elimination, completely predominates, even though concerted migration of bond "b" is possible.

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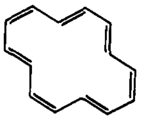
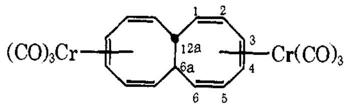
Reaction of [14]Annulene with Tricarbonyltriamminechromium(0). Synthesis and Structure of Hexacarbonyl-*trans*-6a,12a-dihydrooctalenedichromium(0)[1]

Sir:

Although organometallic complexes of cyclobutadiene, benzene, and cyclooctatetraene are well known, it has previously not been possible to prepare such complexes from the higher annulenes.[2] We now report the synthesis and structure determination of a carbonylchromium complex obtained from [14]annulene (**1**).[3] This substance has been shown to possess the hexacarbonyl-*trans*-6a,12a-dihydrooctalenedichromium(0) structure **2**, formally derived from *trans*-6a,12a-dihydrooctalene (**3**), a bicyclic valence isomer of [14]annulene.



1



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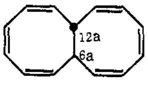

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A solution of [14]annulene (27 mg) in hexane (15 ml) was boiled under reflux with tricarbonyltriamminechromium(0) $[(NH_3)_3Cr(CO)_3]$[4] (300 mg) for 33 hr under nitrogen. Crystals of the complex **2** separated on the walls of the vessel, and one of these was used for the X-ray structure determination. The bulk of the complex **2** was isolated by evaporation, chromatography in benzene on Kieselgel (10 g), rapid elution with hexane–benzene (1:1), and finally crystallization from hexane–benzene. This procedure led to **2** (6 mg, ~10%) as reasonably stable bright red crystals, which decomposed on attempted melting point determination: mass spectrum, m/e 454 $[C_{14}H_{14}Cr_2(CO)_6]$; ultraviolet spectrum, $\lambda_{\max}^{\mathrm{EtOH}}$ 230 sh (relative optical density, 1.00),[5] 283 (0.39), and 352 nm (0.36); $\lambda_{\max}^{\mathrm{benzene}}$ 354 nm (ϵ 9100); infrared spectrum (KBr), strong CO bands at 1955, 1895, and 1880 cm^{-1}.

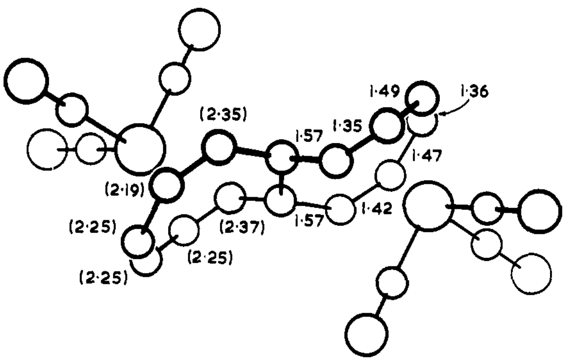

Figure 1. The molecular stereochemistry of hexacarbonyl-*trans*-6a,12a-dihydrooctalenedichromium(0) (**2**). The numbers in parentheses refer to C–Cr bond lengths (in ångströms), and the others to C–C bond lengths (in ångströms).

The nmr spectrum of **2** ($CDCl_3$, 100 MHz), using a time-averaged computer, showed singlets at τ 3.88 and 4.38 due to [14]annulene,[3] formed during determination of the spectrum (see below); in addition, the spectrum exhibited multiplets at τ 3.75–4.3, 4.7–4.95, 5.05–5.3, and 5.45–5.7 (olefinic protons of **2**), as well as at τ 6.3–6.8 (methine protons of **2**).

It is interesting that [14]annulene was regenerated when solutions of **2** in ether, ethyl alcohol, benzene, or deuteriochloroform were allowed to stand at room temperature. The reaction could be followed conveniently by the typical change of the ultraviolet spectrum, and in ether was complete after ~24 hr. Evidently, *trans*-6a,12a-dihydrooctalene (**3**) is thermodynamically less stable than [14]annulene (**1**), and is transformed to this valence isomer.

The structure of the complex **2** was established by an X-ray crystallographic analysis. It crystallizes in the space group $P\bar{1}$, with a = 11.334, b = 7.101, and c = 9.674 Å, α = 102.10, β = 135.51, and γ = 100.14°, and Z = 1. The crystals gave relatively weak diffraction spectra, but 693 independent reflections with $F_{\mathrm{obsd}}{}^2/\sigma(F_{\mathrm{obsd}}{}^2) \geqslant 1.0$ ($\sin\theta_{\max}/\lambda = 0.45$) have been observed by automatic four-circle diffractometer methods (Mo Kα). The structural analysis was based on conventional Fourier and full-matrix least-squares methods, the molecular stereochemistry being shown in Figure 1 [present unweighted discrepancy index, R = 0.12; esd's in bond lengths average 0.02 (Cr–C) and 0.04 Å (C–C and C–O)].

The complex **2** has exact C_i symmetry in the crystal. Each tricarbonylchromium fragment is seen to be bonded to a triene group, the isomerization of [14]annulene to a bicyclic hexaene being dictated by the charge requirements of the metal (18-electron "rule"). Apart from the bond C(6a)–C(12a), which has a length of 1.32 Å (σ = 0.06 Å), carbon-carbon bond lengths are close to ones which could be predicted from related systems.[6] The shortness of C(6a)–C(12a) is largely due to inadequate resolution in the X-ray data, since this cannot be a double bond in view of the mass spectral data, the regeneration of [14]annulene from the complex, and the general stereochemistry of C(6a) and C(12a). Chromium-carbon bond lengths to C(2), C(3), C(4),

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(1) Unsaturated Macrocyclic Compounds. LXXXI. For part LXXX, see F. Sondheimer, *Accounts Chem. Res.*, submitted for publication.

(2) For instance, no complexes could be isolated when [14]annulene or [18]annulene was treated with hexacarbonylchromium(0 thermally or photochemically (E. P. Woo and K. Stöckel, unpublished experiments from these laboratories). On the other hand, carbonylchromium and carbonylmolybdenum complexes of 1,6-methano[10]annulene have been synthesized [E. O. Fischer, H. Rühle, E. Vogel, and W. Grimme, *Angew. Chem.*, **78**, 548 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 518 (1966); P. E. Baikie and O. S. Mills, *J. Chem. Soc. A*, 328 (1969); P. F. Lindley and O. S. Mills, *ibid.*, 1286 (1969)], as well as a carbonylchromium complex of *anti*-1,6:8,13-bismethano[14]annulene [E. Vogel, personal communication; M. J. Barrow and O. S. Mills, *Chem. Commun.*, 220 (1971)].

(3) See F. Sondheimer, *Proc. Roy. Soc., Ser. A*, **297**, 173 (1967).

(4) W. Hieber, W. Abeck, and H. K. Platzer, *Z. Anorg. Allg. Chem.*, **280**, 252 (1955).

(5) Accurate ϵ values could not be obtained in ethyl alcohol, due to the low solubility of **2** in this solvent.

(6) See M. R. Churchill and R. Mason, *Advan. Organometal. Chem.*, **5**, 93 (1967).

and C(5) average 2.24 Å, while, for what may be largely steric reasons, they average 2.36 Å for the bonds Cr–C(1) and Cr–C(6).

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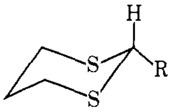
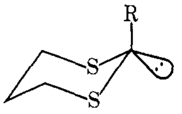
Protonation and Methylation of Conformationally Fixed 2-Lithio-1,3-dithianes. Some Reactions of Remarkable Stereoselectivity

Sir:

Corey and Seebach[1] have studied the deuteration of 2-lithio-1,3-dithiane and Oae and coworkers[2] have compared the rate of base-catalyzed H–D exchange in 1,3-dithianes with that in other dithioacetals. The latter investigators[2] have drawn attention to the finding that, whereas 1,3-dithiane (**1**) exchanges 5.35 times as fast as the acyclic analog diethylthioformal, $H_2C(SC_2H_5)_2$, the (much slower) exchanges of the ethyl compounds **2** and $C_2H_5CH(SC_2H_5)_2$ proceed at nearly the same rate. These observations, and related ones, were rationalized by assuming a favored orientation of the carbanion involved in the exchange with respect to the adjacent C–S segment. In the cyclic compound, it appears that only the equatorial lobe (*cf.* **3**) can assume such a favored orientation and that therefore the 2-ethyl-1,3-dithiane (**2**), which is conformationally biased (anancomeric[3]) with the ethyl group equatorial cannot readily lead to a carbanion stabilized in this way, the unfavorable energy forcing the ethyl into the axial position being about 1.5 kcal/mol.[4]



1, R = H
2, R = C_2H_5



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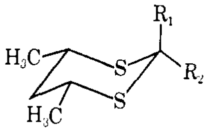
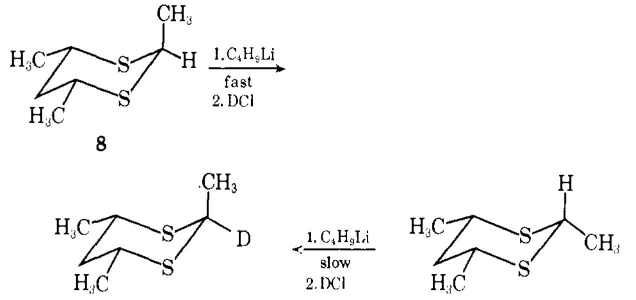


4, $R_1 = R_2 = H$
5, $R_1 = H; R_2 = D$
6, $R_1 = R_2 = D$
7, $R_1 = D; R_2 = H$

$$\mathbf{4}, \xrightarrow{\text{RLi}} \mathbf{3}\text{-Li}, R = H\ (?) \xrightarrow{\text{DCl}} \mathbf{5}$$
$$\mathbf{6}, \xrightarrow{\text{RLi}} \mathbf{3}\text{-Li}, R = D\ (?) \xrightarrow{\text{HCl}} \mathbf{7}$$

Having at our disposal 1,3-dithianes whose conformations are fixed by equatorial methyl groups at C-4 and C-6,[4] we decided to study protonation and alkylation reactions of the lithium salts of such compounds. The results were quite startling. When the lithium derivative of *cis*-4,6-dimethyl-1,3-dithiane (**4**) was treated with DCl, *virtually stereoisomerically pure r*-2-deuterio-*cis*-4,*cis*-6-1,3-dithiane (**5**)[5] was obtained, as evidenced by nmr spectroscopy.[6] In contrast, treatment of the lithium salt of 2,2-dideuterio-*cis*-4,6-dimethyl-1,3-dithiane (**6**) with HCl gave the diastereoisomeric *r*-2-deuterio-*trans*-4,*trans*-6-dimethyl-1,3-dithiane (**7**) in nearly stereochemically pure form. Comparison of the nmr spectra of synthetic mixtures of **5** and **7** with those of samples obtained in the decomposition of the lithium salts with acid suggested that a cross-contamination of about 1% could be clearly detected in the nmr spectrum and that the diastereomeric purity of **5** and **7** as originally obtained must have been at least 99%, probably in excess of 99.5%.

The deuteration of the lithium salts of the 2-methyl-*cis*-4,6-dimethyl-1,3-dithianes **8** and **9** was studied also. Compound **8** appeared to be converted to its lithium salt relatively rapidly; quenching with DCl after treatment of **8** with BuLi in ether at −25° for 2.5 hr led to 80% deuteration; *i.e.*, the product was a mixture of 80% **10** and 20% of undeuterated **8** as shown by nmr. No **9** (or **9**-*d*) was formed, according to gas chromatography. In contrast, lithiation of **9** proceeded sluggishly requiring 24 hr at −22° to give 75% of deuterated product after quenching with DCl. (Only 31% lithiation—as evidenced by subsequent H–D exchange—occurred after 4 hr at −20°.) It is significant that lithiation followed by deuteration of **9** produced, as the exclusive deuterated product, the trans (axial) isomer **10**, which was isolated gas chromatographically and was examined for its deuterium content by both nmr and mass spectrometry. On the other hand, recovered cis isomer **9** was devoid of deuterium as shown mass spectrometrically;[7] *i.e.*, it had never passed through the lithium salt. One may conclude from these two experi-



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[1] E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1075, 1077 (1965); D. Seebach, *Synthesis*, 17 (1969).

[2] S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, **20**, 427 (1964); Y. Yano and S. Oae, *Mech. React. Sulfur Compounds*, **4**, 167 (1969).

[3] M. Anteunis, D. Tavernier, and F. Borremans, *Bull. Soc. Chim. Belg.*, **75**, 396 (1966).

[4] E. L. Eliel and R. O. Hutchins, *J. Amer. Chem. Soc.*, **91**, 2703 (1969).

[5] For nomenclature, see *J. Org. Chem.*, **35**, 2849 (1970).

[6] The AB system for **4** with calculated chemical shifts of 3.41 and 4.03 ppm (J = 14 Hz) (the upfield peaks are broadened) is replaced in **5** by a triplet, ν = 3.97 ppm, J = 2.25 Hz, and in **7** by a slightly broadened triplet, ν = 3.43 ppm. From previous experience (ref 4) the higher field peak may be assigned to the equatorial proton at C-2; it might be noted that the high-field proton in both **4** and **7** is broadened by long-range 1–5 coupling with the equatorial proton at C-5 (zig-zag coupling). In blown-up spectra of **5** and **7**, contamination with **4** (AB pattern, about 1–2%) can be clearly seen, but no cross-contamination of **5** by **7** and *vice versa* is evident. Spectra were recorded on Varian A-60A and XL-100 instruments.

[7] The mass spectra of **8** and **9** show negligible (<0.7%) parent − 1 peaks. Analysis was therefore effected using the various parent, ^{13}C, ^{33}S, and ^{34}S satellite peaks at *m/e* 162, 163, 164, and 165 in **8** and **9**, and the corresponding peaks, shifted by one mass number, and assumed to be of the same relative intensity and sensitivity, in **10**. Lithiation followed by DCl treatment of **9** produced **10** of about 98% isotopic purity.