Cycloaddition Reaction of Diphenylcyclopropenone with Enamines[1,2]

J. CIABATTONI[3] AND G. A. BERCHTOLD[4]

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

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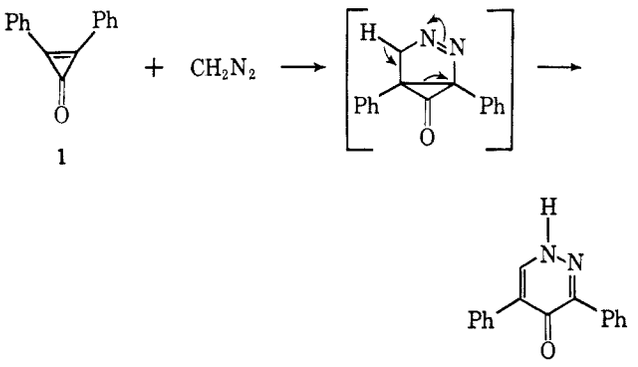
Enamines react with diphenylcyclopropenone (1) to give products arising from a 1,2 cycloaddition of the enamine to the carbon–carbon double bond of 1. When a dienamine is employed, 1,4 cycloaddition is observed. The reactions appear to involve cyclopropanone intermediates which suffer cleavage to form ring-enlarged products.

Cycloaddition reactions to the carbon–carbon double bond of diphenylcyclopropenone (1) have received little attention since the first synthesis of this interesting compound.[5] The only previous cycloaddition reaction involves treatment of 1 with diazomethane, to produce 3,5-diphenylpyridazone-4.[5a,6] This compound presumably arises from an initial 1,3 cycloaddition of



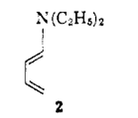
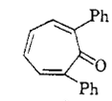
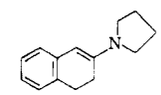
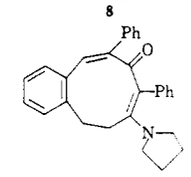
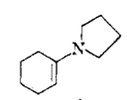
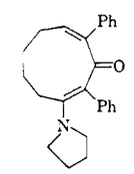
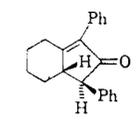
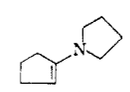
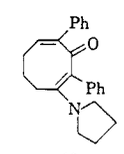
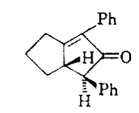
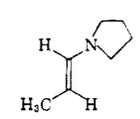
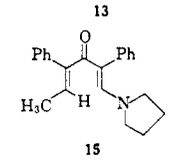
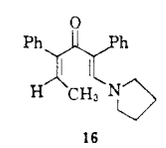
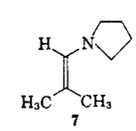
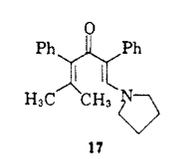
diazomethane to the carbon–carbon double bond followed by ring opening of the cyclopropanone intermediate.

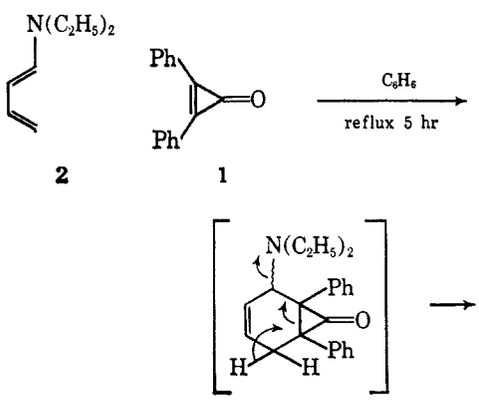
In view of the electrophilic nature of the olefinic double bond of diphenylcyclopropenone (1), the known 1,4 cycloaddition reactions of 1-diethylamino-1,3-butadiene (2),[7] and the 1,2 cycloaddition reactions of simple enamines[8] with electrophilic olefins, the corresponding cycloaddition reactions of enamines with 1 were investigated. This reaction appears to be general for enamines of both cyclic ketones and simple aldehydes (see Table I).

The 2,7-diphenyltropone (8) formed by the reaction of 1-diethylamino-1,3-butadiene (2) with 1 presumably arises from a 1,4 cycloaddition to give a cyclopropanone intermediate which subsequently suffers a 1,4 elimination of the elements of diethylamine with cleavage of the cyclopropanone ring C-2–C-3 bond. Similar attempted cycloaddition reactions of 1 with 1-acetoxy-

TABLE I

PRODUCTS FROM THE REACTION OF ENAMINES WITH DIPHENYLCYCLOPROPENONE (1)

Enamine	Product(s)	Yield, %
 2	 8	68
 3	 10	62
 4	 11  12	8, 12
 5	 13  14	3, 7
 6	 15  16	62 (isomeric mixture)
 7	 17	58



(1) This research has been supported by the National Science Foundation, Grant No. GP-1562.

(2) For a preliminary report of these results, see J. Ciabattoni and G. A. Berchtold, *J. Am. Chem. Soc.*, **87**, 1404 (1965).

(3) National Institutes of Health Predoctoral Fellow (Fellowship No. 5-F1-GM-20,133 from the National Institute of General Medical Sciences).

(4) Alfred P. Sloan Fellow.

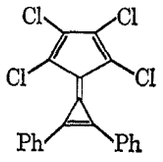
(5) (a) For a review of the chemistry of diphenylcyclopropenone, see R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320 (1965). (b) For a review of other substituted cyclopropenones, see R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1326 (1965); A. Krebs, *Angew. Chem. Intern. Ed. Engl.*, **4**, 10 (1965).

(6) P. T. Izzo and A. S. Kende, *Chem. Ind.* (London), 839 (1964).

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

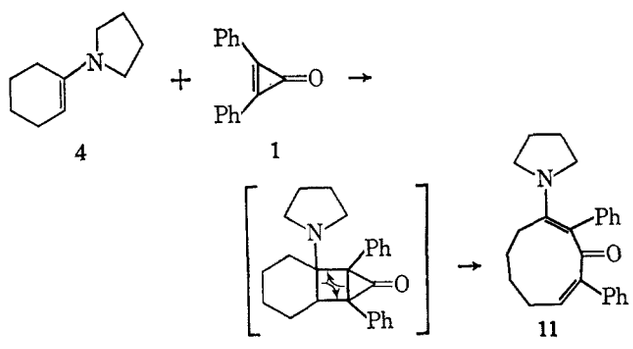
(8) See, for example, K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, **26**, 625 (1961); K. C. Brannock, R. D. Burpitt, V. W. Goodlett, and J. G. Thweatt, *ibid.*, **29**, 813 (1964), and references cited therein.

1,3-butadiene and cyclopentadiene failed. Tetrachlorocyclopentadiene reacts with **1** in methanol to produce **9**.[9]



9

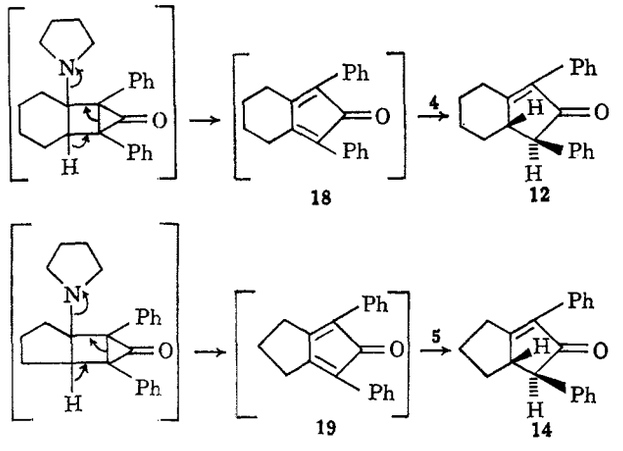
The ring-enlargement products **10**, **11**, and **13** appear to be formed by an initial 1,2 cycloaddition of the electron-rich enamines **3**, **4**, and **5** to the electrophilic double bond of **1**, followed by cleavage of the fused cyclobutane–cyclopropanone ring systems. The acyclic



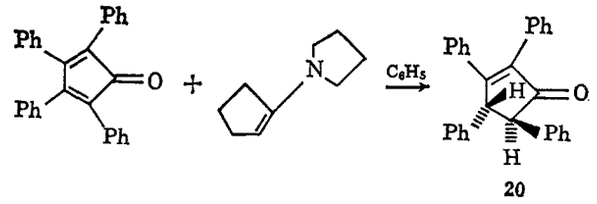
4 **1** **11**

products **15**, **16**, and **17** from enamines **6** and **7** are presumably formed by a similar pathway.

The two unusual reduction products, cyclopentenones **12** and **14**, must be derived from the corresponding cyclopentadienones, **18** and **19**, which are formed by a 1,4 elimination of the elements of pyrrolidine from the previously discussed cyclopropanone intermediates. In view of the fact that the reaction of 1-(N-pyrrolidino)cyclopentene (**5**) with 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone) affords 2,3,4,5-tetraphenylcyclopent-2-en-1-one (**20**), the formation of cyclopentenones **12** and **14** in these reactions is not unreasonable.[10]

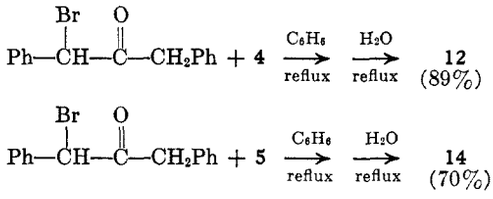


18 **12** **19** **14**

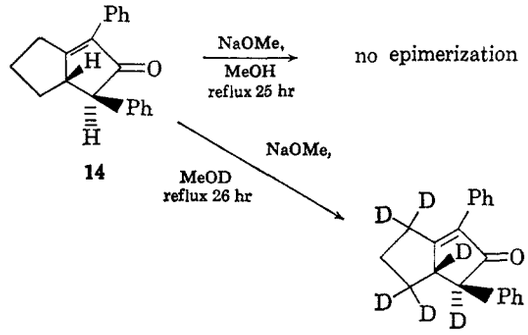


20

Compounds **12** and **14** were synthesized unambiguously in one step by the reaction of 1-bromo-1,3-diphenyl-2-propanone with 1-(N-pyrrolidino)cyclohexene (**4**) and 1-(N-pyrrolidino)cyclopentene (**5**), respectively.

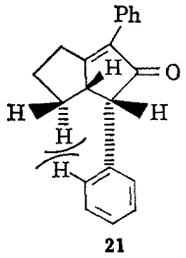


The assignment of *trans* stereochemistry to the two hydrogens on the cyclopentenone rings of **12** and **14** is based on the fact that the more thermodynamically stable isomer is being formed exclusively in these reactions. The attempted epimerization of **14** with sodium methoxide in methanol resulted in complete recovery of **14**. When methanol-d_1 was employed as the solvent, as many as six deuterium atoms per molecule were incorporated.



14

Simple inspection of Dreiding models suggests that the epimer **21** is less stable than **14** owing to a somewhat serious interaction between the *o*-hydrogens of the *endo*-phenyl ring with the C-6 *endo* hydrogen. The same interaction exists in the epimer of **12**.



21

Cookson and Nye's[11] assignment of *trans* stereochemistry to *trans*-2,4,5-triphenyl-3-benzylcyclopent-2-enone (**22**) is based on the coupling constant of $J = 3$ cps for the *trans* vicinal protons on the cyclopentenone ring. An identical coupling constant of $J = 3$ cps was observed for the *trans* vicinal hydrogens of cyclopentenones **12**, **14**, and **20**. The infrared and ultraviolet

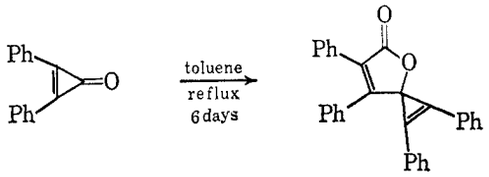
(9) M. Ueno, I. Murata, and Y. Kitahara, *Tetrahedron Letters*, 2967 (1965).

(10) Other workers have also observed this apparent disproportionation reaction between enamines and α,β-unsaturated ketones: *cf.* (a) R. L. Augustine and H. V. Cortez, *Chem. Ind.* (London), 490 (1963); (b) H. O. House, B. M. Trost, R. W. Magin, R. G. Carlson, R. W. Franck, and G. H. Rasmusson, *J. Org. Chem.*, **30**, 2513 (1965).

(11) R. C. Cookson and M. J. Nye, *J. Chem. Soc.*, 2009 (1965).

spectral data of **12** and **14** are in agreement with that reported for **22** [λ_{max}^{EtOH}, mμ (ε), 217 (27,000), 258 (9200), and 315 (230); ν_{max}^{Nujol}, cm^{-1}, 1700 and 1640].[11]

In the course of investigating the reactions of diphenylcyclopropenone, an interesting dimer was isolated. This dimer can be prepared in 78% yield by simply refluxing diphenylcyclopropenone in toluene for several days. On the basis of its spectral data and analysis, the compound has been assigned structure **22**.[12]



22
(78%)

Experimental Section[13]

Reaction of 1-Diethylamino-1,3-butadiene (2) with Diphenylcyclopropenone (1).—Diphenylcyclopropenone[1] (63.1 mg, 0.306 mmole) and 0.30 ml of anhydrous benzene were placed into a 5-ml pear-shaped flask equipped with a reflux condenser and nitrogen gas-inlet tube. To this mixture was added a solution of 39.9 mg (0.319 mmole) of freshly distilled 1-diethylamino-1,3-butadiene[7] in 0.40 ml of benzene. The mixture was heated at 80° for 5 hr under nitrogen. After the addition of 10 ml of ether, the red-brown mixture was extracted four times with 5 ml of a 5% hydrochloric acid solution. The ethereal solution was finally washed with 3 ml of a saturated sodium chloride solution. Removal of the ether afforded 86.6 mg of a crude crystalline solid. Recrystallization from absolute ethanol gave 53.6 mg (67.8%) of 2,7-diphenyltropone (**8**) as yellow plates: mp 132–133°, lit.[14] mp 133°; $\nu_{max}^{CHCl_3}$, cm^{-1}, 3055 (m), 3005 (s), 1620 (s), 1600 (s), 1580 (s), 1490 (m), 1440 (m), 1360 (m), and 1270 (w); $\lambda_{max}^{C_2H_5OH}$, mμ (ε), 229 (21,500), 276 (11,400), and 339 (10,500). The nmr spectrum of **8** in $CDCl_3$ showed complex absorption between 6.8 and 7.8 ppm. The infrared spectrum of **8** was identical with that of an authentic sample,[13] and the melting point of the mixture showed no depression. The mass spectrum of **8** 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[15] in the high mass range due to loss of an *o*-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.

Preparation of Compounds 10, 11, 12, 13, 14, 15, 16, and 17.—These compounds were prepared by reaction of the corresponding enamine with **1** in benzene under nitrogen. The quantities of reagents and the experimental conditions employed are indicated in Table II. All reactions were followed by infrared spectroscopy by observing the disappearance of the 1850-cm^{-1} band of **1**. The work-up procedure involved dilution with ether, extraction with 5% hydrochloric acid and saturated sodium chloride solutions, and drying over anhydrous magnesium sulfate. The crude neutral oil obtained by removal of the ether was chromatographed over Florisil, eluting with benzene–ether mixtures.[16]

TABLE II[a]

Product(s)	Enamine (g, mmoles)	1, g (mmole)	Benzene, ml	Temp, °C	Period, hr
10	**3** (0.206, 1.03)	0.213 (1.03)	2.5	80	10.5
11, 12	**4** (1.023, 6.76)	1.347 (6.53)	12	80	12
13, 14	**5** (1.215, 8.85)	1.508 (7.31)	15	25	3
15, 16	**6** (1.495, 13.4)	2.743 (13.3)	50	80	52
17	**7** (1.325, 10.6)	2.039 (9.88)	40	80	49

[a] Only pyrrolidine enamines have been employed in these reactions. The possibility of increasing the yields of products by the use of a less reactive enamine (*e.g.*, morpholine or piperidine enamine) has not been investigated.

Trituration with pentane–ether (if necessary) followed by recrystallization from hexane afforded the pure product(s). A typical procedure for the preparation of compound **10** is given.

4,5-Benzo-2,9-diphenyl-8-(N-pyrrolidino)cyclonona-2,4,8-trienone (10).—2-(N-Pyrrolidino)-3,4-dihydronaphthalene (**3**) (0.206 g, 1.03 mmoles) and 1.0 ml of dry benzene were placed into a 10-ml pear-shaped flask (with side arm) equipped with reflux condenser and nitrogen gas-inlet tube. To this mixture was added a solution of 0.213 g (1.03 mmoles) of diphenylcyclopropenone in 1.5 ml of anhydrous benzene. The mixture was heated at 80° (reflux) under nitrogen for 10.5 hr. After the addition of 15 ml of ether, the solution was extracted three times with 10 ml of 5% aqueous hydrochloric acid. The ethereal solution was then washed with two 5-ml portions of saturated sodium chloride and dried over anhydrous magnesium sulfate. Removal of the ether afforded 0.361 g of a crude neutral oil. Chromatography over Florisil (ether) gave 0.258 g (61.7%) of **10** as a white glass. After trituration with pentane, the white solid was recrystallized from hexane: mp 136–137°; $\nu_{max}^{CHCl_3}$, cm^{-1}, 3060 (m), 2995 (s), 2885 (s), 2840 (m), 1620 (s), 1495 (s), 1430 (s), 1345 (m), and 1205 (m); $\lambda_{max}^{C_2H_5OH}$, mμ (ε), 227 (25,300), 275 (14,200), and 315 (17,200); mol wt (mass spectrum), 405. The nmr spectrum of **10** in CCl_4 showed absorption at δ 1.6–1.94 (4H, multiplet), 6.46 (1H, broad singlet), and 6,9–7.2 (14H, multiplet).

Anal. Calcd for $C_{29}H_{27}NO$: C, 85.89; H, 6.71; N, 3.45. Found: C, 85.89; H, 6.84; N, 3.46.

2,9-Diphenyl-3-(N-pyrrolidino)cyclonona-2,8-dienone (11) was obtained in 8% yield: 0.185 g; mp 151.5–154.0° (hexane); $\nu_{max}^{CHCl_3}$, cm^{-1}, 1610 (s), 1485 (w), 1430 (s), and 1335 (w); λ_{max}^{EtOH}, mμ (ε), 228 (19,800) and 283 (10,600). The nmr spectrum in $CDCl_3$ shows absorption at δ 1.4–2.3 (12H, multiplet), 3.1–3.7 (4H, A_2B_2 pattern), 5.87 (1H, multiplet), and 7.05 (10H, doublet).

Anal. Calcd for $C_{25}H_{27}NO$: C, 83.99; H, 7.61; N, 3.92. Found: C, 83.69; H, 7.61; N, 3.83.

The **cyclopentenone derivative 12** was obtained in 12% yield, 0.234 g, as a glass: $\nu_{max}^{CHCl_3}$, cm^{-1}, 1700 (s), 1640 (m), 1600 (w), 1495 (m), 1445 (m), 1365 (w), 1345 (w), 1320 (w), and 1295 (w); $\lambda_{max}^{C_2H_5OH}$, mμ (ε), 218 (21,300) and 258 (9270). The nmr spectrum of **12** in $CDCl_3$ showed absorption at δ 1.0–3.15 (9H, broad complex multiplet), 3.27 (1H, doublet, J = 3 cps), and 7.1–7.7 (10H, multiplet).

Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.30; H, 7.01.

2,8-Diphenyl-3-(N-pyrrolidino)cycloocta-2,7-dienone 13 was obtained in 3% yield: 0.070 g; mp 116–120° (hexane); $\nu_{max}^{CHCl_3}$, cm^{-1}, 1610 (s), 1490 (m), 1430 (s), and 1340 (w); $\lambda_{max}^{C_2H_5OH}$, mμ (ε), 231 (16,500) and 287 (12,900). The nmr spectrum of **13** in $CDCl_3$ showed absorption at δ 1.7–2.2 (6H, multiplet), 2.2–2.8 (4H, multiplet), 3.3–3.8 (4H, A_2B_2 pattern), 5.82 (1H, multiplet), and 7.1–7.6 (10H, doublet).

Anal. Calcd for $C_{24}H_{25}NO$: C, 83.92; H, 7.34; N, 4.08. Found: C, 83.67; H, 7.30; N, 4.12.

The **cyclopentenone derivative 14** was obtained in 7% yield, 0.137 g, as white needles: mp 117.0–118.0° (hexane); $\nu_{max}^{CHCl_3}$, cm^{-1}, 1700 (s), 1640 (m), 1600 (w), 1495 (m), 1345 (m), and 1290 (w); $\lambda_{max}^{C_2H_2OH}$, mμ (ε), 228 (20,800) and 262 (9900). The nmr spectrum in $CDCl_3$ showed absorption at δ 1.0–3.2 (7H, broad complex multiplet), 3.33 (1H, doublet, J = 3 cps), and 7.0–7.8 (10H, multiplet).

Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.48; H, 6.63.

1-Methyl-2,4-diphenyl-5-(N-pyrrolidino)-1,4-pentadien-3-one 15 and 16.—The yield of isomeric mixture was 2.600 g (62%): mp 121.0–123.0° (hexane); $\nu_{max}^{CDCl_3}$, cm^{-1}, 1615 (s), 1490 (m),

(12) This dimer has recently been reported by Breslow and coworkers.[5]

(13) All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined with either a Perkin-Elmer, Model 237 or Model 337, infrared recording spectrophotometer fitted with a grating. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 14. The nmr spectra were determined at 60 Mc with a Varian, Model A-60, nmr spectrometer. The values are reported in parts per million downfield from tetramethylsilane. The mass spectra were obtained with a CEC, Model 21-103C, mass spectrometer. The microanalyses were performed by the Scandinavian Microanalytical Laboratory.

(14) T. Mukai, *Bull. Chem. Soc. Japan*, **31**, 852 (1958). We wish to thank Professor Mukai for a sample of **8**.

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

(16) Cyclopentenones **12** and **14** were eluted before compounds **11** and **13**, respectively.

1430 (s), 1340 (w), 1245 (w), and 1220 (w); $\lambda_{max}^{C_2H_5OH}$, mμ (ε), 223 (16,900) and 284 (18,600). The nmr spectrum in $CDCl_3$ showed absorption for two methyl groups, doublets centered at δ 1.75 and 1.77 (3H, *cis* and *trans* =CH—CH_3, J_1 = 7 cps, J_2 = 7 cps) as well as absorption at δ 1.6–2.1 (4H, multiplet), 3.2–3.9 (4H, A_2B_2 pattern), two overlapping quartets centered at δ 5.65 and 5.39 (1H, J = 7 cps, *cis* and *trans* =CH—CH_3), two finely split multiplets at δ 6.38 and 6.64 (1H, >N—CH=) and 6.9–7.4 (10H, multiplet).

Anal. Calcd for $C_{22}H_{23}NO$: C, 83.24; H, 7.30; N, 4.41. Found: C, 83.17; H, 7.36; N, 4.49.

1,1-Dimethyl-2,4-diphenyl-5-(N-pyrrolidino)-1,4-pentadien-3-one (**17**) was obtained in 58% yield: 1.906 g; mp 95.0–95.5° (white needles from hexane); $\nu_{max}^{CHCl_3}$, cm^{-1}, 1610 (s), 1490 (m), 1430 (s), 1385 (w), 1375 (w), and 1340 (m); $\lambda_{max}^{C_2H_5OH}$, mμ (ε), 234 (19,200) and 295 (13,900). The nmr spectrum in $CDCl_3$ showed absorption at δ 1.28 (3H, finely split singlet, J = 1.5 cps), 1.82 (3H, finely split singlet, J = 1.5 cps), 1.7–2.0 (4H, multiplet), 3.2–3.8 (4H, A_2B_2 pattern), 6.12 (1H, multiplet, J = 1.5 cps), and 7.14 (10H, doublet).

Anal. Calcd for $C_{23}H_{25}NO$: C, 83.34; H, 7.60; N, 4.23. Found: C, 83.45; H, 7.55; N, 4.18.

2,3,4,5-Tetraphenylcyclopent-2-en-1-one (**20**).—Into a 100-ml three-necked flask that was equipped with magnetic stirrer, reflux condenser, and gas-inlet tube were added 1.331 g (0.00970 mole) of 1-(N-pyrrolidino)cyclopentene, 1.865 g (0.00485 mole) of tetraphenylcyclopentadienone (tetracyclone), and 40 ml of benzene. The mixture was refluxed for 29 hr under nitrogen, after which the solvent was removed. Upon standing a crystalline material separated: crude mp 159°. The crude solid was washed several times with ether and recrystallized twice from boiling methanol to give 0.348 g of white needles, mp 159.5–160° (lit.[17] mp 161–162°, 158.5–160.0°). Further recrystallization from the mother liquor afforded an additional 0.277 g: over-all yield, 0.625 g (33.3%); $\nu_{max}^{CHCl_3}$, cm^{-1}, 1698 (s), 1620 (w), 1602 (w), 1574 (w), 1498 (m), 1456 (m), 1448 (m), 1348 (s), and 1151 (m); λ_{max}^{MeOH}, mμ (ε), 222 (26,400) and 297 (12,400). The nmr spectrum of **20** in $CDCl_3$ showed absorption at δ 3.72 (1H, doublet, J = 3 cps), 4.54 (1H, doublet, J = 3 cps), and 7.0–7.5 (20H, multiplet).

Synthesis of Cyclopentenone Derivative 12.—Freshly distilled 1-(N-pyrrolidino)cyclohexene (6.561 g, 0.0434 mole) and 25 ml of dry benzene were added to a 100-ml three-necked flask equipped with magnetic stirrer, reflux condenser, gas-inlet tube, and addition funnel. To this stirred mixture was added over a 15-min period a solution of 12.629 g (0.0437 mole) of 1-bromo-1,3-diphenyl-2-propanone[18] in 25 ml of dry benzene. The solution was refluxed for 10 hr under nitrogen, and after the addition of 20 ml of water, refluxing was continued for a further 4 hr. After the addition of 100 ml of ether, the mixture was extracted with three 25-ml portions of 5% hydrochloric acid. The ethereal solution was washed with 25 ml of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Removal of the ether afforded a red-brown oil which was chromatographed over Florisil (benzene–ether 1:1) to give 11.142 g (89%) of **12** as a glass. All efforts to induce crystallization failed. The infrared, ultraviolet, and nmr spectra were identical with those of **12** prepared as described earlier.

Synthesis of Cyclopentenone Derivative 14.—Into a 100-ml three-necked flask equipped with heating mantle, magnetic stirrer, reflux condenser, gas-inlet tube, and addition funnel were added 3.641 g (0.0265 mole) of freshly distilled 1-(N-pyrrolidino)cyclopentene and 25 ml of anhydrous benzene. To this solution was added dropwise over a 30-min period a solution of 7.519 g (0.0260 mole) of 1-bromo-1,3-diphenyl-2-propanone[18] in 25 ml of dry benzene. After refluxing the mixture under nitrogen for 11 hr, 20 ml of water was added and refluxing continued for another 5 hr. After the addition of 100 ml of ether, the mixture was extracted three times with 25 ml of 5% hydrochloric acid. The ethereal solution was washed with 25 ml of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Removal of the ether afforded 6.882 g of **14** as a yellow crystalline solid. Recrystallization from hexane gave 4.968 g (70%) of **14** as a white crystalline material, mp 117.0–117.5°, identical in all respects with compound **14** described earlier. The mass spectrum showed a peak for the molecular ion at m/e 274.

Attempted Epimerization of 14.—A solution of cyclopentenone **14** (0.367 g, 1.34 mmoles) and 13 mg of sodium methoxide (0.24 mmole) in 12 ml of methanol was refluxed under nitrogen for 25 hr. The reaction mixture was added to 5 ml of a solution of 5% hydrochloric acid and extracted with 20 ml of ether. Removal of the ether gave 0.351 g of recovered **14** as a white crystalline solid, mp 116–117° (hexane). A mixture melting point showed no depression.

Attempted Epimerization of 14 in Methanol-d_1.—A solution of **14** (0.349 g, 1.27 mmoles) and 14 mg (0.61 mg-atom) of sodium in methanol-d_1 (95%) was refluxed under nitrogen for 26 hr. The mixture was poured into 5 ml of a solution of 5% acetic acid. The mixture was extracted with ether and the ethereal solution was dried over anhydrous magnesium sulfate. Removal of the ether gave 0.329 g of a white crystalline solid. The nmr and mass spectra clearly indicated the incorporation of six deuterium atoms. The mass spectrum showed peaks at m/e 278, 279, and 280.

Diphenylcyclopropenone Dimer (**22**).—A solution of 0.528 g of diphenylcyclopropenone (**1**) in 5 ml of anhydrous toluene was refluxed for 6 days. After removal of the toluene under reduced pressure the white solid was recrystallized from ether–pentane to afford 0.411 g (78%) of colorless crystals: mp 166.5–167.0 (lit.[5] mp 181–182° dec); $\nu_{max}^{CHCl_3}$, cm^{-1}, 1730 (s), 1490 (w), 1445 (m), 1360 (w), 1315 (w); $\lambda_{max}^{C_2H_5OH}$, mμ (ε), 227 (37,800), 285 (37,900), 296 (41,300), and 312 (30,400). The mass spectrum showed peaks at m/e 412, 384, 356, and 178. The nmr spectrum in $CDCl_3$ showed only complex absorption at δ 7–8.

Anal. Calcd for $C_{30}H_{20}O_2$: C, 87.35; H, 4.89. Found: C, 87.09; H, 4.93.

(17) G. P. Mueller and F. L. MacArtor, *J. Am. Chem. Soc.*, **76**, 4621 (1954).

(18) A. C. B. Smith and N. Wilson, *J. Chem. Soc.*, 1342 (1955).