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.

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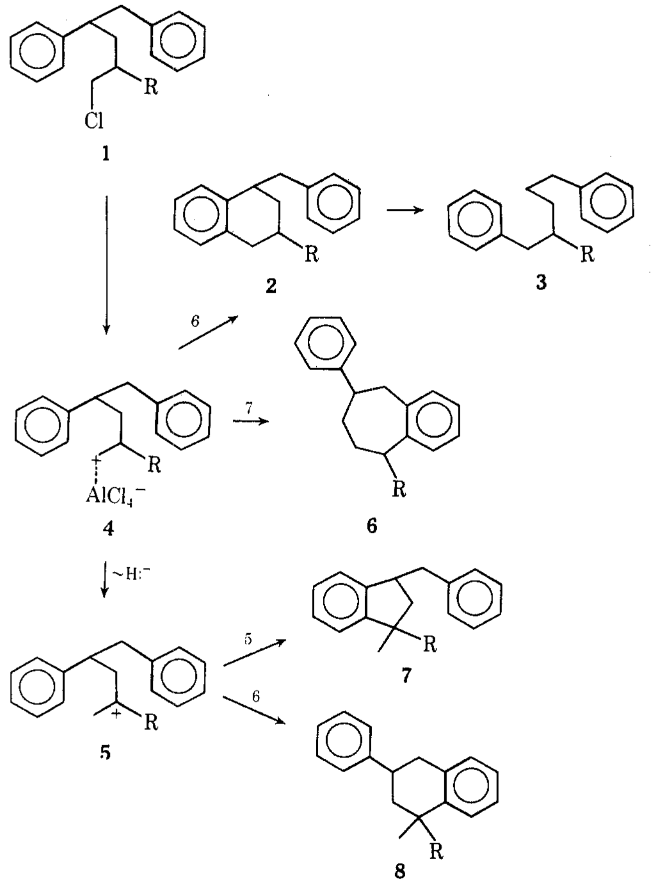
(1) (a) Part XXV of the series, "New Friedel-Crafts Chemistry." Part XXIV: A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **36**, 1040 (1971). (b) Generous support of this research, including a postdoctoral fellowship for A. A. Khalaf, by the Robert A. Welch Foundation, is gratefully acknowledged.

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

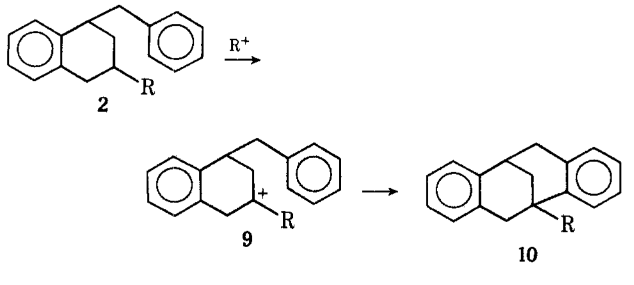
(3) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **31**, 89 (1966).

Scheme I



a series, R = H
b series, R = Me

sulfide solution at room temperature gave 1-benzyltetralin (**2a**) as the major product and some 1,5-diphenylpentane (**3a**), presumably formed from **2a** by dealkylation at the tertiary carbon, followed by hydride exchange (Table I). No 2-phenylbenzosuberane (**6a**), 1-benzyl-3-methylindan (**7a**), or 1-methyl-3-phenyltetralin (**8a**) could be detected, but another product was identified as 2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**10a**). This is produced from 1-benzyltetralin (**2a**) by hydride abstraction followed by bicyclialkylation (**2a** → **9a** → **10a**). When the reaction was carried out in petroleum ether at 70° for 2.5 hr, the amount of **2a** decreased and the amount of **10a** increased, as did also the amount of 1,5-diphenylpentane. No **6a**, **7a**, or **8a** were produced, however.



a series, R = H
b series, R = Me

Treatment of 1-chloro-2-methyl-4,5-diphenylpentane (**1b**) with aluminum chloride in petroleum ether or carbon disulfide at room temperature gave a more complex mixture of products, including 1-benzyl-3-methyltetralin (**2b**), 1-benzyl-3,3-dimethylindan (**7b**), 1,1-dimethyl-3-phenyltetralin (**8b**), 1-methyl-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene (**10b**), and 2-methyl-1,5-diphenylpentane (**3b**, Table I). No 1-methyl-4-phenylbenzosuberane (**6b**) could be detected. The ratio of **10b**/**2b** was much higher than the ratio of **10a**/**2a** produced under similar reaction conditions, reflecting the greater ease of abstracting a hydride ion from the tertiary C-3 carbon of **2b** than from the corresponding secondary carbon of **2a**. The formation of the rearranged cyclialkylation products **7b** and **8b** may also be attributed to the greater driving force for rearrangement of the intermediate primary complex **4b** to the tertiary carbonium ion **5b**, rather than to the secondary carbonium ion **5a**. The more facile formation of a five-membered ring by an intermediate tertiary carbonium ion is also a factor; this has been noted before.[3]

The intermediacy of **2a** and **2b** in the formation of **10a** and **10b** from **1a** and **1b** was confirmed by treating **2a** and **2b** separately with aluminum chloride. The major products, as expected, were as follows: from **2a**, **10a** and **3a**; from **2b**, **10b** and **3b**. No products corresponding to structures **7** and **8** were found.

The 1-chloro-2-methyl-4,5-diphenylpentane (**1b**) used as starting material in the cyclialkylations and bicyclialkylations reported here was a mixture of diastereomers. In order to examine the possibly different behaviors of the individual diastereomers toward cyclialkylation and bicyclialkylation, we have obtained them, as well as the individual diastereoisomeric benzyl tetralins (**9b**), by stereoselective syntheses. The results from these investigations will be reported subsequently.

Experimental Section[4]

1-Chloro-4,5-diphenylpentane (1a).—γ-Chlorobutyrophenone (Aldrich) was treated with benzylmagnesium chloride in dry ether. The reaction mixture was worked up in the usual way and the crude product alcohol was catalytically hydrogenated at low pressure with Pd/C in glacial acetic acid containing perchloric acid to give the title compound: bp 164–165° (2 mm); $n^{25}{}_{\mathrm{D}}$ 1.5572; mass spectrum (70 eV) m/e 258–260 molecular ion; ir compatible with the structure; nmr (CCl$_4$) δ 1.3–1.8 (m, 4 H, CH$_2$CH$_2$), 2.75 [broad s, 3 H, PhCH$_2$CH(Ph)], 3.15 (t, 2 H, J = 7 Hz, CH$_2$Cl), and 6.8–7.2 ppm (m, 10 H, aromatic); mass, calcd for $C_{17}H_{19}{}^{35}Cl$, 258.1175 (found, 258.1170).

1-Chloro-2-methyl-4,5-diphenylpentane (**1b**).—2-Methyl-4,5-diphenylpent-1-ene-5-one was prepared from deoxybenzoin and methallyl chloride by a known procedure[5] and reduced by a modified[3] Wolff–Kishner method to 2-methyl-4,5-diphenylpent-1-ene. Hydroboration, followed by treatment with NaOH–H$_2$O$_2$,[6] gave 2-methyl-4,5-diphenylpentan-1-ol: bp 156–170° (0.6 mm); $n^{25}{}_{\mathrm{D}}$ 1.5580 (a mixture of diastereomers); nmr (CCl$_4$) δ 0.55–0.85 (m, 3 H, CH$_3$), 1.1–1.9 [m, 3 H, C**H**$_2$C**H**(CH$_3$)], 2.65–2.85 [broad s, 3 H, PhCH$_2$CH(Ph)], and 2.95–3.25 ppm (m, 3 H, CH$_2$OH) (the breadth of the peaks is attributable to

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[4] Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. and by A. Bernhardt, Mülheim, Germany. The nmr spectra were determined in CCl$_4$ on a Varian A-60 instrument with TMS as internal standard. Analytical glpc was performed using a Varian Hy-Fi Model 600-D instrument; preparative glpc separations were made with a Wilkens A-700 (Autoprep) instrument. Infrared spectra were recorded on a Beckman IR-5A instrument.

[5] C. M. Suter and A. W. Weston, *J. Amer. Chem. Soc.*, **64**, 534 (1942).

[6] H. C. Brown and B. C. Subba Rao, *ibid.*, **81**, 6433 (1955).

TABLE I

PRODUCTS FROM CYCLIALKYLATION AND BICYCLIALKYLATION OF DIPHENYLALKYL CHLORIDES WITH ALUMINUM CHLORIDE[a]

Diphenylalkyl chloride	Solvent	Temp, °C	Time, hr	Products, %[b]				
				2a	**3a**	**7a**	**8a**	**10a**
1-Chloro-4,5-diphenylpentane (**1a**)	Petroleum ether[c]	25	2.5	47	36	0	0	15
	Petroleum ether[c]	70	1.0	21	51	0	0	27
	CS_2[e]	25	2.5	76	12	0	0	10
				2b	**3b**	**7b**	**8b**	**10b**
1-Chloro-2-methyl-4,5-diphenylpentane (**1b**)	Petroleum ether[d]	25	2.5	9	10	16	19	39
	CS_2[e]	25	2.5	(5)[f]	11	26	(12)[f]	38

[a] Reactants proportions, RCl-$AlCl_3$-solvent = 1 g:0.25 g:5 ml. [b] Relative amounts of products distilling in the diphenylalkane range; about 50% of reaction products were in the monophenylalkane range, owing to dephenylation. The relative amounts were determined by glpc; totals do not add up to 100% because small amounts of known and unidentified products are not included in the table. [c] Glpc analysis: 8 ft × 0.25 in. XF-1165 (30%) on 60–80 mesh Chromosorb W column operated at 230–240° with helium carrier gas at 120 cc/in. [d] Glpc analysis: 16 ft × 0.125 in. DEGA (25%) on 45–60 mesh Chromosorb W column operated at 210° with nitrogen carrier gas at 30 psi. [e] Glpc analysis: 6 ft × 0.25 in. SE-30 silicone gum rubber on 42–60 mesh firebrick column operated at 220° with helium carrier gas at 40 psi. [f] These two products were not resolved by the glpc analysis; the proportion is assumed to be similar to that found in the reaction carried out in petroleum ether, where resolution was successful.

the presence of both diastereomers); ir (neat) 3330 cm^{-1} (broad, OH). The mass spectrum (70 eV) showed no parent peak.

Anal. Calcd for $C_{18}H_{22}O$: C, 85.04; H, 8.66; O, 6.30. Found: C, 84.80; H, 8.54; O, 6.42.

The alcohol was converted to the title compound using a 2:1 molar ratio of thionyl chloride in pyridine, refluxing at 100° for 1 hr: bp 172–174° (1.5 mm); nmr (CCl_4) δ 0.6–0.9 (m, 3 H, CH_3), 1.1–1.9 [m, 3 H, $CH_2CH(CH_3)$], 2.6–2.9 [broad s, 3 H, $PhCH_2CH(Ph)$], and 3.0–3.3 ppm (m, 2 H, CH_2Cl) (the breadth of the peaks is attributable to the presence of both diastereomers); mass spectrum (70 eV) *m/e* 272–274 molecular ion (weak).

Anal. Calcd for $C_{18}H_{21}Cl$: Cl, 12.99. Found: Cl, 12.67.

Reaction of the Diphenylalkyl Chlorides with Aluminum Chloride.—The diphenylalkyl chlorides, dissolved in petroleum ether (bp 60–70°) or carbon disulfide, were added dropwise to anhydrous aluminum chloride suspended in the same solvent. The mixtures were stirred magnetically in a flask to which was attached a reflux condenser protected by a calcium chloride drying tube, either at room temperature for 2.5 hr or, in some experiments with petroleum ether as solvent, at reflux for 1 hr. The proportions of the diphenylalkyl chlorides-$AlCl_3$-solvent were 1 g:0.25 g:5 ml. The reaction mixtures were decomposed with water and worked up in the usual way. The hydrocarbon products were distilled and analyzed by glpc (see Table I).

The bicyclialkylation product, 2,3:6,7-dibenzobicyclo[3.3.1]-nona-2,6-diene (**10a**), was isolated by preparative glpc, using an 8 ft × 0.25 in. XF-1165 column operated at 230–240° with helium carrier gas at a rate of 120 cc/min, mp 73.5–75° (lit.[7] mp 78°). It was identical with the product obtained by cyclialkylation of 1-benzyltetralin as described below.

The homologous product **10b** was isolated from the bicyclialkylation reaction of **1b** (20 g) carried out in carbon disulfide (Table I). After decomposition of the reaction mixture with water in the usual way, the organic products were distilled and the fraction, 4.5 g, bp 145–154° (0.5–1.0 mm), was subjected to chromatography on a 110 × 3 cm column of silica gel (E. Merck, type G, pH 7), eluting with pentane. The white crystalline material obtained from the middle elution fractions was sublimed *in vacuo* to yield 1.3 g of 1-methyl-2,3:6,7-dibenzobicyclo-[3.3.1]nona-2,6-diene (**10b**) as white, fluffy crystals: mp 86.5–89°; nmr (CCl_4) δ 1.48 (s, 3 H, CH_3), 1.8–2.0 (broad, spiked s, 2 H, bridge CH_2), 2.5–3.5 (m, 5 H, benzylic), and 6.7–7.4 ppm (m, 8 H, aromatic); mass spectrum (70 eV) *m/e* 234 (molecular ion), 219 (base peak).

Anal. Calcd for $C_{18}H_{18}$: C, 92.31; H, 7.69. Found: C, 92.33; H, 7.71.

This product was identical with the product obtained by cyclialkylation of 1-benzyl-3-methyltetralin as described below and with the product obtained by sulfuric acid catalyzed dehydration of 4-benzyl-2-methyl-1-tetralol, in work which will be reported separately.

1-Benzyltetralin (**2a**).—α-Tetralone (Aldrich) was treated with benzylmagnesium chloride in dry ether. The crude carbinol was hydrogenated at low pressure with Pd/C catalyst in glacial acetic acid containing perchloric acid. The title compound had bp 143–144° (1.4 mm), $n^{25}D$ 1.5813 [lit.[8] bp 145–146° (0.6 mm)]; ir, nmr, and mass spectra were all consistent with the title formulation.

1-Benzyl-3-methyltetralin (**2b**).—3-Methyl-1-tetralone was synthesized starting with phenylacetone and ethyl bromoacetate as described in the literature:[9] bp 67–68° (0.17 mm) [lit.[9b] bp 132–136° (14 mm)]; $n^{24}D$ 1.5562; ir (film) 1690 cm^{-1} (C=O); nmr (CCl_4) δ 1.03 (d, 3 H, *J* = 7.0 Hz, CH_3), 1.90–3.00 (cluster of multiplets, 5 H, all other nonaromatic), 7.00–7.50 and 7.80–7.98 ppm (both multiplets, 3 H and 1 H, respectively, aromatic).

Reaction of the latter ketone with benzylmagnesium chloride followed by hydrogenation of the resulting 1-benzyl-3-methyl-1-tetralol with hydrogen and Pd/C in glacial acetic acid containing a little perchloric acid[10a] gave the desired 1-benzyl-3-methyltetralin: bp 115–116° (0.2 mm); $n^{23}D$ 1.5694; nmr (CCl_4) δ 0.92 and 0.98 (both doublets in a ratio of 4:1 totaled 3 H, *J* = 6.8 Hz, CH_3), 1.25–3.45 (unresolved, 8 H, all other nonaromatic), and 6.90–7.30 ppm (m with sharp singlet at 7.12, 9 H, aromatic).

Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.29; H, 8.61.

It is to be noted that both glpc and nmr analysis showed the latter hydrocarbon to be a mixture of two diastereomers[10b] in a ratio of about 4:1.

Bicyclialkylation of 1-Benzyltetralin and 1-Benzyl-3-methyltetralin with Aluminum Chloride.—To 5 mmol of the hydrocarbon in 10 ml of carbon disulfide was added 2.5 mmol of anhydrous $AlCl_3$, and the mixture was stirred magnetically at room temperature. After various time intervals, 0.5-ml samples of the solution were withdrawn by pipet and analyzed by glpc.[11] After 56 hr, conversion of both tetralins was about 90% complete. The products were as follows: from 1-benzyltetralin, **10a** (80%), **3a** (20%); from 1-benzyl-3-methyltetralin, **10b** (78%), **3b** (22%).

Synthesis of Authentic Compounds for Comparison or Identification with Products of Cyclialkylations and Bicyclialkylations. 2,3:6,7-Dibenzobicyclo[3.3.1]nona-2,3-diene (**10a**) was synthesized by the procedure of Stetter and Reischl,[7] starting with α,γ-diphenylglutaric acid. In the second step, the reduction of the diketone was accomplished in better yield (90%) by catalytic hydrogenation using 5% Pd/C in glacial acetic acid containing perchloric acid,[10a] rather than by Wolff-Kishner reduction (56.6% yield reported[7]). Our product had mp 74–76° (lit.[7] mp 78°); its ir and nmr spectra were consistent with the assigned structure.

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[7] H. Stetter and A. Reischl, *Chem. Ber.*, **93**, 791 (1960).

[8] H. Beyer and H. Schulte, *Ber.*, **74B**, 98 (1941).

[9] (a) S. Natelson and S. P. Gottfried, *J. Amer. Chem. Soc.*, **61**, 970 (1939); (b) F. Weygand and K. Schroder, *Ber.*, **74**, 1844 (1941).

[10] (a) R. M. Roberts, G. A. Ropp, and O. K. Neville, *J. Amer. Chem. Soc.*, **77**, 1764 (1955). (b) These two diastereomers were synthesized by R. M. Roberts and K.-H. Bantel using a sequence of standard procedures which will be published separately.

[11] Products from 1-benzyltetralin were analyzed on a 5 ft × 0.125 in. SE-30 silicone gum rubber (5%) on 42–60 mesh firebrick column operated at 220° with nitrogen carrier gas at 5 psi. Products from 1-benzyl-3-methyltetralin were analyzed on a 10 ft × 0.125 in. Bentone-34 (5%) and SE-52 (5%) on Chromosorb W column operated at 210° with nitrogen carrier gas at 60 psi.

1,5-Diphenylpentane (**3a**) was prepared by reaction of 4-phenylbutylmagnesium bromide with benzaldehyde, followed by catalytic hydrogenolysis of the carbinol,[10a] bp 83–87° (0.1 mm) (lit.[12] bp 190–192°). The product was purified by preparative glpc (16 ft × 0.25 in. 30% XF-1150 column with helium carrier gas at 190°, 40 psi); the ir and nmr spectra were consistent with the assigned structure.

2-Methyl-1,5-diphenylpentane (**3b**) was synthesized starting with phenylacetone and 3-phenylpropylmagnesium bromide. The 2-benzyl-5-phenyl-2-pentanol so obtained had bp 110° (0.12 mm) and ir and nmr spectra consistent with its formulation. The alcohol was dehydrated by means of pyridine and phosphorus oxychloride,[13] and the mixture of alkene isomers was catalytically hydrogenated as before[10a] to give the title hydrocarbon, bp 102–108° (0.14 mm). It was purified by preparative glpc (16 ft × 0.25 in. 30% XF-1150 column with helium carrier gas at 190°, 40 psi): ir (film) 3080 (m), 2950 (s), 1500 (s), 1462 (s), 1390 (m), 1098 (m), 1035 (m), 912 (m), 745 (s), 700 cm^{-1} (s); nmr (CCl_4) δ 0.86 (d, 3 H, J = 6.0 Hz, CH_3), 1.11–2.00 (m, 5 H, $C^4H_2C^3H_2C^2H$), 2.52 (apparent q, 4 H, benzylic), and 7.10 ppm (s, 10 H, aromatic); mass spectrum (70 eV) m/e (rel intensity) 77 (5), 91 (100), 105 (15), 149 (9), 147 (30), 238 (22), 239 (5), 240 (0.7); mass, calcd. for $C_{18}H_{22}$, 238.1721 (found, 238.1728).

2-Phenylbenzosuberane (**6a**).—2-Benzosuberone[14] reacted with phenylmagnesium bromide to give 2-phenyl-2-benzosuberol: mp 82–83°; 60% yield; ir (Nujol) 3500 (s), 1495 (s), 1460 (s), 1390 (s), 1180 (m), 1100 (m), 1075 (s), 1015 (s), 778 (m), 725 (s), and 702 cm^{-1} (s); nmr (CCl_4) δ 1.66 [s, 1 H, OH (exchangeable with D when treated with D_2O)], 1.50–2.18 (m, 4 H, C^3H_2-C^4H_2), 2.74–2.98 (m, 2 H, C^5-benzylic), 2.88–3.60 (AB pattern, 2 H, J = 14 Hz, C^1H_2), 6.93–7.63 (m, 4 H, aromatic), and 7.10 ppm (s, 5 H, aromatic). 2-Phenyl-2-benzosuberol was subjected to catalytic hydrogenolysis as before[10a] and the product 2-phenylbenzosuberone (**6a**) was purified by preparative glpc (20 ft × 0.25 in. 30% SE-30 silicone gum rubber column operated at 255° with helium carrier gas at 60 psi) to give a viscous oil: n^{24}D 1.5844 (lit.[15] mp 37–38°); nmr (CCl_4) δ 1.30–2.33 (m, 4 H, $C^3H_2C^4H_2$), 2.42–3.43 [m (ABC pattern), 5 H, benzylic], 7.02 (s, 4 H, aromatic), and 7.16 ppm (s, 5 H, aromatic).

1-Benzyl-3,3-dimethylindan (**7b**) was synthesized by reaction of 3,3-dimethyl-1-indanone[3] with benzylmagnesium chloride followed by catalytic reduction of the intermediate carbinol so obtained by hydrogen and Pd/C in glacial acetic acid containing a little perchloric acid:[10a] bp 180–190° (11 mm); $n^{26.8}$D 1.5672; nmr (CCl_4) δ 1.07 and 1.28 (both singlets, 6 H, gem methyls), 1.43–3.75 (unresolved, 5 H, all other nonaromatic), and 7.02–7.15 ppm (both singlets in a ratio of 5:4, 9 H, aromatic); mass, calcd for $C_{18}H_{20}$, 236.1565 (found, 236.1570).

1,1-Dimethyl-3-phenyltetralin (**8b**).—This was prepared by H_2SO_4-catalyzed cyclization of the previously obtained 2-methyl-4,5-diphenylpent-1-ene: bp 132–135° (0.27 mm); $n^{26.8}$D 1.5702; nmr (CCl_4) δ 1.30 and 1.13 (both singlets, 6 H, gem methyls), 1.84 (an apparent doublet, 2 H, C^2H_2), 2.70–3.38 [m with strong singlet at 2.90, 3 H, $CH_2CH(Ph)$], and 6.85–4.70 ppm (m with strong singlet at 7.18, 9 H, aromatic); mass, calcd for $C_{18}H_{20}$, 236.1565 (found, 236.1563).

Registry No.—**1a**, 31444-33-4; **1b**, 31444-34-5; **2b**, 31444-35-6; **3b**, 31444-36-7; **6a**, 2979-01-3; **7b**, 31489-88-0; **8b**, 31444-38-9; **10b**, 31444-39-0; 2-methyl-4,5-diphenylpentan-1-ol, 31489-89-1.

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Cyclialkylation of Phenol with 1,5-Hexadiene

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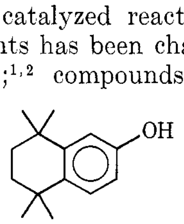
Phenol and 1,5-hexadiene (**6**) in carbon disulfide (4:1 mole ratio) at 30° react in the presence of boron trifluoride etherate to produce 5,6,7,8-tetrahydro-5,8-dimethyl-1- and -2-naphthol (**7** and **8**) and 2,5-diphenoxyhexane (**9**). A study of this reaction suggests that 5-phenoxy-1-hexene (**12**) and 2-(1-hexen-5-yl)phenol (**13**) are initially formed and react further to produce **9** and **7**, respectively. At longer reaction times, $C_{18}H_{26}O$ products are formed by reaction of **9** with **7** or $C_{12}H_{16}O$ ethers formed from **7**. Direct para alkylation by olefins **6** or **12** is excluded. The major para-alkylated product is formed from the alkylation of phenol with diether **9**.

The Lewis acid catalyzed reaction of phenol with cyclialkylating agents has been characterized by a diversity of products;[1,2] compounds **1–4** have been obtained starting with 2,5-dimethyl-1,5-hexadiene while **2** and **5** have been obtained from 2,5-dichloro-2,5-dimethylhexane.



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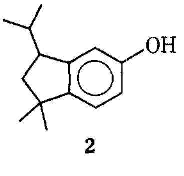

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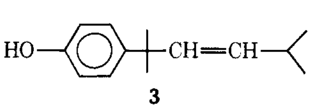

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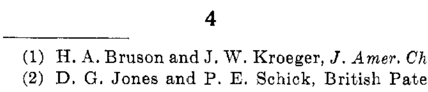

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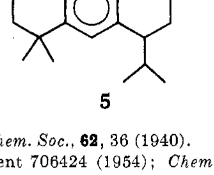

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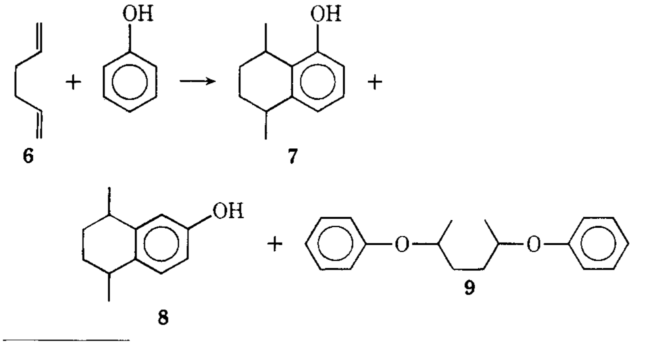
When phenol and 1,5-hexadiene (**6**) (4:1 mole ratio) at 30° reacted in the presence of boron trifluoride etherate for 3 hr, cycliadducts **7** and **8** were recovered in 27 and 8% yields, respectively, based on starting **6**. When the reaction was terminated after 15 min, **7** and diether **9** (25% yield) were the major products.[3] The



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[3] The identification of new compounds is based on ir and proton nmr spectra in addition to microanalyses: see the Experimental Section.