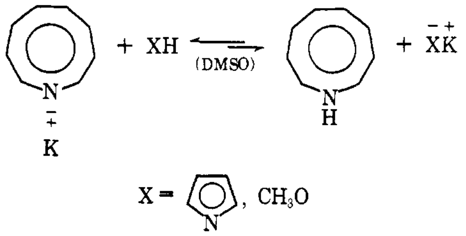
of classifying such systems in terms of overall π delocalization. The rationale here is, of course, that N–H acidity is a sensitive function of overall electron density on nitrogen which, in turn, is heavily controlled by the extent to which the lone pair is delocalized into the π system, *i.e.*, an increase in overall delocalization ought to manifest itself in a corresponding enhancement in N–H acidity. In the present instance the availability of both 1*H*-azonine and its conjugate base **2** allowed for a direct comparison between this system and certain key substances of known acidity. Thus, codissolution in DMSO-d_6 of known quantities of potassium azonide (**2c**) and pyrrole led to such a reduction in the amount of **2c** (nmr) as to require 1*H*-azonine (**1**) to be *ca.* 1.8 pK_a units *more* acidic than pyrrole.[5a] Hence, to the extent that electron delocalization is chiefly responsible for the difference in acidity, the π system of azonine appears to be more extensively delocalized than that of pyrrole. Furthermore, an analogous comparison between 1*H*-azonine and methanol has established **1** as more acidic than the alcohol by *ca.* 0.8 pK_a unit.[5b] In light of these findings and to the extent that pK_a differences between two related substances remain reasonably constant in the various media, we estimate the pK_a (Et_2O) of 1*H*-azonine to be *ca.* 15.5.[6]

Scheme I



In brief summary, we note that the data recorded presently serve to unambiguously classify the azonide system as planar (uv) and aromatic (nmr, thermal stability) and to further consolidate our case for a decidedly aromatic 1*H*-azonine.[1,2,9,10]

Acknowledgment. We are very grateful to the National Science Foundation for support of this work under Grant No. GP 26347. We also wish to thank Professor C. D. Ritchie for helpful discussions relating to the solvation of the metal azonides.

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[5] (a) This quantity was obtained as the average of the values observed from three separate runs (ΔpK_a = 1.6, 1.8, and 2.0) in which the relative molar proportions of **2c** and pyrrole were varied from *ca.* 1:2 to 1:6, respectively. Attempts to establish the equilibrium shown in Scheme I through admixture of known quantities of 1*H*-azonine and potassium pyrrolide invariably led to irreproducible results owing to the pronounced sensitivity of **1** to air. (b) This estimate was obtained by averaging the values obtained from two separate runs (ΔpK_a = 1.0 and 0.7) with the relative molar proportions of **2c** and methanol set at *ca.* 1:1 and 1:3, respectively.

[6] For pyrrole[7] pK_a(ether) = 17.5 and for methanol[8] pK_a(ether) = 16.0.

[7] G. Yagil, *Tetrahedron*, 23, 2855 (1967).

[8] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N.Y., 1965, p 4.

[9] A. G. Anastassiou and H. Yamamoto, *J. Chem. Soc.*, in press.

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A Possible Intermediate in the Tungsten-Catalyzed Olefin Metathesis Reaction

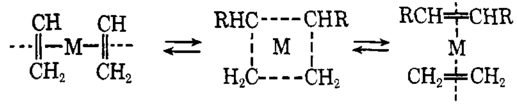
Sir:

Metathesis[1] catalysts promote a reaction in which the carbon–carbon double bonds of two olefins are broken and then remade with the fragments scrambled. A

$$2R_1CH{=}CHR_2 \rightleftarrows R_1CH{=}CHR_1 + R_2CHCHR_2$$

variety of heterogeneous and homogeneous transition[2] metal complexes have been prepared which catalyze this reaction. The most useful catalysts contain either tungsten or molybdenum complexes absorbed on a solid support or as coordination compounds in combination with selected organometallic derivatives.[3]

The mechanism for the reaction has been formulated as a (2 + 2) cycloaddition of the two olefins in the coordination sphere of the metal to form a "quasicyclobutane"[4] intermediate which can decompose by a retro (2 + 2) cycloaddition with a change in the symmetry plane.



$$\begin{array}{c}CH\quad CH\\ \cdots\|{-}M{-}\|\cdots\\ CH_2\quad CH_2\end{array} \rightleftarrows \begin{array}{c}RHC{-}{-}{-}{-}CHR\\ \vdots\ M\ \vdots\\ H_2C{-}{-}{-}{-}CH_2\end{array} \rightleftarrows \begin{array}{c}RCH{=}CHR\\ M\\ CH_2{=}CH_2\end{array}$$

Symmetry correlation diagrams can be drawn which show that the (2 + 2) cycloaddition, a reaction that is not allowed thermally, becomes "allowed" due to the admixture of the metal d orbitals of the proper symmetry with the olefin π orbitals.[5,6]

Katz[7] and Eaton[8] have recently investigated the rhodium-catalyzed rearrangement of strained carbocyclic ring systems. They have demonstrated that these reactions involve a metal–carbon σ-bonded intermediate instead of a direct metal-catalyzed electrocyclic rearrangement.

We now have evidence that a carbon–metal σ-bonded species is a possible intermediate in the tungsten-catalyzed olefin metathesis reaction.

A mechanism for the reaction, based on the intermediates demonstrated by Eaton and Katz, can be formulated as follows: (a) a rearrangement of the complexed olefins to a metallocyclic intermediate followed by (b) a rearrangement of the metallocycle and (c) reversal of step a. The rearrangement of A into B may involve a symmetrical intermediate.

To test this alternate mechanism, a procedure was developed for the production of metallocyclic intermediates under conditions used in the metathesis reaction. Wang and Menapace[9] found that a metathesis catalyst could be formed by the reduction of tungsten hexachloride with 2 equiv of butyllithium. The following mechanism was suggested for the formation of tungsten

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[1] N. Calderon, paper presented at the XXIIIrd IUPAC Meeting, Boston, Mass., Aug 1971, paper 559 and references therein.

[2] G. C. Bailey, *Catal. Rev.*, 3, 37 (1969).

[3] (a) N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Lett.*, 3327 (1967); (b) W. B. Hughes, *J. Chem. Soc. D*, 431 (1969).

[4] C. P. C. Bradshaw, E. J. Howman, and L. Turner, *J. Catal.*, 7, 269 (1967).

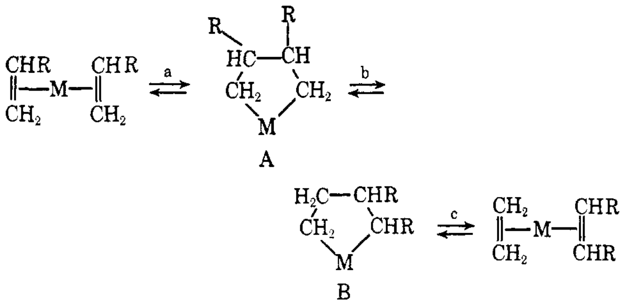
[5] F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967).

[6] G. S. Lewandos and R. Pettit, *Tetrahedron Lett.*, 780 (1971).

[7] T. Katz and S. Cerefice, *J. Amer. Chem. Soc.*, **91**, 6520 (1969).

[8] L. Cassar, P. E. Eaton, and J. Halpem, *ibid.*, **92**, 3515 (1970).

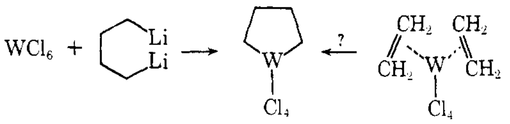
[9] J. L. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).



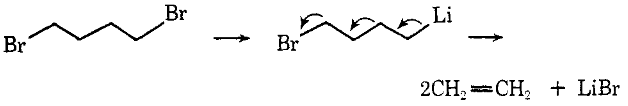
tetrachloride which is the catalytic species. This result

$$\mathrm{WCl_6 + 2BuLi \longrightarrow [W(Cl_4)(Bu)_2] \longrightarrow WCl_4 + C_4H_{10} + C_4H_8}$$

suggested that treatment of tungsten hexachloride with a 1,4-dilithioalkane should produce a metallocyclic intermediate under reaction conditions very similar to those used in this metathesis reaction.



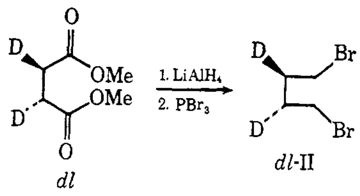
Thus, a solution of 1,4-dilithiobutane[10] (I) in diethyl ether (also containing butyllithium) was prepared from 1,4-dibromobutane and lithium dispersion at −20°. The yield (14–30%) of 1,4-dilithiobutane was determined by quenching a portion of the reaction mixture with chlorotrimethylsilane and determining the amount of 1,4-bis(trimethylsilyl)butane produced by gc analysis (durene as internal standard). The lithium reagent can also be prepared in dipropyl ether in a 7% yield. Some ethylene was formed during the preparation of the 1,4-dilithio reagent by a Grob-type elimination. The ethylene which was formed during the reaction was removed with a stream of nitrogen. No ethylene was formed after the reaction was completed. No 1,4-dilithiobutane was formed if the reaction was run in tetrahydrofuran, diglyme, butyl ether, or dioxane.



When a freshly prepared 0.05 *M* (2 ml) dipropyl ether solution of 1,4-dilithiobutane (also containing 0.52 *M* in BuLi), prepared as above, was added to a 0.16 *M* solution (10 ml) of tungsten hexachloride in benzene contained in a partially evacuated vessel, ethylene evolution began immediately. After 20 min the volume of ethylene maximized at a near quantitative yield (determined by gc, propane internal standard). An equal amount of the 1,4-dilithio reagent in the same amount of benzene used in the reaction above (no WCl_6 present) gave negligible amounts of ethylene after a 2-day period. Similar results could be obtained with diethyl ether as the solvent; however, some ethylene was produced although much more slowly (10^{-5}) without the tungsten hexachloride. A solution of butyllithium in diethyl ether of similar concentration produced only trace amounts of ethylene on treatment with tungsten hexachloride under similar conditions.

To further establish the intermediacy of the metallocycle in the reaction, labeled 1,4-dilithiobutanes (II) were prepared as follows.

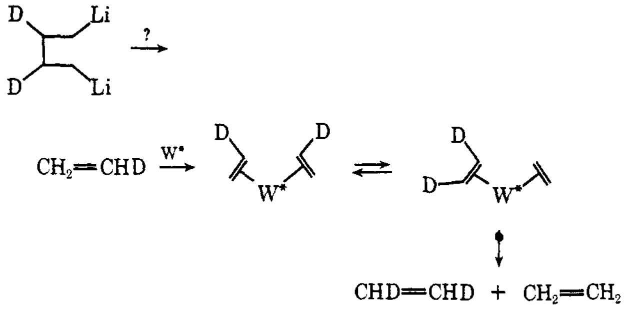
$$\underset{\text{trans}}{\mathrm{CH_3O_2CCH{=}CHCO_2CH_3}} + \mathrm{D_2} \xrightarrow[\text{EtOH–PhH}]{\mathrm{Rh(Ph_3P)_3Cl}^{11}}$$



$$\text{cis} + \mathrm{D_2} \xrightarrow{\;''\;} \text{meso} \longrightarrow \underset{\text{III}}{\text{meso}}$$

A solution of 1,4-dilithio-2,3-dideuteriobutane was prepared from either II or III and added to a benzene solution of tungsten hexachloride (see above). After 20 min the evolved ethylene was purified by vpc.[12] The ethylene mixture was analyzed by its mass spectrum at 15 eV ionization voltage. At this ionization voltage, ethylene shows negligible fragmentation and any nitrogen gas impurity in the sample is not ionized. The ethylene products obtained from the reaction of either II or III with tungsten hexachloride were a mixture which contained 6% D_2, 6% D_0, and 88% D_1 ethylene (mass spectral analysis). This result demonstrated that 12% of the ethylene was arising from a rearranged intermediate. Identical results, within experimental error, were obtained when diethyl ether was used as the solvent.

It is possible that the rearranged products were formed by a secondary reaction, such as the scheme below, instead of being formed directly from the primary product of the reaction.



To check this possibility, a dismutation catalyst was formed using WCl_6 and *n*-butyllithium in ether. This solution produced no ethylene from 1,7-octadiene.[13] This demonstrates that the ether complexes with the catalysts in preference to the olefin and blocks further reaction of the olefins that are formed. Conclusive proof of this point was obtained by examining the stereochemistry of the ethylene produced by the isomeric 2,3-dideuterio-1,4-dilithiobutanes. The *d,l* isomer II produced *trans*-1,2-dideuterioethylene and the

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(10) R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 1739 (1953).

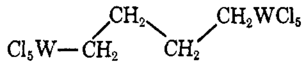
(11) J. A. Osborn, *et al.*, *J. Chem. Soc. A*, 1711 (1966).

(12) Analysis and purifications were performed on a 10-ft 4% paraffin oil on silica gel column at 50°. Ethylene was well separated from the butane and butene which arose from the butyllithium present in solution.

(13) W. B. Hughes, *J. Amer. Chem. Soc.*, **92**, 532 (1970).

meso-isomer III gave *cis*-1,2-dideuterioethylene.[14] If the dideuterioethylenes were produced by multiple turnovers of monodeuterioethylene on the catalyst, both isomers should have given the same olefin mixture or at least some stereochemical mixing.

This stereochemical result also suggests that the intermediate must be cyclic since acyclic species such as the bimetallic intermediate C should give the opposite stereochemical results if it is assumed that the decomposition of such a product would proceed through a "Grob"-type transition state.



C

Although there are some slight differences in solvent composition, the reaction of 1,4-dilithiobutane with tungsten hexachloride produces an intermediate which yields products identical with those produced by the intermediate in the olefin metathesis reaction. All of the evidence points to the structure of this intermediate being that of a metallocycle.

The existence and position of this intermediate in an overall metathesis reaction scheme and the extension of this reaction to other metathesis catalysis are under active investigation.

Acknowledgments. The authors wish to thank Professor Donald G. Farnum for his many helpful discussions, Mr. Dale Carr for technical assistance, and the Research Corporation for partial support of this work.

(14) The 1,2-dideuterioethylenes were analyzed by infrared. Authentic samples of the cis and trans isomers were prepared by the procedure of R. S. Rabinovitch and F. S. Looney, *J. Amer. Chem. Soc.*, **75**, 2652 (1953). Only trace amounts of the cis isomer could be observed in the products from the *d,l* isomer.

(15) NSF Undergraduate Research Participant, Summer 1971.

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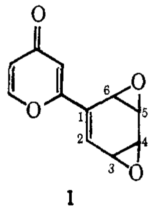
Structure of LL-Z1220. A New Antibiotic Containing a Cyclohexene Diepoxide Ring System

Sir:

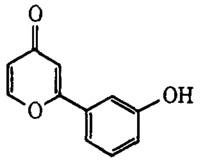
In the antibiotic program conducted in our laboratories, an undetermined fungal species was found to produce a new antibiotic, LL-Z1220,[1] for which a structure having the unique cyclohexene diepoxide ring system **1** is proposed.

When the antibiotic (colorless solid; $C_{11}H_8O_4$; mp 148° dec; $[\alpha]^{25}\mathrm{D}$ −123° (*c* 0.591, $CHCl_3$); $\lambda_{\max}^{\mathrm{CH_3OH}}$ 269 nm (ϵ 16,800); *m/e* 204) was treated with acetic acid–potassium iodide,[2] it yielded a deoxy compound: $C_{11}H_8O_3$; mp 241–243°; $\lambda_{\max}^{\mathrm{MeOH}}$ 278 nm (ϵ 13,900); *m/e* 188. The ir (3380–2700 cm^{-1}) and nmr (OH singlet, 1 H, δ 9.71 in DMSO-d_6) spectra indicated the presence of one OH group in the deoxy compound. It was methylated with dimethyl sulfate in acetone containing potassium carbonate[3] and the product was oxidized with potassium permanganate.[4] A residue from a chloroform extract of the latter reaction was purified by preparative thin layer chromatography to yield crystalline *m*-methoxybenzoic acid.[5]

The $C_5H_3O_2$ moiety of the deoxy compound which was destroyed by the permanganate oxidation had a characteristic three-proton nmr pattern (δ 8.24 (1 H, d, J = 6.0 Hz), 6.83 (1 H, d, J = 2.4 Hz), 6.34 (1 H, doublet of doublets, J = 6.0, 2.4 Hz)). This same pattern was observed for the antibiotic[1] and was that predicted for an α-substituted γ-pyrone.[6] The antibiotic and the deoxy compound had ir absorptions near 1653 cm^{-1} as would be expected for a γ-pyrone.[7] The mass spectrum of the deoxy compound had fragmentations (M − 70) expected for an α-aryl γ-pyrone.[8] All these data are in agreement with structure **2** for the deoxy compound.



1



2

The acetic acid–potassium iodide reaction with **1** to give **2** indicated a carbocyclic six-membered ring in the $C_6H_5O_2$ portion of LL-Z1220. This reagent is known to convert epoxides to carbon–carbon double bonds; however, in this case one of the epoxides yielded a phenolic hydroxyl group. A ^{13}C nmr spectrum of the antibiotic[9] showed the presence of only one carbonyl group (13.1 ppm relative to CS_2), that was assigned to the γ-pyrone, six carbons (29.8, 34.6, 57.5, 59.5, 74.5, and 77.5 ppm) involved in double bonds, and four sp^3 carbon atoms (143.5, 143.7, 144.7, and 146.6 ppm) linked to oxygen.[10] Since by ir analysis the antibiotic contains no hydroxyl function, the two oxygens associated with the C_6 carbocyclic ring must therefore exist as ether groups. The formation of the deoxy compound **2** and a positive reaction to thiosulfate ion[11] indicate at least one of the ether oxygens exists as a conjugated epoxide and suggests **1** as a possible structure for LL-Z1220.

The antibiotic ($CDCl_3$, 100 MHz) showed three protons characteristic of the pyrone ring (δ 7.80 (1 H, d, J = 6.0 Hz), 6.65 (1 H, d, J = 2.5 Hz), 6.38 (1 H, doublet of doublets, J = 6.0, 2.5 Hz)), the additional olefinic

(1) D. B. Borders, F. Barbatschi, A. J. Shay, and P. Shu, *Antimicrob. Ag. Chemother., 1969*, 233 (1970).

(2) O. Ceder, *Acta Chem. Scand.*, **18**, 126 (1964).

(3) P. N. Rao and L. R. Axelrod, *J. Chem. Soc.*, 4769 (1961).

(4) N. D. Cheronis, *Tech. Org. Chem.*, **4**, 271 (1954).

(5) Hans-G. Boit, Ed., "Beilsteins Handbuch der Organischen Chemie," Vierte Auflage, Drittes Erganzungswerk, Vol. 10, Springer-Verlag, Berlin, 1971, pp 244, 245.

(6) P. Peck and H. Abelson, *J. Org. Chem.*, **27**, 3715 (1962); P. Beak and G. A. Carls, *ibid.*, **29**, 2678 (1964).

(7) M. H. Palmer, "The Structure and Reactions of Heterocyclic Compounds," St. Martin's Press, New York, N. Y., 1967, p 212; A. R. Katritzky and A. P. Ambler, *Phys. Methods Heterocycl. Chem.*, **2**, 255 (1963).

(8) H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, **21**, 1855 (1965).

(9) Obtained at 22.63 MHz on a Bruker HFX-90 spectrometer through the courtesy of Bruker Scientific, Elmsford, N. Y.

(10) J. B. Stothers, *Quart. Rev., Chem. Soc.*, **19**, 144 (1965); J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964); D. H. Marr and J. B. Stothers, *ibid.*, **43**, 596 (1965); P. C. Lauterbur, "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, p 489; E. Lippmaa, J. Past, A. Olivson, and T. Saluvere, *Eesti NSV Tead. Akad. Toim. Fuus.-Mat. Tehnikatead. Seer.*, **No. 1**, 58 (1966); *Chem. Abstr.*, **65**, 9967*f* (1967).

(11) W. C. J. Ross, *J. Chem. Soc.*, 2257 (1950).