For analysis, the diester **14** was purified by preparative glpc.

Anal. Calcd for $C_{16}H_{24}O_5$: C, 64.87; H, 8.11. Found: C, 64.71; H, 8.34.

When the adduct **14** was heated under reflux with pyridine for 8 hr, only the starting material could be recovered (ir, nmr, and glpc analysis), showing the trans relationship of the ester groups and the cis fusion of the rings. The diester **14** was also recovered unchanged when allowed to stand in methanol containing sodium.

Photoaddition of Dimethyl Acetylenedicarboxylate to Carvenone. Formation of Diester 15.—The mixture of carvenone (3 g, 0.02 mol) and dimethyl acetylenedicarboxylate (5 g, 0.032 mol) was irradiated in a Pyrex tube for 30 hr. Analysis by tlc on silica (hexane–ethyl acetate, 2:1) as also by glpc showed the formation of only one product. The mixture was chromatographed on basic alumina and elution with benzene afforded the adduct **15** as a pale yellow liquid (750 mg, 12%): ir (neat) 1720 (ester C=O) and 1650 cm^{-1} (C=C); nmr ($CDCl_3$, 100 MHz) δ 0.94 (d, J = 6 Hz), 0.96 (d, J = 6 Hz), 1.1 (d, J = 7 Hz) (total 9 H), 1.46–2.6 (m, 6 H), 3.26 (s, 1 H, bridgehead methine proton), 3.74 (s) and 3.80 (s) (total 6 H); mass spectrum (70 eV) m/e (rel abundance) 294 (14, M$^+$, $C_{16}H_{22}O_5$ requires M$^+$, 294), 263 (17), 262 (23), 234 (30), 204 (67), 202 (25), 193 (20), 192 (46), 191 (33), 189 (24), 177 (25), 175 (26), 164 (33), 153 (11), 152 (40), 110 (50), 59 (55), 43 (43), and 41 (100). The analytical sample was obtained by further purification of **15** by preparative glpc.

Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.31; H, 7.48. Found: C, 65.60; H, 7.63.

The unsaturated diester **15** was recovered unchanged when stirred with pyridine for 6 hr.

Photoaddition of 3-*tert*-Butyl-2-cyclohexenone (2) to Cyclohexene. Formation of 16 and 17.—A solution of 3-*tert*-butyl-2-cyclohexenone (2 g) and cyclohexene (5 ml) in benzene (5 ml) was irradiated in a Pyrex tube for 30 hr. Removal of the solvent and excess olefin under reduced pressure afforded a liquid, which showed two new glpc peaks. The liquid was chromatographed on neutral alumina and elution with n-hexane–benzene (1:1) gave **16** + **17** as a pale yellow liquid (1.15 g, 37%), with the same glpc retention times as in the crude photolysis mixture. The relative ratio of **16** and **17**, as found by glpc, was 5:1, respectively. The analytical sample was obtained as a thick, colorless liquid by distillation of the pale yellow liquid (short-path distillation at 0.05 mm in an oil bath at 80°).

Anal. Calcd for $C_{16}H_{26}O$ (mixture): C, 82.05; H, 11.11. Found: C, 82.22; H, 11.42.

The mixture was separated by preparative glpc. The major component **16** was a crystalline solid: mp 59–61°; ir (CCl_4) 1700, 1385, and 1360 cm^{-1}; nmr ($CDCl_3$, 100 MHz) δ 0.77 (s, 9 H), 1.2–2.2 (m, 16 H), and 2.42 (d, J = 9 Hz, 1 H, bridgehead C-2 methine proton).

The minor fraction **17** was obtained as a thick liquid: ir (CCl_4) 1695, 1388, and 1365 cm^{-1}; nmr ($CDCl_3$, 100 MHz) δ 0.75 (s, 9 H), 1.1–2.2 (m, 16 H), and 2.53 (d, J = 2.5 Hz, 1 H, bridgehead C-2 methine proton). The photoadducts were recovered unchanged when refluxed for 8 hr with pyridine.

Registry No.—**1,** 499-74-1; **2,** 17299-35-3; **3a,** 30462-49-8; **3a** 2,4-DNPH, 30462-50-1; **3b,** 31444-44-7; **3b** 2,4-DNPH, 31444-45-8; **4a,** 30462-51-2; **4a** 2,4-DNPH, 30462-52-3; **4b,** 31444-48-1; **4b** 2,4-DNPH, 31444-49-2; **5a,** 31444-50-5; **5a** bis-2,4-DNPH, 31489-90-4; **5b,** 31444-51-6; **5b** bis-2,4-DNPH, 31442-94-1; **8,** 31442-95-2; **9,** 31442-96-3; **10,** 31442-97-4; **12,** 31442-98-5; **13,** 31442-99-6; **14,** 31443-00-2; **15,** 31443-01-3; **16,** 31443-02-4; **17,** 31443-03-5.

Acknowledgments.—The author is highly thankful to Professor Gurbakhsh Singh, Head of Chemistry Department, Banaras Hindu University, for providing necessary facilities, to Dr. H. S. Sachdev for a generous gift of 1,5-cyclooctadiene, and to Professor R. C. Cookson, Southampton University, England, for mass spectra.

Concerning the Reaction of 1,3,5-Cyclooctatrien-7-yne at Various Temperatures

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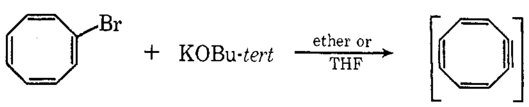
1,3,5-Cyclooctatrien-7-yne (dehydrocyclooctatetraene) has been reported to be best prepared in ether at room temperature to afford the highest yield of adduct with a trapping agent. We now report on how the yields of product from the reaction of this species with a trapping agent vary depending upon (a) when the trapping agent is added and (b) the temperature employed. Our results indicate that, contrary to previous indicated reports, dehydrocyclooctatetraene is best prepared and allowed to react at temperatures other than room temperature.

The recently[1,2] prepared 1,3,5-cyclooctatrien-7-yne (dehydrocyclooctatetraene, I) has been reported[2] to be best prepared in ether at room temperature to afford the highest yield of adduct with a trapping agent. We now report on how the yields of product, from the reaction of this species with a trapping agent, vary depending upon (a) when the trapping agent is added and (b) the temperature employed. Our results indicate that, contrary to previous indicated reports, I is best prepared and allowed to react at temperatures other than room temperature.

The method used[1,2] to prepare I is treatment of bromocyclooctatetraene with potassium *tert*-butoxide at room temperature in ether or tetrahydrofuran (THF). In the absence of any trapping agent, I has been observed[1,2] to react with the base to yield *tert*-butoxycyclooctatetraene or to dimerize to cycloocta[*b*]naphthalene. The intermediate I may, however, be trapped with a variety of trapping agents (*e.g.*, 1,3-diphenylisobenzofuran,[1,2] phenyl azide,[1,2] 1-diethylaminobutadiene,[1,2] and furan[3]), but tetraphenylcyclopentadienone (tetracyclone) was chosen for this study because of its availability and because of the high



I

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[1] A. Krebs, *Angew. Chem., Int. Ed. Engl.*, **4**, 953 (1965).

[2] A. Krebs and D. Byrd, *Justus Liebigs Ann. Chem.*, **707**, 66 (1967).

[3] A. Krebs, personal communication reported in R. W. Hoffman, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, 1967, p 349.

TABLE I

YIELD OF PRODUCT AT 25.0 ± 0.1° WITH ELAPSED TIME BEFORE TETRACYCLONE ADDITION

Time, min	0.0	5.0	15.0	30.0
Yield, %[a]	20.5 ± 0.1	14.3 ± 0.1	8.1 ± 0.1	5.7 ± 0.1
Time, min	45.0	60.0	90.0	120.0
Yield, %[a]	3.0 ± 0.1	1.7 ± 0.1	0.9 ± 0.2	Trace

[a] Average of quintuplicate runs.

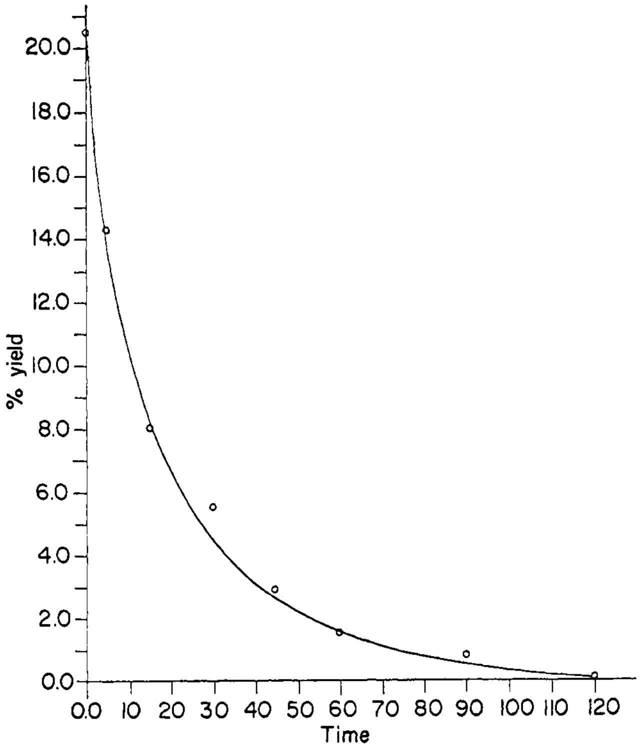
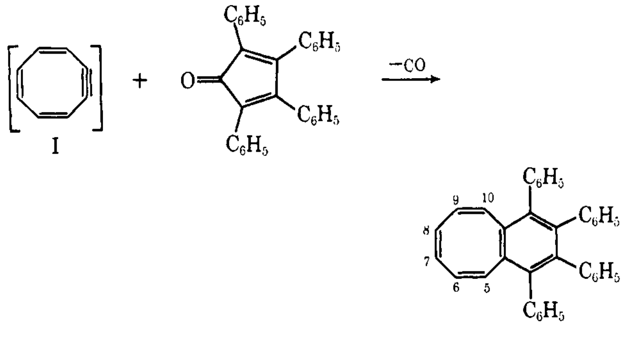


Figure 1.—Reaction of 1,3,5-cyclooctatrien-7-yne with tetracyclone. The yields are the average of quintuplicate runs. Time indicates number of minutes elapsing between introduction of bromocyclooctatetraene and introduction of tetracyclone.

yield[1,2] of 1,2,3,4-tetraphenylbenzocyclooctatetraene obtained by the Diels–Alder reaction of I with tetracyclone.



Preparation of I was accomplished under high vacuum in a specially constructed flask which allowed introduction of the tetracyclone, under vacuum, to the reaction mixture at different time intervals after the formation of I had begun; the mixture was allowed to stir[4] for exactly 30 min and the 1,2,3,4-tetraphenylbenzocyclooctatetraene was isolated. This method gives an indication of the optimum time to introduce a trapping agent to react with I. Using this procedure, the best results at room temperature (25.0 ± 0.1°) were obtained when the tetracyclone was present initially, and the yields of product dropped rapidly with even a 5-min time lapse before the trapping agent was added. These results indicate that I is very reactive and if a trapping agent is not available for immediate reaction, the dehydrocyclooctatetraene disappears by reacting with itself and/or the base. The results of this study (Table I and Figure 1) are presented as the per cent yield of product obtained when the given number of minutes were allowed to elapse between the initiation of the dehydrocyclooctatetraene formation and the introduction of tetracyclone. These results are reasonable in light of similar experiments performed with cycloheptyne and cyclohexyne.[5]

In order to obtain information on what competing reactions are possible for the dehydrocyclooctatetraene once it is formed, all material was recovered and examined for three runs at *t* 30.0. In addition to the 1,2,3,4-tetraphenylbenzocyclooctatetraene and unreacted tetracyclone, the only other products present to any extent were *tert*-butoxycyclooctatetraene and cycloocta[*b*]naphthalene. Thus it appears that besides Diels–Alder reaction with the trapping agent, dimerization and reaction with base are the only other competing pathways for the dehydrocyclooctatetraene.

Once it had been established that the best yields at room temperature were obtained when the trapping agent is present initially, we turned our attention to the effect of temperature. When the reaction between I and tetracyclone is performed under vacuum at 30.0 ± 0.1° in ether with the tetracyclone present initially, the yields of product are increased by more than 50% above the yields obtained at room temperature (Table II). However, when the reaction is performed under vacuum at 0.0 ± 0.1° in ether with the tetracyclone present initially, the yields of product are again increased over room temperature, although not so greatly. These results are presented in Table II where they are compared with the runs at room temperature with the tetracyclone present initially. Evidently two opposing factors are in effect with the temperature change. An increase in reaction rate with increased temperature is the expected kinetic result, and this seems to explain the increased yields of product when the reaction is run at the higher temperature. The intermediate I is highly reactive, however, and apparently lower temperatures prolong the lifetime of this species signifi-

TABLE II

YIELDS OF PRODUCT AT VARIOUS TEMPERATURES WITH TETRACYCLONE PRESENT INITIALLY

Temp, °C	30.0 ± 0.1	25.0 ± 0.1	0.0 ± 0.1
Yield, %[a]	37.4 ± 0.1	20.5 ± 0.1	26.2 ± 0.1

[a] Average of quintuplicate runs.

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[4] Changing the rate of stirring had little effect upon the yield.

[5] J. Schüller, Ph.D. Thesis, University of Heidelberg, 1966, reported in "Dehydrobenzene and Cycloalkynes," ref 3, pp 356, 357.

cantly. In order to establish this, rate studies[6] were also performed at 0.0 ± 0.1°, and the results are recorded below in Table III.

TABLE III
YIELD OF PRODUCT AT 0.0 ± 0.1° WITH ELAPSED TIME BEFORE TETRACYCLONE ADDITION

Time, min	0.0	5.0	15.0
Yield, %[a]	26.2 ± 0.1	19.8 ± 0.1	11.4 ± 0.1

[a] Average of quintuplicate runs.

If these results are compared with the results obtained for the room-temperature (25.0 ± 0.1°) kinetic study, it can be seen that the yields of product are consistently higher for the low-temperature reactions. Therefore, it appears that at lower temperatures the intermediate is less apt to react with itself or the base before colliding fruitfully with a tetracyclone molecule. Thus, room temperature appears to be a low point on the temperature–yield curve generated by these two opposing trends. One possible explanation for these results is that, since dimerization and reaction of I with the base are the only other competing reactions observed for the dehydrocyclooctatetraene, we may consider the reaction between I and tetracyclone to have a lower energy of activation than either of the above competing side reactions, at the lower temperature. Thus the increase in yields at the lower temperature is probably due to a decrease in the rate of formation of the side products, and as a consequence more dehydrocyclooctatetraene is available for reaction with the tetracyclone.

In order to obtain an indication of the effect of time on the yields of product from the reaction of I with tetracyclone, three room-temperature (25.0 ± 0.1°) reactions and three reactions at 30.0 ± 0.1°, all under vacuum and with the tetracyclone present initially, were allowed to run to essential completion. After 70 hr, the yield of 1,2,3,4-tetraphenylbenzocyclooctatetraene obtained from the room-temperature reactions was 79.9 ± 0.1% which corresponds closely to the 72% yield which Krebs obtained[1,2] with no special precautions. However, after the same length of time, the yield of 1,2,3,4-tetraphenylbenzocyclooctatetraene obtained from the higher temperature reactions was 90.9 ± 0.1%. Allowing other reactions to proceed for longer than 70 hr did not increase the yield of product.

Thus the yield of product from the reaction of I with tetracyclone is maximized at 91% if the reaction is performed under vacuum, in ether at 30° with the trapping agent present initially.

Experimental Section

Bromocyclooctatetraene-1,3,5,7.—The preparation of bromocyclooctatetraene was based on the method of Konz and Huisgen[7] and Sargent.[8] Into a 1-l. flask equipped with a mechanical stirrer, dropping funnel, condenser, and nitrogen inlet was placed, under nitrogen, a solution of 52 g (0.5 mole) of freshly distilled cyclooctatetraene in 350 ml of methylene chloride (distilled from phosphorus pentoxide), and the mixture was cooled with a Dry Ice–acetone bath to −60 to −65°. Then within 1 hr, 82 g (1.0 mol) of bromine in 150 ml of absolute methylene chloride was added dropwise with strong stirring. The solution was continuously stirred at −60° for 1 hr, and then 80 g (0.71 mol) of potassium *tert*-butoxide was added in 5- to 10-g portions while the temperature was maintained at −55 to −60°. When addition of the potassium *tert*-butoxide was complete, the solution was stirred at −60° for an additional hour. During the addition, the mixture was strongly stirred and the nitrogen stream increased. The temperature was then raised to −50 to −45°, and the mixture was stirred for 3 hr at this temperature. Then the temperature was raised to −10° within 1 hr and the reaction mixture poured into 750 ml of water and 12.5 ml of acetic acid. The emulsion which formed was treated with 25 g of magnesium sulfate, and a clear phase separated. The organic phase was separated and the aqueous layer saturated with sodium chloride and extracted with a total of 750 ml of ether in three portions. The combined extracts were washed with three 300-ml portions of water, two 300-ml portions of 5% sodium bicarbonate solution, and again with water (one 300-ml portion) and dried over magnesium sulfate. Removing the solvent at room temperature afforded a residue which was then distilled under vacuum. The bromocyclooctatetraene distilled at 26–28° (2×10^{-6} mm): yield 70 g (0.38 mol, 76%); nmr (neat) τ 4.5 (m, 7).

Reaction of I with Tetracyclone at Room Temperature for 70 Hr.—Approximately 200 ml of anhydrous ether was allowed to stand over Na–K alloy on the vacuum line, degassed twice, and then distilled onto fresh Na–K alloy. For the reaction a specially designed flask was used which had a side arm with a 2-ml bulb to hold the bromocyclooctatetraene. After this flask had been flamed and flushed with nitrogen, 1.83 g (0.01 mol) of bromocyclooctatetraene was placed in the side-arm bulb which was then sealed. Potassium *tert*-butoxide (1.12 g, 0.01 mol) and 3.84 g (0.01 mol) of tetracyclone were placed in the bottom of the flask along with a magnetic stirring bar; the flask was immediately placed on the vacuum line and evacuated for a few minutes, and the potassium *tert*-butoxide was heated gently and briefly with a heat gun to remove any moisture present. The ether was then distilled into the flask and the flask sealed at the neck. The ether was allowed to warm to room temperature (25.0 ± 0.1°) in a thermostatically controlled constant temperature bath and the flask tilted to introduce the bromocyclooctatetraene. The flask was kept in the constant-temperature bath and the mixture allowed to react with stirring for 70 hr; the flask was opened and the mixture transferred to a separatory funnel and washed with 100 ml of water. This water wash was separated and washed with 100 ml of ether, and the ether was added to the original mixture. The combined ether solutions were washed successively with 150-ml portions of water until the wash water was clear (only one wash usually required), 150 ml of 10% HCl, and twice more with 150 ml of water. The solution was dried over anhydrous magnesium sulfate, the ether evaporated, and the residue dissolved in carbon tetrachloride and chromatographed on a 45 cm × 4.5 cm silica gel column using carbon tetrachloride as eluent. Evaporation of the carbon tetrachloride afforded a white crystalline material which was recrystallized from glacial acetic acid: yields for the three separate runs were 3.66, 3.67, and 3.67 g (0.0079 and 0.0080 mol, 79.9 ± 0.1%); mp 246° (lit.[2] 241–242°); nmr (CCl_4) τ 2.81–3.31 (A_2B_2 multiplet, 20, ArH), 3.70 and 4.12 (doublet of AB quartet, 2, vinyl adjacent to benzo ring $H_{5,10}$), and 3.92 and 4.30 (high-field doublet of AB quartet superimposed on a singlet at 3.92, 2, vinyl $H_{6,9}$; 2, vinyl $H_{7,8}$).

Anal. Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 93.98; H, 5.80.

Reaction of I with Tetracyclone at 30° for 70 Hr.—The reaction as described above using the same proportions of reactants was carried out with the tetracyclone present initially (*t* 0.0); the temperature was maintained at 30.0 ± 0.1° by a thermostatically controlled constant-temperature bath for the entire reaction time of 70 hr. The yields for the three separate runs were 4.16, 4.17, and 4.18 g (0.0091, 0.0091, and 0.0091 mol, 90.9 ± 0.1%).

Room-Temperature Kinetic Study of the Reaction of I with Tetracyclone.—The kinetic study was performed by setting up the reaction in the manner described below, but allowing various time intervals to elapse between the addition of bromocyclooctatetraene and the addition of tetracyclone. The ether was prepared in the same manner as described above. The reaction vessel used throughout this study consisted of a specially designed 500-ml flask which had two side arms; one side arm had

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[6] We thank the referees for suggesting this study.

[7] R. Huisgen, private communication.

[8] M. V. Sargent, private communication.

a 2-ml bulb to hold the bromocyclooctatetraene, while the other side arm had a larger bulb to hold the tetracyclone. The tetracyclone (3.86 g, 0.01 mol) was placed in the larger bulb and the bulb sealed, except for the *t* 0.0 runs when the tetracyclone was placed in the bottom of the flask. The bromocyclooctatetraene (1.83 g, 0.01 mol) was placed in the smaller bulb which was also sealed. The potassium *tert*-butoxide (1.12 g, 0.01 mol) was placed in the bottom of the flask along with a magnetic stirring bar[4] and the flask immediately placed on the vacuum line and evacuated. The potassium *tert*-butoxide was heated briefly and gently with a heat gun, the flask allowed to cool, and the ether distilled over. The flask was sealed at the neck and placed in a thermostatically controlled constant-temperature bath at 25.0 ± 0.1°, and then the bromocyclooctatetraene was added to the potassium *tert*-butoxide–ether solution. The bromocyclooctatetraene was allowed to react with the base for the prescribed length of time as indicated in Table I; then the tetracyclone was introduced; and the mixture allowed to react for exactly 30 min. The flask was opened and the mixture treated as above. The results obtained were (*t* 0.0) one yield of 0.93 g (20.3%), two of 0.94 g (20.5%), and two of 0.95 g (20.7%); (*t* 5.0) two yields of 0.65 g (14.2%) and three of 0.66 g (14.4%); (*t* 15.0) two yields of 0.37 g (8.1%) and three of 0.38 g (8.3%); (*t* 30.0) one yield of 0.25 g (5.5%), two of 0.26 g (5.7%), and two of 0.27 g (5.9%); (*t* 45.0) one yield of 0.13 g (2.8%) and four of 0.14 g (3.1%); (*t* 60.0) two yields of 0.07 g (1.5%), two of 0.08 g (1.7%), and one of 0.09 (2.0%); (*t* 90.0) two yields of 0.03 g (0.7%), one of 0.04 g (0.9%), and two of 0.05 g (1.1%); (*t* 120.0) only trace amounts were obtained in all five cases. For three runs at *t* 30.0, all material was recovered and examined. The product (0.25, 0.26 and 0.26 g, 0.054 and 0.057 mol, 5.4 and 5.7%) and the unreacted tetracyclone (3.10, 3.10, and 3.12 g, 0.806 and 0.811 mol, 80.6 and 81.1%) were eluted from the chromatography column with carbon tetrachloride (the product is eluted first), and then the column was stripped by elution with acetone. Evaporation of the acetone and tlc on a silica gel plate using 3:1 carbon tetrachloride–acetone showed two main bands and a number of lesser ones. The two main bands were separately extracted, filtered, and subjected to nmr and mass spectroscopy; they proved to be *tert*-butoxycyclooctatetraene[2] and cycloocta[*b*]naphthalene.[2]

Various Temperature Kinetic Studies of the Reaction of I with Tetracyclone.—The reaction as described above using the same proportions of reactants was carried out with the tetracyclone present initially (*t* 0.0) but keeping the reaction mixture at the temperatures indicated below for the reaction period of 30 min. Quintuplicate runs were made with the temperature maintained at 30.0 ± 0.1° (just below the reflux temperature of ether) by means of a thermostatically controlled constant-temperature bath. Yields for this reaction were three of 1.71 g (37.3%) and two at 1.72 g (37.5%). On a separate set of determinations the reaction mixture was kept in a thermostatically controlled constant-temperature bath at 0.0 ± 0.1° for the 30-min reaction period. Yields for this reaction were three of 1.20 g (26.2%) and two of 1.21 g (26.4%).

Low-Temperature Kinetic Study of the Reaction of I with Tetracyclone.—The reaction as described above using the same proportions of reactants was carried out with the temperature of the thermostatically controlled constant-temperature bath maintained at 0.0 ± 0.1°, adding the tetracyclone at different time intervals after the bromocyclooctatetraene was added to the base and allowing the reaction to proceed after the addition of the tetracyclone for exactly 30 min. The results obtained were (*t* 0.0) three yields of 1.20 g (26.2%) and two of 1.21 g (26.4%); (*t* 5.0) one yield of 0.90 g (19.6%), three of 0.91 g (19.8%), and one of 0.92 g (20.0%); (*t* 15.0) one yield of 0.51 g (11.1%), two of 0.52 g (11.3%), and two of 0.52 g (11.6%).

Registry No.—I, 4514-69-6; tetracyclone, 479-33-4; bromocyclooctatetraene-1,3,5,7, 7567-22-8; 1,2,3,4-tetraphenylbenzocyclooctatetraene, 4514-72-1.

Acknowledgments.—We thank Professors Huisgen and Sargent for making their procedure for the preparation of bromocyclooctatetraene available to us, and, Badische Anilin- & Soda-Fabrik, A.-G., for a generous gift of cyclooctatetraene.

Friedel–Crafts Cyclialkylations and Bicyclialkylations with Diphenylalkyl Chlorides[1]

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Cyclialkylation of 1-chloro-4,5-diphenylpentane (**1a**) by $AlCl_3$ produced 1-benzyltetralin (**2a**) and no 2-phenylbenzosuberane, showing the preference of six-ring formation over seven-ring formation. No products expected to result from initial rearrangement of the primary chloride to a secondary carbonium ion preceding cyclialkylation were found, *e.g.*, no 1-benzyl-3-methylindan or 1-methyl-3-phenyltetralin. A second major product was found to be 2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**10a**), which is formed from **2a** by hydride abstraction and bicyclialkylation. Similar treatment of 1-chloro-2-methyl-4,5-diphenylpentane (**1b**) with $AlCl_3$ gave 1-benzyl-3-methyltetralin (**2b**) and 1-methyl-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**10b**); more extensive bicyclialkylation of **2b** to **10b** was found, in line with the greater ease of abstraction of a tertiary hydride ion from **2b**. Two other products from **1b** were 1-benzyl-3,3-dimethylindan (**7b**) and 1,1-dimethyl-3-phenyltetralin (**8b**), resulting from initial rearrangement of the primary chloride to a tertiary carbonium ion preceding cyclialkylation.

In an earlier publication[3] we described the cyclialkylation of 1-chloro-3,4-diphenylbutane to yield 2-phenyltetralin as the almost-exclusive product, thus demonstrating the preference for six-membered ring (tetralin) formation over five-membered ring (indan) formation, either directly or *via* rearrangement to a secondary carbonium ion intermediate. We remarked then that interesting tests for competing direct cyclialkylations and those involving rearrangements of primary phenylalkyl chlorides to secondary and tertiary carbonium ion intermediates would be provided by studies of reactions of 1-chloro-4,5-diphenylpentane (**1a**) and 1-chloro-2-methyl-4,5-diphenylpentane (**1b**) with aluminum chloride. The present paper describes such studies.

Possible cyclialkylations, and rearrangements followed by cyclialkylations, of these phenylalkyl chlorides are outlined in Scheme I. The numbers over the arrows refer to the ring size produced in the cyclialkylation step.

Treatment of 1-chloro-4,5-diphenylpentane (**1a**) with aluminum chloride in petroleum ether or carbon di-

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(1) (a) Part XXV of the series, "New Friedel-Crafts Chemistry." Part XXIV: A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **36**, 1040 (1971). (b) Generous support of this research, including a postdoctoral fellowship for A. A. Khalaf, by the Robert A. Welch Foundation, is gratefully acknowledged.

(2) On leave of absence from the Chemistry Department, Assiut University, Assiut, U. A. R.

(3) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **31**, 89 (1966).