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

I
(A = C₅H₇O₂)

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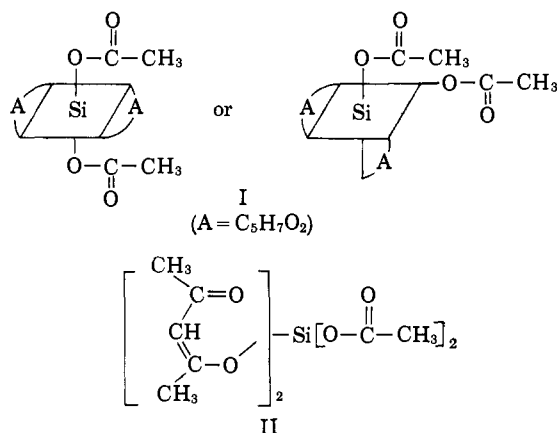
is the first example of a neutral silicon chelate having β-diketo ligands prepared from a tetrafunctional silicon reagent.[7]

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) West[2] 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.

Ronald M. Pike, Ronald R. Luongo

Department of Chemistry, Lowell Technological Institute
Lowell, Massachusetts

Cycloaddition Reaction of Enamines with Diphenylcyclopropenone[1]

Sir:

We wish to report a facile condensation of diphenylcyclopropenone (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 cyclopropenone, respectively. Addition of 0.447 mmole of freshly distilled 2[2] in 0.5 ml. of benzene to 0.427 mmole of 1[3] 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,

(1) This research was supported by National Science Foundation Grant No. GP-1562.
(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°, $\lambda_{max}^{C_2H_5OH}$ (in mμ) 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.; $\nu_{max}^{CHCl_3}$ (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 sample[4] 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-phenyltropones in the high mass range[5] 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), $\lambda_{max}^{C_2H_5OH}$ (in mμ) 227 (ϵ 25,300), 275 (ϵ 14,200), and 315 (ϵ 17,200); $\nu_{max}^{CHCl_3}$ 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 cyclopropenones 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
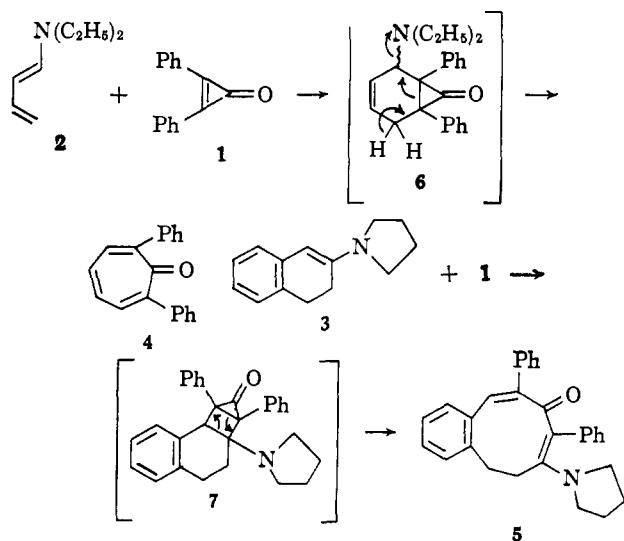
(4) T. Mukai, *Bull. Chem. Soc. Japan*, **31**, 852 (1958). We wish to thank Professor Mukai for a generous sample of 2,7-diphenyltropone.
(5) J. M. Wilson, *et al.*, *Tetrahedron*, **19**, 2247 (1963).
(6) See, for example: K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, **26**, 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 cyclopropenones 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 cyclopropenone: P. T. Izzo and A. S. Kende, *Chem. Ind.* (London), 839 (1964).

elements of diethylamine and ring cleavage, respectively. Whether the reaction proceeds by a concerted cycloaddition or by a Michael-type addition followed by ring closure of the dipolar intermediate is open to question. Further investigations of these cycloaddition reactions will be reported at a later date.

Joseph Ciabattoni,[8] Glenn A. Berchtold[9]

Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

## The Phosphine Oxide Catalyzed Isomerization of Epoxides

Sir:

During the course of our work on the opening of epoxides with tertiary phosphines in the presence of *m*-chlorobenzaldehyde[1] we have found that tertiary phosphine oxides catalyze the isomerization of *cis*- and *trans*-4-octene oxides to 4-octanone. We have also discovered that *trans*-stilbene oxide is similarly isomerized to a mixture of deoxybenzoin and diphenylacetaldehyde while *cis*-stilbene oxide undergoes prior or simultaneous isomerization to *trans*-stilbene oxide which is then converted to deoxybenzoin and diphenylacetaldehyde.

In a typical experiment, 0.61 g. (0.0047 mole) of *trans*-4-octene oxide, 1.03 g. (0.0047 mole) of tributylphosphine oxide, and 2.0 g. (0.0142 mole) of *m*-chlorobenzaldehyde were placed in a glass tube and the solution was thoroughly degassed with nitrogen. The tube was then sealed and heated at 160° for 10 days. Analysis (g.l.p.c.) of the reaction mixture showed that 85% of the 4-octene oxide had been isomerized to 4-octanone. Samples of the 4-octanone, collected from the analytical g.l.p.c., were identical in every respect with the authentic material. *cis*-4-Octene oxide was also isomerized under these conditions although at a somewhat slower rate. The conversion of either epoxide to ketone did not occur in the absence of *m*-chlorobenzaldehyde. This is thought to be a solvent effect because other epoxides do isomerize in the absence of this aldehyde. Triphenylphosphine oxide also catalyzes the isomerization of epoxides but the reaction is much slower. Most of our work has therefore been confined to tributylphosphine oxide.

There are at least two mechanisms which may be written for the isomerization of 4-octene oxide by phosphine oxide (eq. 1 and 2). These mechanisms differ in that the first involves hydride transfer with synchronous departure of phosphine oxide whereas the second utilizes phosphine oxide as both a nucleophile and a base and involves the intermediacy of the enolate ion.
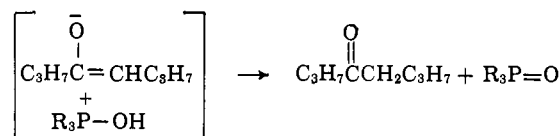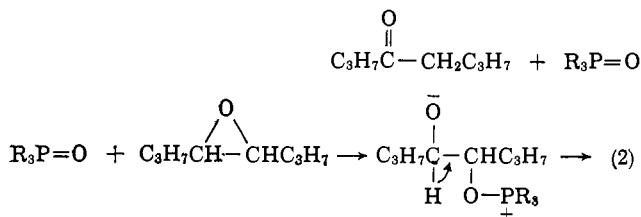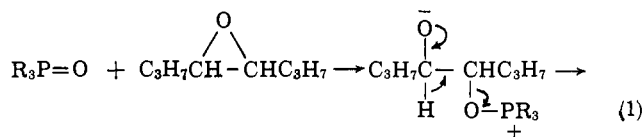
Dimethyl sulfoxide also reacts with epoxides to give α-hydroxy ketones.[2] The fact that the phosphine

$$(CH_3)_2S{=}O + RCH\overset{O}{\overset{/\backslash}{-}}CHR \rightarrow RCH\overset{OH}{\overset{|}{-}}\overset{O}{\overset{\|}{C}}{-}R + (CH_3)_2S$$
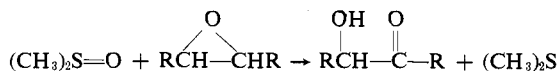
(1) (a) A. J. Speziale and D. E. Bissing, *J. Am. Chem. Soc.*, **85**, 1888 (1963); (b) A. J. Speziale and D. E. Bissing, *ibid.*, **85**, 3878 (1963); (c) D. E. Bissing and A. J. Speziale, *ibid.*, in press.

(2) T. Cohen and T. Tsuji, *J. Org. Chem.*, **26**, 1681 (1961).

oxide reaction does not take the same course emphasizes the extreme affinity of phosphorus for oxygen. In addition, the dimethyl sulfoxide reaction requires equimolar quantities of the reactants while the phosphine oxide reaction is truly catalytic.

$$R_3P{=}O + C_3H_7CH\overset{O}{\overset{/\backslash}{-}}CHC_3H_7 \rightarrow C_3H_7\overset{\overset{-}{O}}{\underset{\underset{H}{|}}{C}}{-}\underset{\underset{O{-}PR_3}{|}}{CHC_3H_7} \rightarrow$$

$$C_3H_7\overset{O}{\overset{\|}{C}}{-}CH_2C_3H_7 + R_3P{=}O \quad (1)$$

$$R_3P{=}O + C_3H_7CH\overset{O}{\overset{/\backslash}{-}}CHC_3H_7 \rightarrow C_3H_7\overset{\overset{-}{O}}{\underset{\underset{H}{|}}{C}}{-}\underset{\underset{O{-}PR_3}{|}}{CHC_3H_7} \rightarrow \quad (2)$$

$$\left[C_3H_7\overset{\overset{-}{O}}{\overset{|}{C}}{=}CHC_3H_7 + R_3P{-}OH \right] \rightarrow C_3H_7\overset{O}{\overset{\|}{C}}CH_2C_3H_7 + R_3P{=}O$$

The reactions of *cis*- and *trans*-stilbene oxide with tributylphosphine oxide were also investigated. Tributylphosphine oxide and *trans*-stilbene oxide react to give deoxybenzoin and diphenylacetaldehyde in the ratio of 9:1 (by n.m.r.). Deoxybenzoin was isolated in a 67% yield while the presence of diphenylacetaldehyde was detected and confirmed only by n.m.r. Deoxybenzoin is presumably formed *via* a mechanism similar to that suggested for the formation of 4-octanone. Diphenylacetaldehyde probably arises *via* phenyl migration rather than hydride transfer. The same product ratio was also obtained in the presence of *m*-chlorobenzaldehyde. When an n.m.r. spectrum of the mixture was taken after 30% reaction, the only detectable products were deoxybenzoin and diphenylacetaldehyde in the reported ratio. On completion of the reaction the epoxide had disappeared and the ratio of the ketone to aldehyde had remained unchanged.

cis-Stilbene oxide, under the above conditions, gave the same products in exactly the same proportions. However, the n.m.r. spectrum of the partially completed reaction showed a new peak which was proved to be due to *trans*-stilbene oxide. Thus, *cis*-stilbene oxide undergoes isomerization to *trans*-stilbene oxide either prior to or concomitantly with formation of deoxybenzoin and diphenylacetaldehyde. It is not known whether the *cis*-epoxide gives ketone and aldehyde directly. Since the ratio of deoxybenzoin to diphenylacetaldehyde is independent of the stereochemistry of the starting epoxide, it is reasonable that the *cis*-epoxide is isomerized to *trans*-stilbene oxide more rapidly than to ketone and aldehyde.

The isomerization of *cis*-stilbene oxide is interesting and quite possibly involves a reasonably stable pentacovalent phosphorus intermediate.[3]

The stability of the pentacovalent phosphorus intermediate I may be enhanced because the phenyl groups

(3) (a) F. Ramirez, S. B. Bhatia, R. B. Mitra, Z. Hamlet, and N. B. Desai, *J. Am. Chem. Soc.*, **86**, 4394 (1964); (b) F. Ramirez, R. B. Mitra, and N. B. Desai, *ibid.*, **82**, 2651 (1960); (c) F. Ramirez, A. V. Patwardhan, N. B. Desai, N. Ramanathan, and C. V. Greco, *ibid.*, **85**, 3056 (1963).