Anal. Calcd for $C_{22}H_{22}N_4$ (342.3): C, 77.16; H, 6.48; N, 16.36. Found: C, 77.34; H 6.33; N, 16.47; mol wt (osmometric in benzene), 346.

5-Methyl-1-phenacyl-4-phenylpyrazole (**5**) was synthesized by addition of 0.6 ml of 2 *N* phenyllithium in ether–benzene to a suspension of 107 mg of 5-methyl-4-phenylpyrazole-1-acetic acid in the same solvents. After refluxing for 5 hr the reaction mixture was poured into 50 ml of iced aqueous NH_4Cl. The organic layer was washed, dried, and evaporated to a dark oil which crystallized to give 55 mg (39%) of **5**, mp 145°. Recrystallization gave white crystals, mp 148–149°, ir identical with that of the material isolated from photolysis of **1**.

1-Benzoyl-4-methyl-5-phenylpyrazole (**4**) was prepared by addition of 89 mg of benzoyl chloride and 65 mg of pyridine to a solution of 100 mg of 5-methyl-4-phenylpyrazole[3] in CH_2Cl_2. After 1 hr water was added and the organic phase was washed with carbonate and acid, dried, and evaporated to an oil. Addition of pentane gave 80 mg of yellowish crystals, mp 65–67°. Repeated recrystallization at 0° from ether–pentane gave colorless crystals of **4**: mp 68–69°; λ_{max}^{MeOH} 233 mμ (ε 17,000), 283 (11,000); ν^{KBr} 1680 cm^{-1} (CO); δ^{CDCl_3} 2.4 (s, 3), 7.1–7.5 (m, 8), 8.0–8.4 (m, 3).

Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68. Found: C, 77.80; H, 5.33; N, 10.58.

Photolysis of 1 in Methanol.—Irradiation of solution of 500 mg of **1** in 300 ml of methanol as described above for 35 min caused complete disappearance of the starting ketone. The nmr spectrum of the total mixture revealed the presence of compounds **4**, **5**, and **6** together with another component **11** (δ 2.3, 3.8); using 15.1 mg of standard B, the integral steps for CH of standard, CH_3 of **4**, CH_2 of **5**, CH_2CH_2 of **6**, and NCH_3 of **11** were 10.3, 13.9, 6.6, 5.1, and 11.3 mm, respectively. Chromatography (35 g of silicic acid) was carried out to isolate the last compound. After preliminary fractions containing **4** and **5**, 1,5-dimethyl-4-phenylpyrazole (**11**) was eluted with benzene–ether 9:1, giving 36 mg of oil. The compound was purified by vpc (30% SE-30; 20 ft, 225°); the sample was identical (nmr, ir, vpc) with that described below.

Photolysis of 5-Methyl-4-phenyl-1,2-diazabicyclo[3.2.0]-2-hepten-6-one[11] (**8**).—A solution of 1.0 g of slightly impure bicyclic ketone **8** (mp 43–48°) in 350 ml of methanol was irradiated as described for **1**. After 17 hr, the solution was evaporated; the nmr spectrum showed only peaks due to **11** (80% based on total integral) and unreacted **8**.

In a second run, a solution of 62 mg of **8** (0.31 mmol) in 300 ml of methanol was irradiated for 2.7 hr. The nmr spectrum of the product mixture plus 31 mg of standard A showed peaks due to **11**, unreacted starting material, and standard in a molar ratio of 0.15:0.14:0.14, representing a yield of **11**, based on starting material consumed, of 90%. A small impurity peak was present at δ 1.35.

The residue from the 1-g run was chromatographed on 36 g of silicic acid (benzene–5% ether); fractions containing 590 mg of oil containing **11** were collected, followed by 200 mg of material containing some unreacted **8**. The early fractions crystallized on standing for 10 days at 5°; sublimation [60° (0.2 mm)] followed by repeated recrystallization from ether–pentane gave 285 mg of white plates of **11**, mp 65–66°; λ_{max}^{MeOH} 241 (ε 16,000); δ^{CDCl_3} 2.33 (s, 3), 3.8 (s, 3), 6.9–7.4 (s, 5), 7.52 (s, 1); *m/e* 172 (base peak).

Anal. Calcd for $C_{11}H_{12}N_2$ (172.2): 76.71; H, 7.02; N, 16.27. Found: C, 76.78; H, 7.21; N, 16.36.

A sample of this material was treated with methyl iodide in a sealed tube at 100° for 50 hr, giving 1,2,3-trimethyl-4-phenylpyrazolium iodide, mp 156–157° (lit.[6] mp 148–149°), mixture melting point with earlier sample[6] recrystallized from ethanol–ether, 156–157°.

Photolysis of 3-Acetoxy-2-acetyl-5-methyl-4-phenyl-1,2-diazabicyclo[3.2.0]-6-heptanone (**12**).—A solution of 250 mg of **12**[11] in 300 ml of methylene chloride was irradiated as described above; 3 hr was required for disappearance of the 1800-cm^{-1} ir band. After evaporation the residue was extracted with ether; 70 mg of dark polymer remained insoluble. The pink ether soluble oil was chromatographed on alumina. The benzene eluent gave 120 mg of oil, ir ($CHCl_3$) 1750 and 1670 cm^{-1}, consisting mainly of one compound. The nmr spectrum contained peaks attributed to **13** (see discussion) and also minor peaks due to 1-acetyl-3-methyl-4-phenylpyrazole. Further chromatography of the oil on silicic acid gave fractions which crystallized to give 1-acetyl-3-methyl-4-phenylpyrazole, mp 59–60° (lit.[3] mp 66–67°).

After photolysis of **12** in methanol solution for 2 hr and evaporation, nmr analysis (using fractions of total integral) indicated the presence of **13** (40%) and the dimethylpyrazole **11** (20%); with internal standard B, the yields were 36 and 20%, respectively. Injection of this mixture at 150° onto a vpc column (8 ft × 0.25 in., SE-30) produced peaks due to the dimethylpyrazole (**11**) and 1-acetyl-3-methyl-4-phenylpyrazole in a ratio of 1:1.5, indicating nearly complete pyrolysis of **13** to the acetylpyrazole.

Registry No.—**4**, 21297-76-7; **5**, 21297-77-8; **6**, 21297-78-9; **11**, 1706-46-3.

(11) J. A. Moore, F. J. Marascia, R. W. Medeiros, and R. L. Wineholt, *J. Org. Chem.*, **31**, 34 (1966).

A Practical Synthesis of Tetraphenylcyclopentadiene from Tetracyclone

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1,2,3,4-Tetraphenylcyclopentadiene (**1**) and related tetraarylcyclopentadienes are valuable as intermediates for the synthesis of a variety of other compounds, particularly fulvenes, diazo compounds, and ferrocenes. The usual synthesis of **1** involves a rather lengthy procedure[2,3] and is intrinsically inapplicable to the synthesis of unsymmetrical derivatives of **1**. Since tetracyclone (**2**, tetraphenylcyclopentadienone) and a large number of both symmetrical and unsymmetrical analogs of **2** can be prepared readily,[4] the conversion of **2** to **1** represents a process of real synthetic utility. A detailed study of the reduction of ketone **2** has been reported, the major objective of which was to find a practical conversion of **2** to **1**; all conditions investigated gave unexpectedly complex mixtures, the best yield of **1** (18%) being obtained by an inverse lithium aluminum hydride reduction followed by a chromatographic separation.[5]

We have now found that the reduction of **2** to **1** can be carried out very cleanly and essentially quantitatively by the use of excess lithium aluminum hydride in the presence of aluminum chloride, as described in the Experimental Section. This procedure should be applicable to the synthesis of a wide variety of unsymmetrical substitution products of **1**. As an illustration, we have carried out the reduction of 3-(*p*-methoxyphenyl)-2,4,5-triphenylcyclopentadienone (**3**)[6] to 2-(*p*-methoxyphenyl)-1,3,4-triphenylcyclopentadiene (**4**) in good yield. Diene **4** has been available previously by way of a complex multi-step synthesis.[7]

During the course of this work, we also investigated briefly the reduction of tetracyclone (**2**) with sodium

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(2) J. Wislicenus and H. Carpenter, *Ann.*, **302**, 223 (1898).

(3) K. Ziegler and B. Schnell, *ibid.*, **445**, 266 (1925).

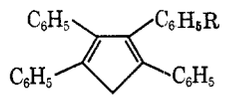
(4) M. A. Ogliarusso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 293 (1965).

(5) N. O. V. Sonntag, S. Linder, E. I. Becker, and P. E. Spoerri, *J. Amer. Chem. Soc.*, **75**, 2283 (1953).

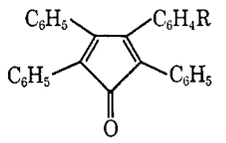
(6) S. B. Coan, D. E. Trucker, and E. I. Becker, *ibid.*, **75**, 900 (1953).

(7) L. Mehr, E. I. Becker, and P. E. Spoerri, *ibid.*, **77**, 984 (1955).

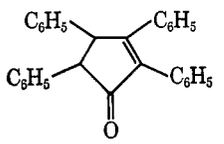
borohydride in ethanol solution at room temperature. Using an equimolar amount of borohydride, the purple color of ketone **2** was discharged only after 10 min; work-up at this stage afforded the enone **5**[5] in 34% yield. Infrared monitoring of a similar reduction showed the persistence of carbonyl absorption even after 20 hr of reaction time. On the other hand, use of a large excess of borohydride (5 mol equiv) led to the disappearance of all carbonyl absorption after 1 hr of reduction time. Work-up afforded an inseparable mixture of alcohols which could be dehydrated cleanly by treatment with iodine in refluxing benzene to give diene **1** in an overall yield of 55% from **2**.



1, R = H
4, R = *p*-OCH_3



2, R = H
3, R = *p*-OCH_3



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Experimental Section[8]

1,2,3,4-Tetraphenylcyclopentadiene (1) from Tetracyclone (2). A. By Lithium Aluminum Hydride–Aluminum Chloride Reduction.—To a stirred solution of ketone **2** (0.384 g, 1 mmol) in dry ether (20 ml) was added aluminum chloride (0.266 g, 2 mmol), followed by lithium aluminum hydride (0.076 g, 2 mmol). After refluxing for 7 hr, excess hydride was decomposed by the addition of dilute hydrochloric acid. Evaporation of the dried ($MgSO_4$) ether solution left a residue of crystalline diene **1** (0.0352 g, 93%), mp 174–176°. Recrystallization from hexane afforded pure **1** (0.178 g) as first-crop fluffy needles, mp 180–182° (lit.[5] mp 180°); its qualitative ultraviolet spectrum was in accord with reported values.[5]

B. By Sodium Borohydride Reduction and Subsequent Dehydration.—Sodium borohydride (0.500 g, 13 mmol) was added at room temperature to a stirred solution of ketone **2** (1.00 g, 2.6 mmol) in ethanol (50 ml). After 1 hr, infrared monitoring of an aliquot showed the disappearance of carbonyl absorption and the development of a strong hydroxyl band at 2.8 μ. The solvent was evaporated *in vacuo*, the residue was treated with dilute hydrochloric acid, and the organic product (a complex mixture by tlc) was extracted into ether. The washed (aqueous $NaHCO_3$) and dried ($MgSO_4$) extract was evaporated, and the residue (0.91 g) was dissolved in benzene (50 ml). Iodine (0.100 g) was added and the solution was refluxed for 1 hr, after which the solution was cooled and shaken with aqueous $NaHSO_3$ to reduce the iodine. Evaporation of the dried solution, followed by crystallization from ethanol, yielded diene **1** (0.55 g), mp 180–182°.

2-(*p*-Methoxyphenyl)-1,3,4-triphenylcyclopentadiene (4).—3-(*p*-Methoxyphenyl)-2,4,5-triphenylcyclopentadienone (**3**, 0.103 g, 0.25 mmol)[6] was reduced as described above (method A for **1** from **2**), using aluminum chloride (0.133 g, 1 mmol) and lithium aluminum hydride (0.038 g, 1 mmol) as the reagents. The crude crystalline diene **4** (0.090 g) showed essentially one spot by tlc and no hydroxyl or carbonyl absorption in the infrared. Crystallization from hexane gave diene **4** (0.064 g, 64%) as needles, mp 128–130°. Recrystallization from hexane raised the mp to 132–133° (lit.[7] melting point 130–131°).

Registry No.—**1**, 15570-45-3; **2**, 479-33-4.

(8) Melting points are uncorrected and were determined using a Thomas-Hoover apparatus.

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Photochlorination of Methylenecyclopropane

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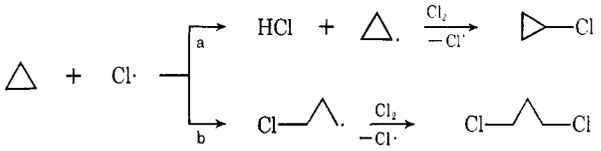
Photochlorination of cyclopropane[1] is a useful method for preparing chlorocyclopropane because abstraction of a cyclopropyl hydrogen by chlorine atom, a, to give hydrogen chloride and cyclopropyl free radical competes successfully with the simultaneous reaction, b, that gives 3-chloropropyl free radical.



Consider photochlorination of methylenecyclopropane (**1**). The greater strain in **1**,[2] which is relieved on ring opening, should cause b to occur more rapidly than with cyclopropane. Also, the exocyclic double bond of **1** can be expected to provide allylic-like resonance stabilization of the transition state for the substitution reaction,[4] but, because of orthogonality, similar stabilization of the transition state for the ring-opening reaction is not allowed. Therefore, it seems reasonable to expect that both reactions will occur more rapidly with **1** than with cyclopropane. However, prediction of the relative importance of these two pathways is uncertain.

We photochlorinated **1** in order to determine the relative importance of substitution and ring opening and, not incidentally, to see if the reaction might prove to be a convenient synthesis of 1-chloro-2-methylenecyclopropane (**2**). No **2** was obtained, but 3-chloro-2-chloromethyl-1-propene (**3**) was the major product. In addition, two other dichlorinated products, 1-chloro-1-chloromethylcyclopropane (**4**) and 2,4-dichloro-1-butene (**5**), as well as small amounts of products of further chlorination, 2-chloromethyl-1,3-dichloro-1-propene (**6**) and 2-chloromethyl-1,2,3-trichloropropane (**7**), were isolated and identified. The composition of these products from a typical reaction is summarized in Table I.

Formation of **3** and **4** can be explained as occurring by initial attack of chlorine atom at the double bond of

(1) J. D. Roberts and P. H. Dirstine, *J. Amer. Chem. Soc.*, **67**, 1281 (1945).

(2) The strain energies of cyclopropane and methylenecyclopropane are 27.5 and 41.0 kcal/mole, respectively.[3]

(3) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968). See also: R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, **90**, 4315 (1968); N. C. Baird and M. J. S. Dewar, *ibid.*, **89**, 3966 (1967); and H. A. Skinner and G. Pilcher, *Quart. Rev.* (London), **20**, 264 (1966).

(4) In deuterium oxide at 152°, 2-methylenecyclopropanecarboxylate undergoes deuterioxide-catalyzed exchange of its α hydrogen 10^6 times faster than cyclopropanecarboxylate.[5]

(5) A. T. Bottini and A. J. Davidson, *J. Org. Chem.*, **30**, 3302 (1965).