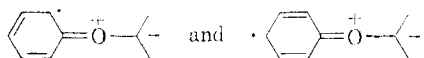


observed 15 Å. away from the nickel atom. The -NH- group is found to be as effective as the N=N group in transmitting spin density effects. However, substitution of an oxygen atom for the N=N linkage in III reduces spin densities on the terminal phenyl ring by a factor of about five. This strong attenuating effect of the oxygen atom can also be seen in IV from comparison of the observed spin densities on the six- and seven-membered rings. A rather similar spin density distribution was observed for the phenyl ring of the analog of IV in which oxygen is replaced by sulfur. These studies clearly establish that π -electron spin densities are transmitted through hetero atoms linking conjugated systems.

The sign of the spin density of the C γ atom of IV is positive (see I, II and III), whereas the spin density of C-1 of the phenyl ring must be negative. It would appear then that structures such as



contribute significantly to the electronic structure of the molecule since they would place positive spin densities on the ortho and para carbon atoms. However, as expected from consideration of contributing valence bond structures, simple alternation of sign of the spin density distribution takes place across the group in III, where each of the



bridging nitrogen atoms contributes only a single p π electron.

Details of spin density distribution measurements and valence bond calculations on these and other aminotroponimineates will be published shortly.

CONTRIBUTION No. 699

CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND Co.
WILMINGTON 99, DELAWARE

R. E. BENSON
D. R. EATON
A. D. JOSEY
W. D. PHILLIPS

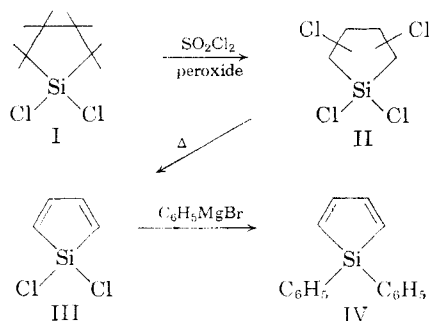
RECEIVED JULY 10, 1961

A NEW CLASS OF ORGANOSILICON COMPOUNDS. SILICON ANALOGS OF CYCLOPENTADIENE

Sir:

We are hereby reporting the first unequivocal synthesis of a series of silicon compounds which are analogs of cyclopentadiene.¹

1,1-Dichlorosilacyclopentadiene (III) has been prepared by the reaction sequence depicted



(1) Hexaphenylsilacyclopentadiene has been mentioned (E. H. Bray and W. Hübel, *Chem. and Ind.*, 1250 (1959)), but no details of its preparation or structure proof are given.

Treatment of silicon tetrachloride with the di-Grignard reagent of 1,4-dibromobutane produced I (b.p. 142-3°).² Treatment of the latter with two equivalents of sulfur chloride in the presence of benzoyl peroxide formed an isomeric mixture of tetrachlorosilacyclopentanes (II) (b.p. 63-70° (2.5 mm.)). *Anal.*, Calcd. for C₄H₆SiCl₄: C, 21.42; H, 2.67; Cl, 63.39. Found: C, 21.64; H, 2.54; Cl, 63.33. When II was passed through a packed tube heated at 525-540°, 1,1-dichlorosilacyclopentadiene (III) was obtained as a colorless liquid boiling at 130° (dec.) *Anal.* Calcd. for C₄H₆SiCl₂: C, 31.78; H, 2.64; Cl, 47.00. Found: C, 31.94; H, 2.81; Cl, 47.09.

Compound III reacted with phenylmagnesium bromide to form 1,1-diphenylsilacyclopentadiene (IV) m.p. 55-56°. (*Anal.* Calcd. for C₁₆H₁₄Si: C, 82.05; H, 5.98. Found: C, 81.91; H, 5.99) and with lithium aluminum hydride to form silacyclopentadiene (b.p. 60-62°). The infrared spectrum of IV showed typical Si C₆H₅ absorption at 1590, 1490, 1430, and 1120 cm.⁻¹. Compound IV formed an adduct with hexachlorocyclopentadiene, m.p. 41-42° [*Anal.* Calcd. for C₂₁H₁₄SiCl₆: C, 49.70; H, 2.76; Cl, 42.01. Found: C, 49.67; H, 3.09; Cl, 42.20] and tetracyanoethylene.

The way is now clearly open for an investigation of the stability of the anion of silacyclopentadiene and concomitant implications with regard to aromaticity and the Hückel rule.³

It is also obvious that a route may now be opened for the formation of "sandwich" structures of the ferrocene type from silacyclopentadiene. Experiments are already underway in our Laboratory to investigate these points. A broad research program is envisioned.

The authors are grateful to the National Science Foundation for fellowship aid which made this work possible.

(2) R. J. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954).

(3) E. Hückel, *Z. Elektrochem.*, **43**, 752, 827 (1937).

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
WEST LAFAYETTE, INDIANA

ROBERT A. BENKESER
RICHARD F. GROSSMAN
GARTH M. STANTON

RECEIVED AUGUST 7, 1961

THE ROLE OF ACETATE, MALONATE AND SUCCINATE IN THE BIOSYNTHESIS OF CAROLIC ACID¹

Sir:

The mold tetronic acids have a unique structural relationship both to ascorbic acid and to fatty acids. Lybing and Reio² indicated that part of the carolic acid molecule was derived by the "head to tail" condensation of acetate, commonly observed in mold metabolites. Evidence that this polyacetic condensation actually involves malonate is now reported; a role for a C₄ dicarboxylic acid in carolic acid formation also has been demonstrated.

Carolic acid was isolated³ from cultures of *Penicillium charlesii* NRRL 778, grown on ordinary

(1) Supported in part by a grant from the National Science Foundation.

(2) S. Lybing and L. Reio, *Acta Chem. Scand.*, **12**, 1575 (1958).

(3) P. W. Clutterbuck, W. N. Haworth, H. Raistrick, F. Reuter and M. Stacey, *Biochem. J.*, **28**, 94 (1934); P. W. Clutterbuck, H. Raistrick and F. Reuter, *ibid.*, **29**, 300 (1935).