

not observed. The spectral and chromatographic data of isolated plastoquinone-3 do not agree in every detail with PQC or PQD. However, a compound called "R 253" ($\lambda_{\text{max}}^{\text{EtOH}}$ 253 ($E_{1\text{cm}}^{1\%}$ 15); R_f values of 0.69 on silica gel G in 1% ether in chloroform, and 0.53 on silica gel G thin layer plates in 15% trichloroethyl acetate in benzene), also reported by Crane² from spinach chloroplasts, does compare favorably with plastoquinone-3 in ultraviolet absorption data and chromatographic behavior. Also, a quinone isolated by Eck and Trebst³ from chestnut tree leaves and tentatively identified as plastoquinone-4 shows properties quite similar to those of plastoquinone-3; plastoquinone-4, kindly provided by Professor Trebst, and plastoquinone-3 are not identical.

Plastoquinone-3 is surprisingly unstable. During isolation, the elution time from the decalco column was very critical. Plastoquinone-3 largely decomposed within 1 hr. upon exposure to sunlight to give a number of leucomethylene blue sensitive compounds and changes in room light; chromatography was performed under a red safety lamp.

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Bis(2,4-pentanediono)diacetatosilicon(IV)

Sir:

We wish to report the preparation of bis(2,4-pentanediono)diacetatosilicon(IV) which is representative of a new class of hexacoordinate silicon chelate compounds having β -diketone ligands.

Silicon acetylacetonates were first reported by Dilthey,¹ who prepared a number of derivatives of the tris(2,4-pentanediono)siliconium ion, $(\text{C}_5\text{H}_7\text{O}_2)_3\text{Si}^+$, formed by treating silicon tetrachloride with acetylacetone. Salts such as $(\text{C}_5\text{H}_7\text{O}_2)_3\text{Si}^+ \cdot \text{HCl}_2^-$ and $(\text{C}_5\text{H}_7\text{O}_2)_3\text{Si}^+ \cdot \text{FeCl}_4^-$ were isolated and characterized. The assigned octahedral structure for this class of chelates was later confirmed by infrared analysis,² partial resolution,³ and more recently by nuclear magnetic resonance data.⁴

We have found that use of organocarboxysilanes in place of the previously employed tetrachlorosilane leads to the formation of a new class of hexacoordinate acetylacetonate silicon derivatives. Tetraacetoxysilane was treated with acetylacetone in a 1:2.1 mole ratio in chloroform solvent under a nitrogen atmosphere. A temperature rise of approximately 30–60° was noted on mixing the reagents. Subsequent heating of the reaction mixture at 70° for 2 hr. produced a light yellow solid. Collection of the solid by filtration under suction followed by recrystallization from a chloroform-petroleum ether mixture gave white, crystalline bis(2,4-pentanediono)diacetatosilicon(IV) (I), m.p. 178–180° dec. *Anal.* Calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_8\text{Si}$: C, 48.82; H,

5.85; Si, 8.16; equiv. wt., 86.1; mol. wt., 344.39. Found: C, 48.52; H, 5.98; Si, 8.19; equiv. wt., 88.0; mol. wt., 346. The recrystallized material is stable for an indefinite period when stored in a sealed container, but turns yellow in color when exposed to the atmosphere for several hours.

The nonionic nature of the chelate I was demonstrated by treatment of the material with ferric chloride in chloroform under conditions similar to those employed by Dilthey¹ for the preparation of the salts mentioned above. No reaction was detected, either by a rise in temperature or by the precipitation of an iron salt.

The infrared spectra of metal acetylacetonates have been studied extensively by many investigators. Nakamoto⁵ has compiled much of these data. The key assignments in Table I are made based on the infrared spectrum of I.

Table I. Infrared Absorption Bands

Frequency, cm^{-1}	Assignment
1705	Normal $>\text{C}=\text{O}$ absorption in the $\text{CH}_3\text{COO}-$ group
1575	$\text{C}=\text{C}$ stretch
1550	$\text{C}=\text{O}$ stretch
1050	$\equiv\text{Si}-\text{O}-\text{C}\equiv$
830	$\pi(\text{C}-\text{H})$
693	Ring deformation + (Si—O)
665	$\text{C}-\text{CH}_3$ bonding + (Si—O)

All but the band at 1705 cm^{-1} are observed, in general, for the metal acetylacetonates. The assignments are made based on the conclusions of Nakamoto.⁵ The intensification and very large shift of the $\text{C}=\text{O}$ absorption band from 1625, observed in acetylacetone, to 1550 cm^{-1} in compound I is typical of metal chelates formed with acetylacetonate ligands.

Holm and Cotton⁶ have reported that the feature of the ultraviolet spectra of metal acetylacetonate compounds is the very strong absorption band occurring usually from about 270 to 300 $\text{m}\mu$ with ϵ_{max} generally greater than $20,000\text{ l. mole}^{-1}\text{ cm}^{-1}$. The spectrum of I in chloroform solvent shows λ_{max} 279 $\text{m}\mu$, ϵ 20,041 $\text{l. mole}^{-1}\text{ cm}^{-1}$. This increase in the extinction coefficient over that of acetylacetone (ϵ_{max} 10,600 $\text{l. mole}^{-1}\text{ cm}^{-1}$) is typical of the chelates investigated previously.⁶

Further evidence to support the chelate structure of I was obtained by carrying out the above-described reaction at a relatively low temperature. The reaction temperature was not allowed to exceed 5° by addition of the acetylacetone in a dropwise manner. After the addition was complete, the reaction mixture was stirred for an additional 15 min. at 0–5°. A white, chalky precipitate was obtained. A portion of this material was isolated by filtration and dried under reduced pressure (10 mm.) at room temperature, m.p. 150° dec. The infrared spectrum showed *no absorption* in the 1500–1600 or 650–700 cm^{-1} regions which are indicative of bidentate chelation of the acetylacetone group to a metal atom. This material (II) may be the diacetoxysilyl ester of the normal enolate of acetylacetone. *Anal.* Calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_8\text{Si}$: Si, 8.16; equiv. wt.,

(5) See K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 216, and references therein.

(6) R. N. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).

(1) W. Dilthey, *Ber.*, **36**, 926 (1903).

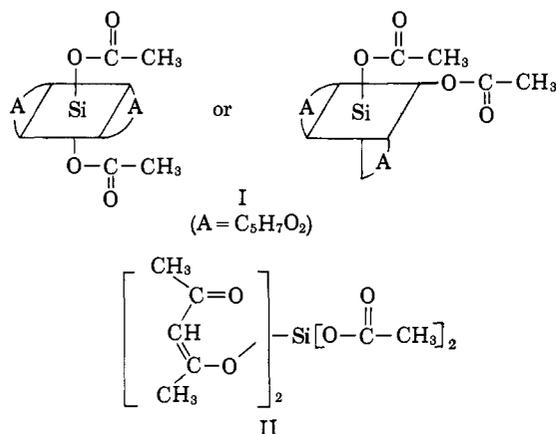
(2) R. West, *J. Am. Chem. Soc.*, **80**, 3246 (1958).

(3) S. K. Dahr, V. Doron, and S. Kirschner, *ibid.*, **80**, 753 (1958).

(4) R. E. Herter, *Chem. Ind.* (London), 1397 (1963).

86.1. Found: Si, 8.14; equiv. wt., 89.3. The *remaining material* formed at 0–5° was then heated, with stirring, to 70° for 2 hr. Isolation and recrystallization of the resulting product gave a material having an infrared absorption spectrum similar to that summarized for compound I in Table I.

Based on the evidence reported in this communication we have assigned structure I to bis(2,4-pentanediono)-diacetatosilicon(IV). We believe that this compound



is the first example of a neutral silicon chelate having β -diketo ligands prepared from a tetrafunctional silicon reagent.⁷

Attempts to separate the possible *cis* and *trans* isomers and to resolve the former are underway. Extension of this synthetic route to the preparation of other silicon- β -keto type chelates and an investigation of the chemistry of this new class of hexacoordinate silicon complexes is in progress.

(7) West² has reported the synthesis of the neutral organosilicon chelates, CH₃Si(C₅H₇O)₂Cl and C₆H₅Si(C₅H₇O)₂Cl, prepared by treatment of methyltrichloro- and phenyltrichlorosilane with acetylacetone.

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Cycloaddition Reaction of Enamines with Diphenylcyclopropanone¹

Sir:

We wish to report a facile condensation of diphenylcyclopropanone (1) with 1-diethylamino-1,3-butadiene (2), and 2-(N-pyrrolidino)-3,4-dihydronaphthalene (3) to yield products which appear to be derived from 1,4- and 1,2-cycloaddition of the enamine to the cyclopropanone, respectively. Addition of 0.447 mmole of freshly distilled 2² in 0.5 ml. of benzene to 0.427 mmole of 1³ in 0.5 ml. of benzene under a nitrogen atmosphere followed by heating at 80° for 5 hr. produced a red-brown mixture. Dilution with 20 ml. of ethyl ether, extraction with 5% hydrochloric acid and saturated sodium chloride solution, removal of the solvent, and recrystallization from absolute ethanol afforded 2,7-diphenyltropone (4) in 68% yield as yellow plates,

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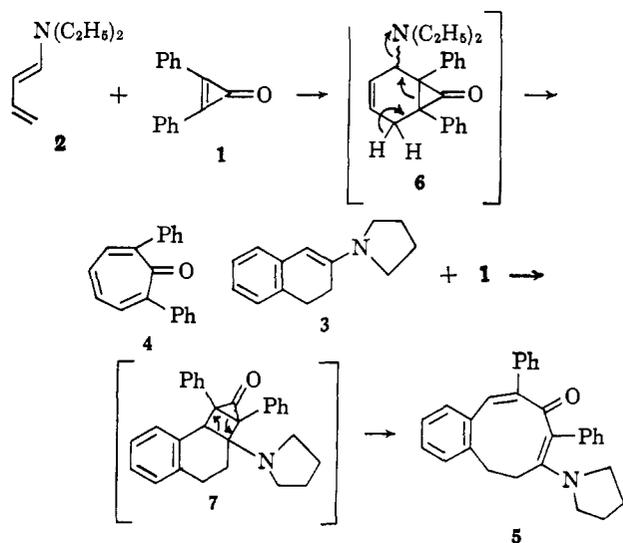
(2) S. Hünig and H. Kahanek, *Chem. Ber.*, **90**, 238 (1957).

(3) R. Breslow, J. Posner, and A. Krebs, *J. Am. Chem. Soc.*, **85**, 234 (1963).

m.p. 132–133°, $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ (in m μ) 229 (ϵ 21,500), 276 (ϵ 11,400), and 339 (ϵ 10,500). The n.m.r. spectrum of 2 in CDCl₃ showed complex absorption between 6.8 and 7.8 p.p.m.; $\nu_{\text{max}}^{\text{CHCl}_3}$ (in cm.⁻¹) 3055 (m), 3005 (s), 1620 (s), 1600 (s), 1580 (s), 1490 (m), 1440 (m), 1360 (m), and 1270 (w). The infrared spectrum of 2 was identical with that of an authentic sample⁴ and the melting point of the mixture was not depressed. The mass spectrum of 4 showed peaks of nearly equal intensity at *m/e* 258, 257, 230, and 229. This is in agreement with the established fragmentation pattern for 2-phenyltropone in the high mass range⁵ due to loss of an *ortho* hydrogen atom of a phenyl substituent from the molecular ion and subsequent loss of carbon monoxide from both the molecular ion and the M - 1 fragment.

Reaction of 1 with 3 under similar conditions (reflux period 10.5 hr.) produced 4,5-benzo-2,9-diphenyl-8-(N-pyrrolidino)cyclonona-2,4,8-trienone (5) in 62% yield after similar work-up and isolation by chromatography on Florisil, m.p. 136–137° (hexane), $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ (in m μ) 227 (ϵ 25,300), 275 (ϵ 14,200), and 315 (ϵ 17,200); $\nu_{\text{max}}^{\text{CHCl}_3}$ 3060 (m), 2995 (s), 2885 (s), 2840 (m), 1620 (s), 1495 (s), 1430 (s), 1345 (m), 1205 (m); mol. wt. (mass spectrum) 405. *Anal.* Found: C, 85.89; H, 6.84; N, 3.46. The n.m.r. spectrum of 5 in CCl₄ showed absorption at δ 1.6–1.95 (4 H, multiplet), 2.0–3.0 (4 H, A₂B₂ pattern), 3.1–3.5 (4 H, multiplet), 6.46 (1 H, broad singlet), and 6.9–7.2 (10 H, multiplet). Structure 5 is the only structure consistent with these data.

In view of the known 1,4-cycloaddition reactions of 2 with electrophilic olefins,² the 1,2-cycloaddition reactions of simple enamines with electrophilic olefins,⁶ and the previously reported reactions of cyclopropanones which appear to proceed by cycloaddition to a cyclopropanone intermediate,⁷ it would appear that 4 and 5 are formed by initial cycloaddition to the cyclopropanones 6 and 7 followed by elimination of the



(4) T. Mukai, *Bull. Chem. Soc. Japan*, **31**, 852 (1958). We wish to thank Professor Mukai for a generous sample of 2,7-diphenyltropone.

(5) J. M. Wilson, *et al.*, *Tetrahedron*, **19**, 2247 (1963).

(6) See, for example: K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, **26**, 625 (1961); K. C. Brannock, R. D. Burpitt, V. W. Goodlett, and J. G. Thweatt, *ibid.*, **29**, 813 (1964), and references cited therein.

(7) The products from the reaction of cyclopropanones with diazomethane, for example, appear to be formed from the cyclopropanone obtained from a 1,3-cycloaddition of diazomethane to the carbon-carbon double bond of the cyclopropanone: P. T. Izzo and A. S. Kende, *Chem. Ind. (London)*, 839 (1964).