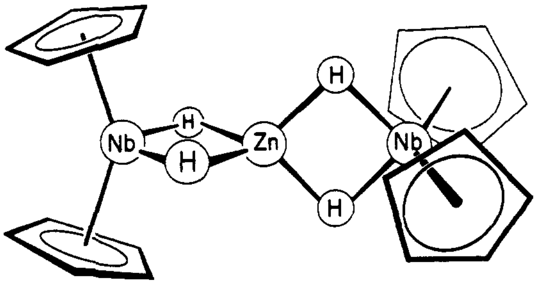

Figure 3. The proposed structure of $[(C_5H_5)_2NbH_2]_2Zn$ (7).

$$Cp_2NbH_3 \xrightarrow[-C_2H_6]{Et_3Al} \underset{\mathbf{6}}{Cp_2NbH_2AlEt_2} \qquad (5)$$

$$2Cp_2NbH_3 \xrightarrow[-2C_2H_6]{Et_2Zn} \underset{\mathbf{7}}{(Cp_2NbH_2)_2Zn} \qquad (6)$$

$$Cp_2MH_3 \xrightarrow[-PhCH_3]{(PhCH_2)_4Hf} Cp_2MH_2Hf(CH_2Ph)_3 \qquad (7)$$

$$M = Nb \text{ or } Ta$$

Nmr data (25 to −50°) for these compounds require location of the group IIb, IIIa, or IVb metal on the twofold axis of the Cp_2MH_2 moiety. The proposed structure for **7** is presented in Figure 3.

Catalysis of olefin reactions by group IVb complexes is often promoted by Lewis acids. It is of interest to determine the effect of Et_3Al on the ethylene reaction with a group V complex[5]

$$Cp_2Nb(C_2H_4)H \xrightarrow{C_2H_4} Cp_2Nb(C_2H_4)C_2H_5 \qquad (8)$$

Under conditions (45°, $P\ C_2H_4 \simeq 5$ atm) where reaction 8 proceeds to 35% completion, ethylene is unreactive with $Cp_2Nb(C_2H_4)HAlEt_3$. Triethylaluminum *deactivates* the hydride ligand toward the ethylene insertion reaction. Investigation of the effects of Lewis acids on other transition metal hydride reactions is in progress.

Acknowledgment. I thank Drs. E. L. Muetterties and G. W. Parshall for helpful discussions, Jean V. Carrier for C and H determinations, Flora C. Youngken and James J. Skowkowski for cryscopic molecular weight determinations, L. J. Rizzardi for most of the nmr spectra, and W. N. Cawthray for experimental assistance.

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Received May 9, 1973

Bis Deprotonation of Bridged Bicyclic Sulfones. Electronic Interactions in Rigid Bridgehead α-Sulfonyl Dicarbanions as a Function of Carbon Framework Unsaturation[1]

Sir:

Conformationally constrained cyclic α-sulfonyl carbanions do not share with their acyclic counterparts the intrinsic ability to maintain configurational stability owing to an enhanced propensity for symmetrization *via* effectively planar conformations.[2] Bridgehead α-sulfonyl carbanions[3] have no such capability and furthermore may be viewed as essentially pyramidal intermediates with the carbon lone pair orbital directed along the bisector of the OSO angle. LCAO–MO–SCF calculations have shown this particular alignment to be the most stable of a number of conformations examined.[4] In this connection, the recent availability of variously unsaturated derivatives of 9-thiabicyclo[4.2.1]nonane 9,9-dioxide (**1**) such as **2**–**5**[5–7] has attracted our attention not only as valuable synthetic intermediates[5a,b,8] but also as possible sources of interesting stereochemically rigid α-sulfonyl dicarbanions. Herein we detail the unique electronic interactions which operate upon bis deprotonation of these bridged bicyclic sulfones.

Preliminary information on the capability of **1**–**5** for dianion formation and the inherent stability of these species was gained by adding *n*-butyllithium in pentane (25% excess) to 0.1 *M* solutions of these sulfones in anhydrous tetrahydrofuran cooled to −70° under a dry nitrogen atmosphere. A large excess of DOAc (>95% isotopic purity) was subsequently introduced and the sulfone recovered by silica gel chromatography.[9] The results, summarized in Table I, reveal three points of major significance: (a) generation of $\mathbf{1}^{2-}$ is comparatively sluggish (moderate level of exchange after 60 min), (b) $\mathbf{4}^{2-}$ is relatively unstable; and (c) $\mathbf{5}^{2-}$ is exceptionally highly colored, the intense purple hue being independent of the method of dianion generation.[10]

Comparable experiments, but with substitution of methyl iodide for the DOAc, led exclusively to 1,6-dimethyl sulfones.[11] Yields of the dimethyl products ran as follows: **1** (91%), **2** (88%), **3** (80%), **4** (50%), **5** (95%). No evidence was gained for the formation of monomethylated sulfones.

From the available data, it is apparent that in the dianions generated from **2**–**5** there are transitions of sufficiently low energy as to be observed in the visible region of the electronic spectrum. To rationalize this we have carried out semiempirical calculations of the extended Hückel (EH) type.[12–14] Based on

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[1] Unsaturated Heterocyclic Systems. XCII. The preceding paper in this series is L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *J. Amer. Chem. Soc.*, **95**, 4647 (1973).

[2] (a) E. J. Corey, H. König, and T. H. Lowry, *Tetrahedron Lett.*, 515 (1962); (b) D. J. Cram and T. A. Whitney, *J. Amer. Chem. Soc.*, **89**, 4651 (1967); (c) L. A. Paquette, J. P. Freeman, and M. J. Wyvratt, *ibid.*, **93**, 3216 (1971).

[3] (a) W. von E. Doering and L. K. Levy, *ibid.*, 77, 509 (1955); (b) L. A. Paquette and R. W. Houser, *ibid.*, 91, 3870 (1969); (c) E. J. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969).

[4] S. Wolfe, A. Rauk, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, **91**, 1568 (1969).

[5] (a) L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *ibid.*, **93**, 1048 (1971); (b) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *ibid.*, **95**, 2230 (1973); (c) J. Gasteiger and R. Huisgen, **94**, 6541 (1972).

[6] W. L. Mock, *ibid.*, **92**, 3807 (1970).

[7] E. D. Weil, K. J. Smith, and R. J. Gruber, *J. Org. Chem.*, 31, 1669 (1966).

[8] L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 9224 (1972).

[9] Suitable control experiments established that the integrity of the isotopic purity was maintained during the chromatographic purification. Furthermore, the sulfones could be recovered quantitatively by this technique.

[10] Other base–solvent systems examined include potassium *tert*-butoxide in dimethyl sulfoxide or tetrahydrofuran (25°).

[11] All new compounds gave acceptable (±0.3%) combustion data and compatible spectra.

[12] The Slater exponents and ionization potentials were those reported in the literature[13] except in the case of H for which a Slater ex-

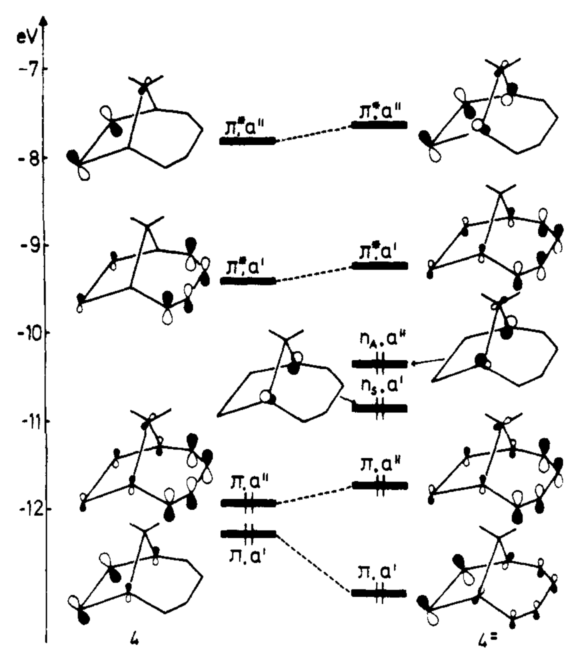


Figure 1. Partial correlation diagrams of **5** (left) and $\mathbf{5}^{2-}$.

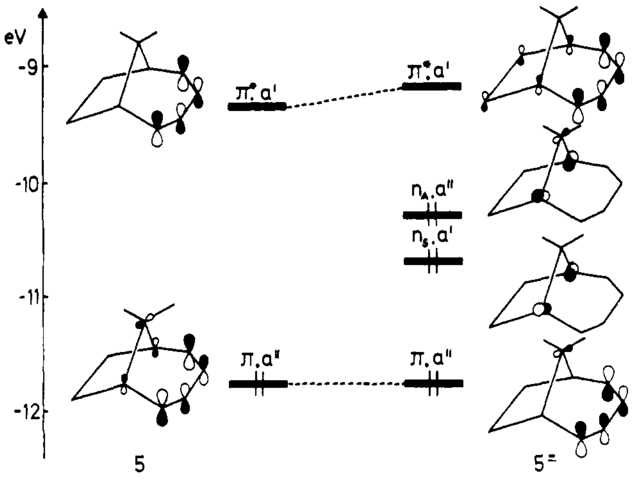
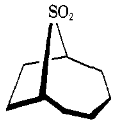
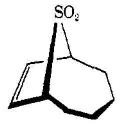
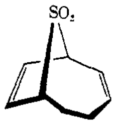
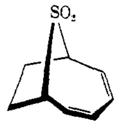
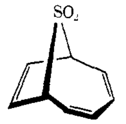


Figure 2. Partial correlation diagrams of **4** (left) and $\mathbf{4}^{2-}$.

Table I. Results of Deuteration Experiments

Sulfone	X, min^a	Y, min^b	Color of solution	Yield of recovered sulfone, %	d_2,^{c} %
 **1**	2	60	Colorless	98	79
 **2**	2	6	Yellow	90	91
	2	60	Yellow	99	94
 **3**	2	6	Yellow	96	86
	2	60	Yellow	96	93
 **4**	1	1	Yellow-greenish	34	90–95
	2	1	Yellow-greenish	27	
	2	9	Yellow-green-brown	0	
 **5**	2	6	Deep purple	68	90–95
	2	60	Deep purple	68	90–95

[a] The time utilized for addition of the *n*-butyllithium solution. [b] The time allowed to elapse during stirring of the dianion solutions at −70° before addition of excess DOAc. [c] Deuterium analyses were performed by nmr and the percentage figure therefore represents an average value of d_0, d_1, and d_2. All experiments were conducted in duplicate, and good reproducibility was observed.

these calculations, Figures 1 and 2 show correlation diagrams of the highest occupied and lowest unoccupied orbitals of **4** and $\mathbf{4}^{2-}$ and **5** and $\mathbf{5}^{2-}$. The energy level scheme for **5** reveals little interaction between the ethylene and butadiene moieties. Photoelectron spectroscopic measurements have established that a similar electronic situation exists in bicyclo[4.2.1]nona-2,4,7-triene.[15]

Removing two protons from the bridgehead positions of **5** generates two lone pairs which give rise to two linear combinations, one n_s which is symmetric with respect to the plane of symmetry, and one n_a which is antisymmetric to this plane. Owing to the dominance of through space interaction over through bond interaction,[16] the n_s combination emerges 0.4 eV below the n_a combination. For reasons of symmetry, interaction between the π and n orbitals is small. Thus the net effect of the removal of two bridgehead protons from **5** is formation of two high lying lone pair combinations n_s and n_a. These two combinations give rise to two allowed $\pi^* \leftarrow$ n transitions of low energy.

In the case of **4** and $\mathbf{4}^{2-}$, the MO diagram (Figure 1) is quite similar to that in Figure 2 with the exception that the π and π^* orbitals of the ethylene moiety are lacking.

The visible spectra of $\mathbf{4}^{2-}$ and $\mathbf{5}^{2-}$ were successfully determined in tetrahydrofuran solution at −80° (Figure 3). For $\mathbf{4}^{2-}$ two bands are observed with some fine structure in the first band (605 and 550 nm).[17] For $\mathbf{5}^{2-}$ only a very broad band is seen at 545 nm; however, from the shape of the curve, it would seem that there exists a second band hidden under the long wavelength tail. These data accommodate very well the MO schemes derived by EH calculation. The low ϵ values[17] argue for a $\pi^* \leftarrow$ n transition in both instances. In actuality, two tran-

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ponent of 1.3 was chosen. For the geometry of 4, $\mathbf{4}^{2-}$, **5**, and $\mathbf{5}^{4-}$, standard bond lengths and angles were assumed.[14]

(13) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 3872 (1962).

(14) Tables of Interatomic Distances and Configurations in Molecules, *Chem. Soc., Spec. Publ.*, No. 11 (1958).

(15) P. Bischof, R. Gleiter, and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1425 (1970).

(16) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(17) The experimentally determined values were $\mathbf{5}^{2-}$, λ_{max} 545 nm (ϵ 970); $\mathbf{4}^{2-}$, λ_{max} 605 (ϵ 56), 550 (85), and 442 nm (860). For experimental reasons (excess of *n*-butyllithium, low temperature), the ϵ values have qualitative character.

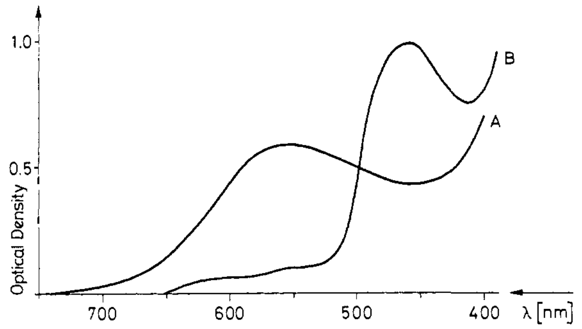
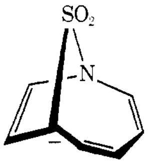


Figure 3. Visible spectra of 5^{2-} (A) and 4^{2-} (B) recorded at −80° in tetrahydrofuran solution.

sitions ($\pi^* \leftarrow n_a$ and $\pi^* \leftarrow n_s$) of low energy are expected. Also for the transition of lowest energy ($\pi^* \leftarrow n_a$) a smaller ϵ value is predicted than for the one with higher energy ($\pi^* \leftarrow n_s$) as is seen.

Significantly, the qualitative picture arising from the EH calculations denotes unequivocally that *the color observed for 5^{2-} is not due to any transition involving the sulfur atom of the SO_2 group.* Rather, the role of the sulfone function is merely to render the bridgehead positions acidic. Successive replacement of the bridgehead positions of 5^{2-} by nitrogen atoms to yield 6^- and 7 has also been considered. As anticipated from first-order perturbation theory,[18] the positions of the lone pairs on the energy scale are now lowered, while the π and π^* orbitals remain approximately constant. The calculated values for 6^- are $n_a = -10.62$ and $n_s = -12.14$ eV and for 7 $n_a = -12.53$ and $n_s = -13.87$ eV on the EH energy scale. Thus, in 7 the transitions of lower energy are predicted to be $\pi^* \leftarrow \pi$ in nature.



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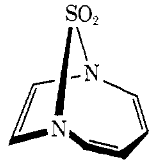

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[18] E. Heilbronner and H. Bock, "Das HMO-Modell und seine Anwendung," Vol. 1, Verlag Chemie, GmbH, Weinheim/Bergstr., 1968.

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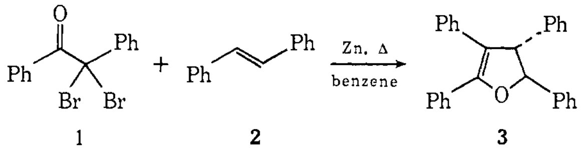
Received April 19, 1973

Ketocarbenoids by α Elimination. Intermolecular Trapping by Olefin Cycloaddition

Sir:

Since the classic work of Buchner and Curtius in 1885,[1] diazo esters and ketones have remained nearly the exclusive source of carbonyl-conjugated carbenes and carbenoids.[2] Recently, however, we described the first example of a ketocarbenoid generated by α elimination in high yield and the efficient trapping of that intermediate by intramolecular C–H insertion.[3] We should now like to report the successful intermolecular trapping by olefin cycloaddition of a ketocarbenoid so generated.[4]

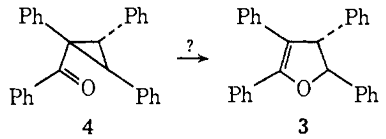
Treatment of an equimolar mixture of α,α-dibromodesoxybenzoin (**1**)[5] and *trans*-stilbene (**2**) with excess zinc dust in refluxing benzene for 1 day gives the dihydrofuran **3** in 27% yield as the major, isolable product (eq 1). The dihydrofuran structure of this 1:1 adduct



(1)

follows directly from its spectral properties[6] and from its facile conversion to tetraphenylfuran by bromination–dehydrobromination[7] (85% yield). Assignment of the trans stereochemistry rests on nmr coupling constant arguments[8] and should be considered tentative. Attempts to prepare the diastereomer of **3** from *cis*-stilbene by an identical procedure gave the same *trans*-dihydrofuran (**3**); no conclusion may be drawn about the stereospecificity of this reaction, however, since recovered stilbene was shown to be partially isomerized.

Dihydrofuran **3** represents the product of formal dipolar addition of benzoylphenylcarbene to stilbene. Although not without precedent, the trapping of ketocarbenes as 1,3 dipoles has been reported only rarely.[9] One must appreciate, however, that the observed product of such apparent dipolar additions may in fact derive from rearrangement of an initially formed cyclopropyl ketone (see eq 2). Zinc bromide, a presumed



(2)

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[1] E. Buchner and T. Curtius, *Chem. Ber.*, **18**, 2371, 2377 (1885).

[2] W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971; V. Dave and E. W. Warnhoff, *Org. React.*, **18**, 217 (1970).

[3] L. T. Scott and W. D. Cotton, *J. Amer. Chem. Soc.*, **95**, 2708 (1973).

[4] The preparation of cyclopropyl ketones and esters by the reaction of *polarized* double bonds with α-haloenolates is generally regarded as a two-stage process involving Michael addition followed by SN2 cyclization, *e.g.*, F. Gaudemar-Bardone and M. Gaudemar, *C. R. Acad. Sci., Ser. C*, 274, 991 (1972). We have purposely avoided the use of trapping agents which might qualify as good Michael acceptors.

[5] Dibromodesoxybenzoin was prepared by the acid-catalyzed bromination of desoxybenzoin in ether and recrystallized from ethanol, mp 112° (lit. mp 112°, J. R. A. Pollock and R. Stevens, Ed., "Dictionary of Organic Compounds," 4th ed, Oxford University Press, New York, N. Y., 1965, p 939).

[6] Compound **3**: mp 118–120° (pentane); ir (CCl_4) 1645 (C=C) and 1240 cm^{-1} (C—O), no carbonyl; nmr (CCl_4) δ 7.70–6.90 (m, 20), 5.42 (d, 1, $J = 6.0$ Hz), and 4.35 ppm (d, 1, $J = 6.0$ Hz); uv max (EtOH) 298 mμ (ϵ 9400); mass spectrum (70 eV) M^+ at *m/e* 374. *Anal.* Calcd for $C_{28}H_{22}O$: C, 89.81; H, 5.92. Found: C, 89.67; H, 5.79.

[7] Bromination of **3** at room temperature with 1.0 equiv of bromine in 1:1 ether–carbon tetrachloride followed by dehydrobromination with refluxing ethanolic potassium hydroxide for 1 hr gave tetraphenylfuran (85% yield) which was identical with an authentic sample.

[8] The coupling constant between the benzylic hydrogens in **3** ($J = 6.0$ Hz) agrees well with the corresponding coupling constant in the structurally similar heterocycles *trans*-2,3-diphenyl-2,3-dihydro-4,5,6,7-tetrachlorobenzo[*b*]furan ($J = 5.7$ Hz) and *trans*-3,4,5-triphenyl-4,5-dihydroisoxazole ($J = 5.6$ Hz); the cis isomer of the latter has a much larger coupling constant ($J = 9.7$ Hz): G. Binsch, R. Huisgen, and H. König, *Chem. Ber.*, **97**, 2893 (1964).

[9] R. Huisgen, G. Binsch, and H. König, *Chem. Ber.*, **97**, **2868**, 2884, 2893 (1964), and references cited therein.