soc.*, **93**, 2572 (1971).

(2) *Cf.* T. E. Hogen-Esch and J. Smid, *ibid.*, **88**, 307 (1966), regarding the 9-fluorenyl anion. It is not entirely certain, however, that because the 9-fluorenyl anion forms a solvent-separated ion pair with DME, the same will necessarily be true for the much more basic 2-dithianyl anion.

(3) For a possible explanation, see S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972).

(4) G. Barbarella, A. Garbesi, and A. Fava, *Helv. Chim. Acta*, **54**, 341, 2297 (1971). The implication here is for an essentially infinite preference for one pair of α hydrogens over the other (diastereotopic) pair in base-catalyzed H–D exchange of tetrahydrothiophene methyl sulfonium hydroxide. In repeating this experiment (O. Hofer, unpublished observations) we find a preference by a factor of 30.

(5) We have assumed in this communication, so far without direct proof, that the protonation and alkylation reactions of the 2-dithianyllithium compounds proceed with retention rather than inversion of configuration. This assumption is implicit in Schemes I and II.

(6) Compounds 1 and 2 were prepared as described in ref 1 except that the 2,2-dideuterio-*cis*-4,6-dimethyldithiane required for the preparation of 1 was obtained rather conveniently by an exchange of the 2-lithio compound (Scheme I) with excess dimethyl-d_6 sulfoxide.

(7) We have assumed that the isotope effects for the axial and equatorial positions are the same. This assumption is not highly critical: for $(\text{IE})_a = {}^1/_2(\text{IE})_e$, $k_e/k_a = 12.1$; for $(\text{IE})_a = 2(\text{IE})_e$, $k_e/k_a = 0.05$.

(8) *Cf.* D. Y. Curtin and D. B. Kellom, *J. Amer. Chem. Soc.*, **75**, 6011 (1953).

(9) The different results reported elsewhere on the basis of run 1 only (E. L. Eliel, *Pure Appl. Chem. Suppl.*, 7, 219 (1971)) were based on a misinterpretation of the data.

(10) Dr. S. Wolfe (personal communication) has suggested we point out that, because of this noncorrespondence, it is no longer permissible to compare experimentally determined kinetic preferences in abstraction of diastereotopic protons with data calculated theoretically on the basis of the stability of the resulting ions (ref 3).

(11) Higher kinetic stereoselectivity is found in the case referred to in ref 4; much higher selectivity has been reported by R. R. Fraser and F. J. Schuber, *Chem. Commun.*, 397 (1969), in a sulfoxide derived from a diphenyl system.

(12) *Cf.* J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 241.

compound (Scheme I) is, to an appreciable extent, formed by carbanion inversion of an axial lithium compound following the initial kinetically controlled lithiation.

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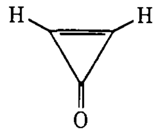
The Isolation and Characterization of Pure Cyclopropenone

Sir:

Cyclopropenone (**1**) is one of the simplest possible



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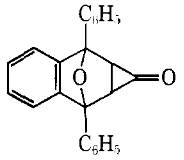
organic compounds, and it is a substance of great theoretical interest. Many stable derivatives of this system have been prepared and explored over the past few years,[1] and we have reported[2,3] the preparation of solutions of parent cyclopropenone and some characterization of the chemistry of this compound. However, there are many purposes for which only the pure isolated substance would be suitable. We now wish to describe the preparation and isolation of pure recrystallized cyclopropenone and some further chemical and physical characterizations of this compound.

The synthesis follows the general sequence we have already described.[2,3] Thus, treatment of 16.3 g of tetrachlorocyclopropene in 150 ml of purified paraffin oil with 69.5 g of tri-*n*-butyltin hydride under argon for 1 hr, followed by collection of the volatile products, affords 7.65–8.25 g of a colorless liquid consisting of 85% of dichlorocyclopropenes, 7–8% of 3-chlorocyclopropene, and 6–8% of trichlorocyclopropenes. This mixture was stirred at 0° for 3 hr with 60 ml of CH_2Cl_2 and 6.0 ml of water. Then 10 g of $NaHCO_3$ was added cautiously, followed by 70 g of Na_2SO_4. The solution was separated at 0° and dried with an additional portion of anhydrous Na_2SO_4, and the solvent was carefully removed at reduced pressure. The residue was distilled at 0.45 Torr, yielding 2.98–3.35 g of colorless cyclopropenone, bp 30° (0.45 Torr). The only impurity is *ca.* 5% of dichloroacrolein which can be removed by recrystallizing the cyclopropenone from 5 ml of dry ether at −78°. The overall yield of purified cyclopropenone, showing no trace of impurities in the nmr, is 2.01–2.26 g (41–46% overall from tetrachloropropene), mp −29 to −28°, *m/e* 54.0107 (calcd 54.0105).

Pure cyclopropenone is stable at least over many weeks below its melting point, but on standing at room temperature it is converted to an insoluble polymer with infrared absorption at 1750 cm^{-1}. Polymerization is very rapid on heating of the neat liquid to 80°, but solutions in organic solvents are stable at room temperature. The spectra of purified cyclopropenone are similar to those we have reported[2,3] for the solutions previously, but in the ultraviolet spectrum we can now identify a band at 276 nm (ϵ 31) as the $n-\pi^*$ transition, while the $\pi-\pi^*$ maximum occurs below 190 nm.[4] On protonation of cyclopropenone in strong acid the nmr coupling constants change, going from $J_{^{13}C-H} = 217 \pm 1$ and $J_{H-H} = 3.9 \pm 0.1$ Hz in $CDCl_3$ to $J_{^{13}C-H} = 250 \pm 1$ and $J_{H-H} = 1.3 \pm 0.1$ Hz in concentrated H_2SO_4. Observing these coupling constants in aqueous sulfuric acid of intermediate concentrations, and assuming the validity of H_0 for these compounds, we deduce a pK_{BH^+} of -5.2 ± 0.3 for cyclopropenone.[5]

On catalytic hydrogenation of cyclopropenone in tetralin with platinum the only detectable product is acetone, produced along with recovered cyclopropenone if the hydrogenation is stopped partway. With 1,3-diphenylisobenzofuran, cyclopropenone reacts quantitatively at room temperature to form an adduct **2**, mp 151–153°, *m/e* 324, with infrared bands at 1875 and 1815 cm^{-1} and an nmr singlet at δ 2.75 in addition to the aromatic protons. This singlet shows $J_{^{13}C-H} = 173 \pm 1$ and $J_{H-H} = 9.0 \pm 0.2$ Hz. A similar cyclopropanone is formed on reaction of cyclopropenone with 9,10-dimethylanthracene, affording compound **3**, *m/e* 260. Again the infrared spectrum is characteristic, with bands at 1838 and 1802 cm^{-1}, and the cyclopropane protons are found at δ 2.17 in the nmr. Both **2** and **3** form hemiketals on treatment with methanol. Treatment of cyclopropenone with diphenyldiazomethane in methylene chloride affords a 28% yield of the unusual diazo ketone **4**, by cycloaddition to the carbon–carbon double bond and opening of the rings. **4** shows the expected infrared bands at 2096 and 1628 cm^{-1} and on treatment with HCl it is converted to **5**, mp 109–110°, identified by characteristic mass, nmr, infrared, and uv spectra.



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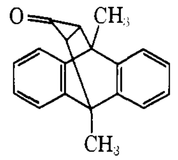

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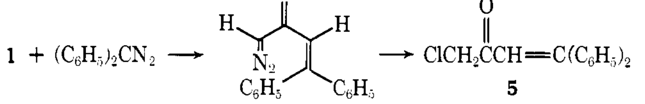

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[1] Diphenylcyclopropenone: R. Breslow, R. Haynie, and J. Mirra, *J. Amer. Chem. Soc.*, **81**, 247 (1959); R. Breslow, J. Posner, and A. Krebs, *ibid.*, **85**, 234 (1963); R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1320 (1965). Dialkylcyclopropenones: R. Breslow and R. Peterson, *ibid.*, **82**, 4426 (1960); R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, T. Murata, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1326 (1965). Methylcyclopropenone: R. Breslow and L. J. Altman, *ibid.*, **88**, 504 (1966).

[2] R. Breslow and G. Ryan, *ibid.*, **89**, 3073 (1967).

[3] R. Breslow, G. Ryan, and J. T. Groves, *ibid.*, **92**, 988 (1970).

[4] These findings are consistent with the results of preliminary gas-phase electron impact studies on **1** by M. Robin of Bell Laboratories.

[5] *Cf.* values[1] of −2.3 for dimethylcyclopropenone and −3.5 for methylcyclopropenone.