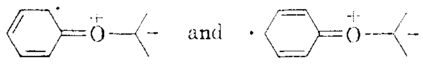
observed 15 Å. away from the nickel atom. The -NH- group is found to be as effective as the N=N group in transmitting spin density effects. However, substitution of an oxygen atom for the N=N linkage in III reduces spin densities on the terminal phenyl ring by a factor of about five. This strong attenuating 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 Cγ 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

>C—N=N—C<

bridging nitrogen atoms contributes only a single p π electron.

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

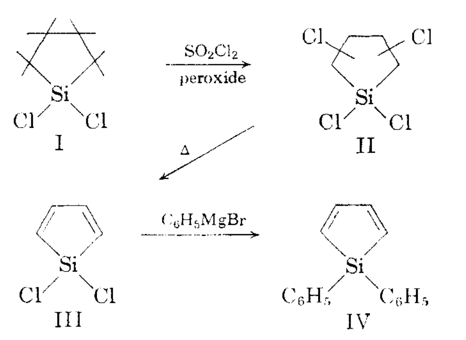
CONTRIBUTION NO. 699
CENTRAL RESEARCH DEPARTMENT — R. E. BENSON
EXPERIMENTAL STATION — D. R. EATON
E. I. DU PONT DE NEMOURS AND CO. — A. D. JOSEY
WILMINGTON 99, DELAWARE — W. D. PHILLIPS
RECEIVED JULY 10, 1961

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) Hexaphenysilacyclopentadiene has been mentioned (E. H. Braye 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 sulfuryl chloride in the presence of benzoyl peroxide formed an isomeric mixture of tetrachlorosilacyclopentanes (II) (b.p. 63–70° (2.5 mm.). *Anal.*, Calcd. for $C_4H_6SiCl_4$: 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 $C_4H_4SiCl_2$: 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 $C_{16}H_{14}Si$: 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 C_6H_5 absorption at 1590, 1490, 1430, and 1120 cm.$^{-1}$. Compound IV formed an adduct with hexachlorocyclopentadiene, m.p. 41–42° [*Anal.* Calcd. for $C_{21}H_{14}SiCl_6$: 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 — ROBERT A. BENKESER
PURDUE UNIVERSITY — RICHARD F. GROSSMAN
WEST LAFAYETTE, INDIANA — GARTH M. STANTON
RECEIVED AUGUST 7, 1961

THE ROLE OF ACETATE, MALONATE AND SUCCINATE IN THE BIOSYNTHESIS OF CAROLIC ACID[1]

Sir:

The mold tetronic acids have a unique structural relationship both to ascorbic acid and to fatty acids. Lybing and Reio[2] 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 C_4 dicarboxylic acid in carolic acid formation also has been demonstrated.

Carolic acid was isolated[3] from cultures of *Penicillium charlesii* NRRL 778, grown on ordinary

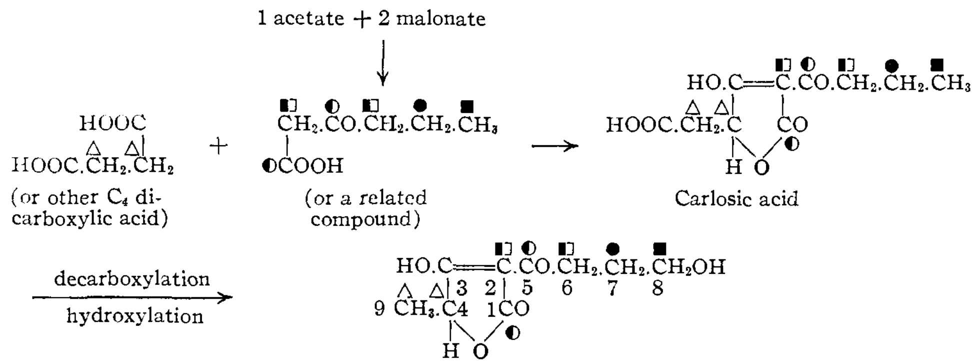
(1) Supported in part by a grant from the National Science Foundation.
(2) S. Lybing and L. Reio, *Acta Chem. Scand.*, **12**, 1575 (1958).
(3) P. W. Clutterbuck, W. N. Haworth, H. Raistrick, F. Reuter and M. Stacey, *Biochem. J.*, **28**, 94 (1934); P. W. Clutterbuck, H. Raistrick and F. Reuter, *ibid.*, **29**, 300 (1935).

TABLE I

Precursor	% of total activity[a]								
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
Acetate-1-C^{14}	35.3	—	—	—	35.9	—	28.6	—	—
Acetate-2-C^{14}	—	41.6	—	—	—	33.0	—	21.4	—
Malonate-1,3-C^{14}	50.6	—	—	—	46.7	—	—	—	—
Malonate-2-C^{14}	—	53.6	—	1.8	—	40.0	—	—	—
Succinate-2,3-C^{14}	3.9	19.8[b]	2.6	38.4	3.5	—	—	—	25.8

[a] Values below 1.0% are indicated by a dash. [b] The exact significance of this value is not clear. The figure is derived indirectly by difference from a mixture of C_2 and C_9 so that any deficit in the C_9 determination will make C_2 appear to be higher than it really is.

glucose after separate addition of acetate-1- and 2-C^{14}, malonate-1,3- and 2-C^{14} and succinate-2,3-C^{14}. The per cent. incorporations of radioactivity were, respectively, for acetates, 25.4 and 32.2; for malonates, 10.8 and 30.6; and for succinate, 5.7. The labeled carolic acids were degraded by hydrolysis to $CO_2(C_1)$, butyrolactone ($C_{5,6,7,8}$) and acetoin ($\overset{2,9}{CH_3}-\overset{3,4}{CHOH}-\overset{3,4}{CO}-\overset{2,9}{CH_3}$). To obtain separate C^{14} values for each carbon atom, butyrolactone was reduced to butyric acid for degradation by successive Schmidt reactions.[4] Acetoin was degraded by the method of Gross and Werkman.[5] Carolic acid also was converted to α-bromo-γ-methyltetronic acid which gave C_9 as the methyl and C_4 as the carboxyl of acetate on Kuhn-Roth oxidation and Schmidt degradation. The observed C^{14} distributions are given in Table I.



Carolic acid

■, carbon from acetate methyl only; ●, carbon from acetate carboxyl only; ◧, carbon from acetate methyl or malonate methylene; ◐, carbon from acetate or malonate carboxyl; △, carbon from succinate methylene.

Carbons 3, 4, and 9 are not significantly labeled by either acetate or malonate. Lybing and Reio[2] reported a similar finding for carolic acid derived from acetate-1-C^{14} with *P. charlesii* P 146. Although labeling of carbons 3, 4 and 9 by acetate would have been expected from operation of the citric acid cycle, Lybing and Reio suggested that these atoms originate from one of the C_4 dicarboxylic acids of the cycle. The experiment with succinate-2,3-C^{14} shows clearly that this compound is an important precursor of carolic acid, and that C_4 and C_9 can, in fact, be derived from a dicarboxylic acid.

The results with labeled acetate, by themselves, would indicate that carbons 1, 2, 5, 6, 7, and 8 are derived by "head to tail" condensation of three acetate units. However, although malonate is well utilized for carolic acid biosynthesis, the malonate carbons contribute to only four of the six "acetate derived" carbons, namely, 1, 2, 5, and 6. The six carbon chain evidently is derived from one acetate unit and two malonate units, as is the case in fatty acid synthesis. Malonate apparently is not converted to acetate to any significant extent so that the unique role of acetate in initiating the synthesis of the fatty acid chain is clearly demonstrated. A similar participation of both acetate and malonate has been reported for the biosynthesis of penicillic acid[6] and of stipitatonic acid.[7] A possible outline of the pathway for carolic acid synthesis is shown in the accompanying reaction sequence. This hypothesis is strengthened by our finding that neither carbon of acetate significantly labels the COOH group of carlosic acid, also isolated in these experiments.

(4) E. F. Phares, *Arch. Biochem. Biophys.*, **33**, 173 (1951).

(5) N. H. Gross and C. H. Werkman, *Arch. Biochem.*, **15**, 125 (1947).

(6) R. Bentley and J. G. Keil, *Proc. Chem. Soc.*, 111 (1961); J. G. Keil, *Federation Proc.*, **20**, 80 (1961).

(7) R. Bentley, *Federation Proc.*, **20**, 80 (1961).

DEPARTMENT OF BIOCHEMISTRY AND NUTRITION
GRADUATE SCHOOL OF PUBLIC HEALTH
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA
RONALD BENTLEY
J. G. KEIL
D. S. BHATE

RECEIVED MAY 25, 1961

PURIFICATION AND CHARACTERIZATION OF SHEEP PROLACTIN

Sir:

Sheep prolactin preparations previously have been shown to be mixtures of three electrophoretic components,[1,2] each reported to possess equal crop-sac-stimulating activity.[1] Recently, however, other workers[3] found a noticeable difference in the

(1) R. D. Cole and C. H. Li, *Biochim. Biophys. Acta*, **33**, 563 (1959); R. D. Cole, *J. Biol. Chem.*, **236**, 1369 (1961).

(2) J. G. Pierce and M. E. Carstens, *J. Am. Chem. Soc.*, **80**, 3482 (1959).

(3) K. A. Ferguson and A. L. C. Wallace, *Acta Endocrinol.*, Suppl. **51**, 293 (1960).