

and to Dr. N. Danieli for the mass spectra.

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Received May 4, 1965

### Sativene, Parent of the Toxin from *Helminthosporium sativum*

Sir:

We have previously reported on the isolation and constitution of helminthosporal (1),<sup>1,2</sup> the toxin responsible for widespread destruction and losses of cereal crops.<sup>3</sup> In Western Canada this has amounted to 3–13% of the wheat crop over the last 25 years.<sup>4</sup> The suggestion was made that helminthosporal, itself not a direct farnesyl pyrophosphate cyclization product, might be derived by oxidative cleavage of a carbon-carbon bond in a hypothetical precursor, sativene (2), with an as yet unencountered carbon skeleton. Evidence was provided from labeling experiments to justify this.<sup>5</sup>

A search among the oxygenated compounds produced by the mold has not yet revealed the presence of any substance with an intact sativane skeleton, although more immediate precursors, such as prehelminthosporol, have been identified.<sup>6</sup> Attention was then given to the very small hydrocarbon fraction accompanying this oxygenated material.

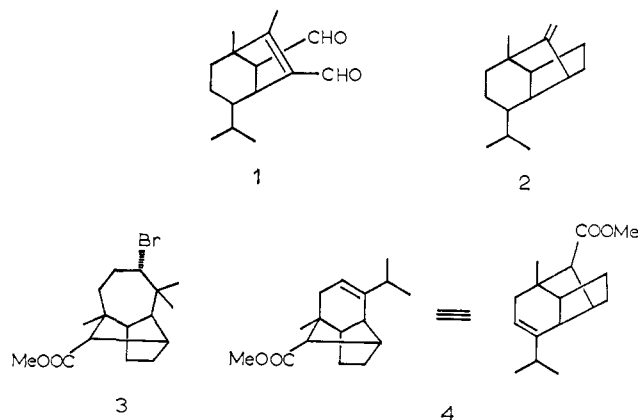
Separation by gas-liquid chromatography gave a homogeneous substance in the yield of 0.5 mg./l. of culture fluid. This compound,  $[\alpha]_D -186 \pm 3^{\circ 7}$  (*Anal.* Found: C, 88.68; H, 11.67; mol. wt., 204<sup>7</sup>), showed absorption at 3060, 1660, and 885  $\text{cm}^{-1}$  ( $\text{CCl}_4$ ), compatible with an exocyclic methylene group. This interpretation was confirmed by the n.m.r. spectrum ( $\tau$  5.60 and 5.28; 2 H) which also showed signals at 9.13 (3 H, d,  $J \sim 5$  c.p.s.), 9.10 (3 H, d,  $J \sim 5$  c.p.s.), and 8.95 (3 H, s). These additional bands suggested the presence of a methyl attached to quaternary carbon, and of an isopropyl group. The derived diol ( $\text{OsO}_4$ ), m.p. 63–64°,  $[\alpha]_D -68^{\circ}$  (*Anal.* Found: C, 74.88; H, 10.72; mol. wt. 238<sup>7</sup>), showed no absorption above 200  $\text{m}\mu$  in the ultraviolet, requiring the presence of but one double bond in the original hydrocarbon, and periodate cleavage of the diol gave material absorbing at 1740  $\text{cm}^{-1}$ .

The sum of the available evidence was thus compatible, but merely compatible, with structure 2. Too little material remained for further, degradative, studies to be considered.

Recently the conversion of longifolene into the bromo ester 3 was reported, together with its ring contraction, under the influence of silver ion to isopropyl derivatives including 4.<sup>8,9</sup> We have prepared 3:

on distillation from iron powder at 180° (0.2 mm.) 4 is obtained (45%). Hydrogenation gave the saturated methyl ester reduced with lithium aluminum hydride to the alcohol,  $[\alpha]_D +77^{\circ}$  (*Anal.* Found: C, 81.49; H, 11.28);  $\alpha$ -naphthylurethan, m.p. 105–106° (*Anal.* Found: C, 80.38; H, 8.63; N, 4.26). The alcohol was acetylated and pyrolyzed in the vapor phase at 550°<sup>11</sup> to give (+)-sativene,  $[\alpha]_D +191 \pm 3^{\circ}$ , identical in infrared spectrum ( $\text{CCl}_4$ ) and n.m.r. spectrum with the natural hydrocarbon. It was converted into the diol, m.p. 63–64°,  $[\alpha]_D +68^{\circ}$ , enantiomeric with the diol from the naturally occurring hydrocarbon.

This partial synthesis<sup>12</sup> establishes unequivocally the nature of the natural hydrocarbon isolated from the culture fluid. Its production by the mold adds significant credibility to the biosynthetic scheme suggested for these substances,<sup>5</sup> though it does not require that the specific hydrocarbon itself be the progenitor of the toxins.<sup>16</sup>



(9) We wish to express our most sincere thanks to Professor Ourisson (Strasbourg) for making experimental data<sup>10</sup> available to us prior to publication, and for his generous scientific good will.

(10) D. Helmlinger, Thesis, University of Strasbourg, 1964.

(11) See, for example, D. H. R. Barton and P. de Mayo, *J. Chem. Soc.*, 887 (1953).

(12) Formally, in view of the synthesis of longifolene,<sup>13</sup> this represents the final stages of a total synthesis. Also, since the absolute stereochemistry of longifolene is known,<sup>14</sup> this confirms the absolute stereochemistry of helminthosporal (1), established by Corey and Nozoe.<sup>15</sup>

(13) E. J. Corey, M. Ohno, R. B. Mitra, and P. A. Vatakencherry, *J. Am. Chem. Soc.*, **86**, 478 (1964).

(14) G. Ourisson, *Bull. soc. chim. France*, **22**, 895 (1955).

(15) E. J. Corey and S. Nozoe, *J. Am. Chem. Soc.*, **85**, 3527 (1963).

(16) The authors are glad to acknowledge support for this work under Grant No. EF-00419-01 from the National Institutes of Health.

(17) Holder of a National Research Council of Canada Scholarship.

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Received May 24, 1965

### Organic Syntheses by Means of Noble Metal Compounds. XII.<sup>1</sup> Reaction of the Cyclooctadiene-Palladium Chloride Complex with Ethyl Malonate

Sir:

It is known that a nucleophilic attack of a hydroxide anion on the ethylene-palladium chloride complex gives acetaldehyde.<sup>2</sup> The reactions of other nucleo-

(1) Part XI: J. Tsuji and S. Hosaka, *J. Polymer Sci.*, in press.

(2) J. Smidt, *Angew. Chem.*, **74**, 93 (1962).

(1) Terpenoids: Part XI.

(2) P. de Mayo, E. Y. Spencer, and R. W. White, *Can. J. Chem.*, **39**, 1608 (1961); **41**, 2996 (1963).

(3) R. A. Ludwig, *Can. J. Botany*, **35**, 291 (1957).

(4) B. J. Sallans, *Can. Plant Disease Survey*, **38**, 11 (1958).

(5) P. de Mayo, R. Robinson, E. Y. Spencer, and R. W. White, *Experientia*, **18**, 359 (1962).

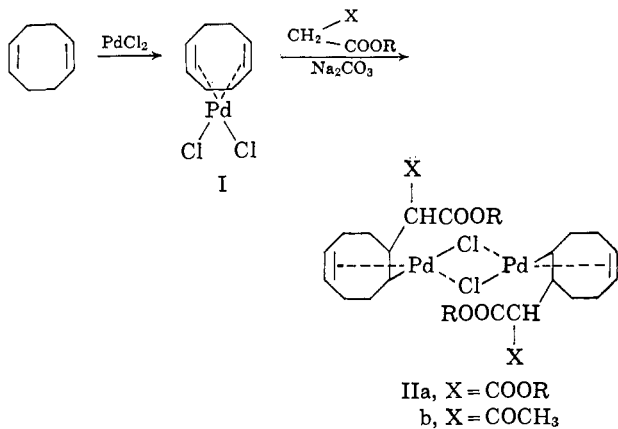
(6) P. de Mayo, E. Y. Spencer, and R. E. Williams, *Can. J. Chem.*, **43**, 1357 (1965).

(7) Rotations were determined in chloroform. Molecular weights (mass spectrum) were determined by N. S. McIntyre and R. Ryhage.

(8) G. Ourisson, Simonsen Lecture, *Proc. Chem. Soc.*, 274 (1964).

philes such as amines<sup>3</sup> and acetate anion<sup>4</sup> with olefin-palladium chloride complexes have also been reported. Consideration of these reactions leads us to undertake a study of reactions of these complexes with carbanions, since no attempt has been made as yet to study the nucleophilic attack of carbanions on the complex.

We at first selected the 1,5-cyclooctadiene-palladium chloride complex (I). When the complex I was treated with an excess of ethyl malonate in the presence of sodium carbonate at room temperature, the yellow complex gradually turned whitish, indicating the formation of a new complex. The new complex was recrystallized from ethyl acetate. By analogy with  $\mu, \mu$ -dichlorobis(8-methoxy-4-cyclooctenyl)dipalladium,<sup>5</sup> we propose that the new complex has the structure  $\mu, \mu$ -dichlorobis(8-dicarbethoxymethyl-4-cyclooctenyl)dipalladium (IIa), m.p. 155–156°. *Anal.* Calcd. for  $(C_{15}H_{23}O_4PdCl)_2$ : C, 43.99; H, 5.66; Cl, 8.66; Pd, 26.0. Found: C, 43.84; H, 5.70; Cl, 8.73; ash, 25.3. Ethyl acetoacetate behaved in the same way giving the complex IIb, m.p. 157–158°. *Anal.* Calcd. for  $(C_{14}H_{21}O_3PdCl)_2$ : C, 44.31; H, 5.57; Cl, 9.34; Pd, 28.1. Found: C, 44.23; H, 5.49; Cl, 9.36; ash, 27.8. For a complete structure determination, an X-ray crystallographic study is in progress.

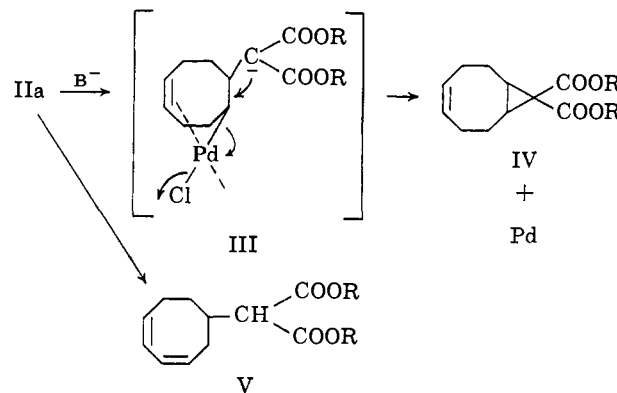


Decomposition of the complex IIa with base was then studied. The addition of methylsulfinyl carbanion<sup>6</sup> to a dimethyl sulfoxide solution of the complex IIa gave a substituted malonate anion (III), which in turn attacked the carbon  $\sigma$ -bonded to the palladium, giving rise to metallic palladium and diethyl bicyclo[6.1.0]non-4-ene-9,9-dicarboxylate (IV), b.p. 120° (bath temperature) (0.2 mm.), which was converted to bicyclo[6.1.0]nonane-9,9-dicarboxylic acid by hydrogenation and hydrolysis; m.p. 208–209°, undepressed with an authentic sample prepared by the reaction of cyclooctene with ethyl diazomalonate,<sup>7</sup> followed by hydrolysis. *Anal.* Calcd. for  $C_{11}H_{16}O_4$ : C, 62.31; H, 7.61. Found: C, 62.50; H, 7.55.

On the other hand, the attack of weaker bases such as trimethylamine or sodium carbonate in boiling benzene induced a simple decomposition of the complex IIa, giving ethyl 3,5-cyclooctadienylmalonate (V). *Anal.* Calcd. for  $C_{15}H_{22}O_4$ : C, 67.64; H,

8.33; mol. wt., 266. Found: C, 67.48; H, 8.31; mol. wt., 266 (mass spectroscopy). The positions of the double bonds were determined by ultraviolet [ $\lambda_{max}^{MeOH}$  229 m $\mu$  ( $\epsilon$  4900)] and n.m.r. spectra. Hydrogenation followed by hydrolysis gave cyclooctylmalonic acid; m.p. 123–124°, undepressed with an authentic sample. *Anal.* Calcd. for  $C_{11}H_{16}O_4$ : C, 61.66; H, 8.47. Found: C, 61.58; H, 8.38.

Thus, these reactions show not only a facile nucleophilic attack of carbanions on the palladium chloride complex, but also new methods of formation of cyclopropanes and of carbon to carbon bonds. The



reaction of various palladium chloride complexes with carbanions will be reported in a forthcoming paper.

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Received April 29, 1965

### Alkyl lithium-Amine Crystalline Complexes

*Sir:*

From previous studies of solution properties, we proposed that lithium alkyls (RLi) can form specific coordination complexes containing neutral Lewis bases (B), e.g., ethers and *t*-amines, with a 1:2 base:lithium ratio ( $R_2Li_2 \cdot B$ ).<sup>1,2</sup> We have now isolated crystalline complexes of the lithium alkyls and characterized them as containing the 1 base unit/pair of lithium atoms.

In the earlier work, solution properties had indicated that steric requirements of the base were important to the complexation and, hence, using a cyclic ether like tetrahydrofuran could be more efficacious than using the more basic triethylamine (I).<sup>1c</sup> Comparison of the solution properties using several amines of lower steric requirements, primarily methylamines and cyclic amines, has revealed that quinuclidine(II) is particularly effective in complexing lithium alkyls, just as this base is particularly effective in complexing trimethylboron.<sup>3</sup> For example, although I shows no interaction with the *t*-butyllithium reagent,<sup>1c</sup> II precipitates this bulky reagent from solution. Several amine-lithium reagent complexes are relatively insoluble, but by far the least soluble are those with the dibasic triethylenediamine, TED (III).<sup>4</sup> By an-

(1) (a) J. F. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, **85**, 2171 (1963); (b) Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *ibid.*, **85**, 3517 (1963); (c) F. A. Settle, M. Haggerty, and J. F. Eastham, *ibid.*, **86**, 2076 (1964).

(2) Solution properties of a lithium alkyl-amine system have also been studied by T. L. Brown, R. L. Geteis, D. A. Bafus, and J. A. Ladd, *ibid.*, **86**, 2135 (1964).

(3) H. C. Brown and S. Sujishi, *ibid.*, **70**, 2871 (1948).

(3) E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, 370 (1961).

(4) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **133**, 377 (1960).

(5) J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 3413 (1957).

(6) E. J. Corey and N. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

(7) H. Musso and U. Biethan, *Chem. Ber.*, **97**, 2282 (1964).