studies will be reported in the full paper.

Acknowledgment. We thank the U.S. Department of Energy, Basic Energy Sciences, for support of this research. M.S.W. acknowledges support as a Dreyfus Teacher-Scholar Grant recipient, 1975-1980, and N.S.L. as a Fannie and John Hertz Foundation Fellow. We thank Dr. Jerry Iseler of the M.I.T. Lincoln Laboratories for donating InP samples.

Dianions of 2-Methyl-2-butene: Evidence for the Stability of a "Y-Aromatic" Species

Nancy S. Mills*

Department of Chemistry, Trinity University San Antonia, Texas 78284

James Shapiro and Mark Hollingsworth

Department of Chemistry, Carleton College Northfield, Minnesota 50112 Received November 10, 1980

Recently the suggestion was made that certain cross-conjugated species, such as dianion 1,¹ may possess a novel aromatic character, the so-called "Y aromaticity".2,3

We wish to report that metalation of 2-methyl-2-butene with 2 equiv of base gave initial formation of the linearly conjugated dianion 2, with facile and complete isomerization to the thermodynamically more stable cross-conjugated dianion 3.



The preparation of dianions in systems in which either a linear or a cross-conjugated dianion could form allows the evaluation of the relative stabilities of each species and an estimation of the aromaticity of the cross-conjugated dianion. As further evidence, the ¹H NMR chemical shift of the parent anion (1) was measured and is in agreement with its proposed aromatic character.

Metalation was carried out by adding 1 equiv of alkene to 2 equiv of the n-butyllithium-tetramethylethylenediamine (TME-DA) complex⁴ under argon at 25 °C. The reaction mixture was usually quenched after 4 days. An alternative preparation involved the addition of 1 equiv of alkene to 2 equiv of Schlosser's base mixture (n-butyllithium/potassium tert-butoxide^{5,6}) in pentane under argon at 25 °C with quenching after 2 days. The n-butyllithium/TMEDA system resulted in formation of a dark reddish brown solid, while the anion prepared with Schlosser's base system was orange.

Evidence for dimetalation and the sequential formation of dianions 2 and 3 comes from ¹H NMR spectral observations and alkylation and silylation results. Obtaining the spectral parameters was possible only in the *n*-butyllithium/TMEDA metalating system because the dianions were moderately soluble in TMEDA. When Schlosser's base mixture was used, the dianions formed were insoluble in the pentane-based solvent and could not be observed directly. Attempts to dissolve the solid anions in dioxane resulted in immediate decomposition of solvent and anion, presumably by proton abstraction from the solvent by the anion.⁷ Although overlap with solvent complicated interpretation of the spectra, the following ¹H NMR shifts (δ) and coupling constants (italics) were deduced.



Justification of the assignment of the spectral parameters of linear dianion 2 was obtained by comparison with the butadiene dianion whose methine protons resonate at δ 4.8.¹ The most obvious structural feature of the spectrum of the cross-conjugated dianion is the 1:3:3:1 quartet (J = 6 Hz) for the vinyl proton at δ 3.42.

The linearly conjugated dianion began to appear after 10 h, reached its maximum concentration after 57 h, and disappeared by 126 h. The cross-conjugated ion appeared at 22.5 h and rapidly grew at the expense of the other dianion. Peaks from dianion 3 were still visible at 241 h, although they were beginning to be obscured by peaks from decomposition of solvent. Dianion 2 was trapped ater 23 h as the bis(trimethylsilyl) derivative by quenching with (chlorotrimethyl)silane. Adducts 4a were present as 30% of the product mixture, with the remainder due primarily to various products from monoaddition (65%) and to diaddition products from dianion 3 (5%). Trapping of dianion 3 was accomplished



by reaction with (chlorotrimethyl)silane after 96 h to give adducts 5a and 6a, in 23% and 17% yield, respectively, with no formation of 4a. Products from monoaddition comprise the remainder of the product mixture.

Interestingly, when 2-methyl-2-butene was metalated with Schlosser's base mixture and alkylated with either methyl iodide or (chlorotrimethyl)silane, the linear dianion 2 was not observed. In both cases, equal amounts of dialkylated products 5a,b and 6a,b formed. In an attempt to trap 2 before it isomerized to 3, the reaction mixture from metalation with Schlosser's base system was quenched with methyl iodide at times ranging from 20 to 5760 min. There was no product from linear dianion.

For evaluation of the influence of the cation on the reaction of the dianion, we reacted 2-methyl-2-butene with Schlosser's base mixture followed by reaction with LiBr to give the dilithiated dianion.⁸ Evidence for the success of the counterion switch comes from the color of the solution of the anion in THF. When the cation was potassium, the solution was reddish brown, while the anion in THF after treatment with LiBr was brownish black, the same color as a solution of the anion from the n-butyllithium/ TMEDA system in THF. Reaction of the dilithiated dianion (2 days old) with chlorotrimethylsilane gave 5a and 6a as the only

Klein, J.; Medlik, A. J. Chem. Soc., Chem. Commun. 1973, 275-6.
 Finnegan, R. A. Ann. N.Y. Acad. Sci. 1969, 152, 242-66.
 Gund, P. J. Chem. Educ. 1972, 49, 100-3.

 ⁽⁴⁾ Peterson, D. J. J. Org. Chem. 1969, 32, 1717-20.
 (5) Schlosser, M.; Rauchschwalbe, G. J. Am. Chem. Soc. 1978, 100, 3258-60 and references therein.

⁽⁶⁾ Lochmann, L, Lim, D.; Coupek J. Collect. Czech. Chem. Commun. 1970, 35, 733-6.

⁽⁷⁾ Bates, R. B.; Kroposki, L. M.; Potter, D. E. J. Org. Chem. 1972, 37, 560-2 (8) Schlosser, M.; Hartmann, J. Angew. Chem. 1973, 85, 544-5.



Figure 1. Correlation of π -electron density and ¹H NMR chemical shift for aromatic ions (\oplus),^{9,11} the terminal protons of linear delocalized anions, C₃H₅-C₃H₁₁ (\blacksquare),¹² and the δ protons of linear delocalized ions, C₃H₇-C₉H₄₄ (\blacksquare),¹² The linear correlations of π -electron density and ¹H NMR chemical shift for the terminal protons and for the δ protons of linear anions also hold when those electron densities are calculated by the Pople method for odd linear ions,¹³ and are significantly different from that shown by dianion 1 and the aromatic ions.

diadducts. It might be argued that in the Schlosser-prepared system the cross-conjugated dianion is in equilibrium with the linearly conjugated dianion, and the exclusive formation of product from the cross-conjugated dianion reflects only its greater reactivity. The observation that the linear dianion can be trapped when the counterions are TMEDA-chelated lithium suggests that if that dianion was present when the counterions were THFchelated lithium it would also be trapped under the same reaction conditions.

One of the characteristics of an aromatic system is the presence of a diamagnetic ring current, present in both charged and neutral species. A plot of charge density at each carbon vs. chemical shift from benzene shows a straight-line relationship from benzene and the cyclic aromatic ions with six π electrons.⁹ The trimethylenemethane dianion ($\delta 0.23$)¹⁰ shows the same linear relationship, which is significantly different from the relationship shown by the nonaromatic linear ions (Figure 1). By this method of evaluation, the trimethylenemethane dianion shows the same relationship between charge density and chemical shift as do benzene and the cyclic aromatic ions, and insofar as chemical shift is used as an indication of aromaticitiy, it is as aromatic as the above species. This is the first time that such a linear relationship has been reported for an acylic system.

We are presently looking at the preference for other crossconjugated dianions to determine if the phenomenon is a general one.

1.78 which was present in the metalating system without alkene.
(11) Olah, G. A.; Staral, J. S.; Liang, G.; Paquette, L. A.; Melega, W. P.;
Carmody, M. J. J. Am. Chem. Soc. 1978, 99, 3349-55.
(12) West, P.; Purmort, J. T.; McKinley, S. V.; J. Am. Chem. Soc. 1968,

90, 797-8. Thompson, T. B.; Ford, W. T. *Ibid.* 1979, *101*, 5469-64 for C₃H⁻. Bates, R. B.; Grosselink, D. W.; Kaczynski, J. A. *Tetrahedron Lett.* 1967, 205-10 for C₃H₂⁻. Bates, R. B.; Deines, W. H.; McCombs, D. A.; Potter, D. E. *J. Am. Chem. Soc.* 1969, *91*, 4608 for C₇H₁₁⁻. Bates, R. B.; Brenner, S.; Mayall, B. I. *Ibid.* 1973, 94, 4765-7. (13) Dewar, M. J. S. "The Molecular Orbital Theory of Organic

Chemistry"; McGraw-Hill: New York, 1969; p 184.

Acknowledgment is made to the Research Corporation, the donors to the Petroleum Research Fund, administered by the American Chemical Society, and the Robert A. Welch Foundation (W-794) for support of this work.

A New Geometrical Form for Tin. Synthesis and Structure of the Tetramethylammonium Chloride Adduct of the Spirobis(dithiastannole) $[(CH_3)_4N]^+[(C_7H_6S_2)_2SnCl]^-$

Arjun C. Sau, Roberta O. Day, and Robert R. Holmes*

Department of Chemistry, University of Massachusetts Amherst, Massachusetts 01003 Received June 5, 1980

Although pentacoordinated tin compounds are not prevalent, X-ray structural work shows that the methylstannanes $(CH_3)_3$ -SnCl,¹ (CH₃)₃SnF,² and (CH₃)₂SnF₂³ possess intermolecular tin-halogen bonding. For (ethyl L-cysteinato-S,N)(chlorodimethyl)stannate(IV), (CH₃)₂Sn(Cl)SCH₂CH(NH₂)CO₂C₂H₅, an X-ray study⁴ showed that the tin atom is pentacoordinated owing to the formation of an intramolecular donor-acceptor nitrogen-tin bond. For all of these examples, the geometry around tin is trigonal bipyramidal.

We report here the preparation and X-ray study of the first tin compound having a rectangular-pyramidal geometry. The compound, tetramethylammonium 2-chloro-5,5'-dimethyl-2,2'spirobis(1,3,2-benzodithiastannole) (1), was formed by the reaction of bis(toluene-3,4-dithiolato)tin(IV), Sn(TDT)₂, with 1 equiv of $(CH_3)_4N^+Cl^-$ in methyl cyanide at room temperature. Additional members (2-4) were also prepared.



The structure of the monocyclic dithiastannole derivative 5, $[(C_2H_5)_4N][C_7H_6S_2)Ph_2SnCl]$, which offers an interesting comparison with 1, was also determined by X-ray crystallography. It was prepared by treating diphenyl (toluene-3,4-dithiolato)tin, $(C_7H_6S_2)$ SnPh₂, with 1 equiv of Et₄N⁺Cl⁻ in methyl cyanide at 25 °C.

Crystal Data. $[(CH_3)_4N]^+[(C_7H_6S_2)_2SnCl]^-(1)$ (bright yellow, mp 206-210 °C): monoclinic, space group Cc (C_s^4 -No. 9),^{5a} with a = 14.126 (4), b = 11.485 (6), c = 14.609 (5) Å; $\beta = 100.37(3)^{\circ}$; Z = 4. $[(C_2H_5)_4N]^+[(C_7H_6S_2)Ph_2SnCl]^-$, (5) (colorless, mp 156–157 °C): monoclinic, space group $P2_1/c$ (C_{2h}^5 -No. 14),^{5b} with a = 12.344 (4), b = 11.975 (5), c = 19.120 (5) Å; $\beta = 96.41$ (2)°; Z = 4.

Data for both compounds were collected on an Enraf-Nonius CAD4 automated diffractometer by using graphite monochromated Mo K $\bar{\alpha}$ radiation and the θ -2 θ scan mode, out to a maximum $2\theta_{MoK\bar{\alpha}}$ of 50. Both structures were solved by using standard Patterson and difference Fourier techniques and were refined by using full-matrix least squares⁶ (anisotropic for non-

⁽⁹⁾ Schaefer, T.; Schneider, W. G. Can. J. Chem. 1963, 41, 966-81. Franenkel, G.; Carter, R. E.; McLachlan, A.; Richards, J. H. J. Am. Chem. Soc. 1960, 82, 5846-50.

⁽¹⁰⁾ The values reported for dianion 1 by Klein and Medlik, δ 1.78 (ref 2), differs from the chemical shift we found. We also observed a peak at δ

⁽¹⁾ Hossain, M. B.; Lefferts, J. L.; Molloy, K. C.; Van der Helm, D.;

⁽¹⁾ Hossain, M. B., Ericles, J. E., Moly, K. C., Van der Hein, D.,
Zuckerman, J. J. *Inorg. Chim. Acta* 1979, *36*, L409.
(2) Clark, H. C.; O'Brien, R. J.; Trotter, J. J. Chem. Soc. 1964, 2332.
(3) Schlemper, E. O.; Hamilton, W. C. *Inorg. Chem.* 1966, *5*, 995.
(4) Domazetis, G.; Mackay, M. F.; Magee, R. J.; James, B. D. *Inorg.*

Chim. Acta 1979, 34, L247

^{(5) (}a) "International Tables for X-ray Crystallography", Kynoch Press: Birmingham, England, 1969; Vol. I, p 99. (b) *Ibid.*, p 89.