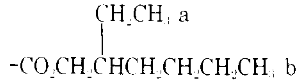
silica gel precoated aluminum plates; UV lamp development); NMR (CCl_4) δ 3.98 (m, 6 H, superposition of three doublets of OCH_2 groups), 2.5–2.0 (m, 6 H, CH of the 2-ethyl-1-hexyl group and CH of the ring), 1.67–1.10 (br signals, 30 H, ring CH_2, and esteric CH_2 groups), 0.83 (m, 18 H, superimposed triplets of the CH_2CH_3 groups); IR ($CHCl_3$) 2980 (CH_3 stretching), 2915 (CH_2 stretching), 2890–2880 (CH stretching), 1735 (C=O stretching, saturated CO_2R),[17] 1265–1000 (cyclohexane ring deformation bands);[17] *m/e* 552 (M^+).

The ^{13}C NMR spectrum of compound **4d** is composed of nine major signals corresponding to the different types of carbons, as the anticipated tenth carbon is apparently not sufficiently resolved. A definite broadening of certain signals, e.g., those centered at 30.35, 23.86, and 10.98 ppm, may be due to dynamic equilibrium between different conformations of **4d** under the conditions of measurement (25 °C). For chair–chair interconversion compound **4d** should be preferably in an axial–equatorial–equatorial (a,e,e) conformation, whereas for the energetically less likely chair–boat interconversion, all the ester groups should be equatorially disposed (e,e,e conformation). Examination of the spectrum indeed shows the presence of several narrow signals at 63.94, 31.95, 29.30, 23.40, 22.70, 19.76, and 14.47 ppm, which may be due to the presence of small amounts of the e,e,e conformer. Assignment of the major signals in the ^{13}C NMR spectrum of **4**, based on assignments in the spectrum of the starting monomer **1d**, is as follows: 10.97 (CH_3 b), 14.01 (CH_3 a), 23.86 ($CH_2CH_2CH_3$), 28.96 (CH_2CH_3 a), 30.35 (CH_2CH), 38.74 (–CH–), 67.11 (OCH_2), the designation of the a and b positions of CH_3 in the ester group being


$$\begin{array}{l}\qquad\qquad\;\; CH_2CH_3\ \text{a}\\ \qquad\qquad\;\; |\\ \text{-}CO_2CH_2CHCH_2CH_2CH_2CH_3\ \text{b}\end{array}$$

1,3,5-Cyclohexanetricarboxylates obtained from other acrylates were analyzed by the same methods.

Registry No.—**4d**, 67208-88-2; benzylpotassium, 2785-29-7; potassium, 7440-09-7; isobutyl alcohol, 78-83-1; cyclohexanol, 108-93-0; 2-ethyl-1-hexanol, 104-76-7; 1-borneol, 507-70—; 1-dodecanol, 112-53-8.

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Base-Catalyzed Alkylation of Cyclopentadiene Rings with Alcohols and Amines

Stephen S. Hirsch[1,2] and William J. Bailey*

Department of Chemistry, University of Maryland, College Park, Maryland 20742

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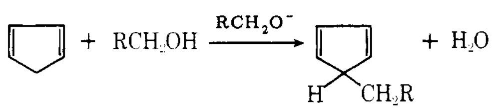
Multiple alkylations of several compounds possessing cyclopentadiene rings were accomplished by the action of alcohols in the presence of their corresponding alkoxides. Several new 1,3-dialkylindenes and 3,5-dialkyl-1,2,4-triphenylcyclopenta-1,3-dienes were synthesized. 1,2,3,4,5-Pentabenzylcyclopenta-1,3-diene was prepared for the first time. It was also demonstrated that 9-benzylfluorene resulted from the action of benzylamine and sodium amide on fluorene.

Since active methylene groups of cyclopentadienes were shown to be alkylated by alcohols and base,[3,4] a research program was undertaken to expand the scope of this reaction. In general form the reaction may be depicted as shown in eq 1, a simplified formulation which disguises informative aspects of the mechanism.[3] However, an examination of this mechanism suggested that more than one, but not necessarily all, of the unsubstituted ring carbon atoms of variously constituted cyclopentadiene moieties should be capable of substitution.



(1)

It has already been demonstrated that each hydroxyl group of certain glycols will alkylate a fluorene molecule to afford bis(9-fluorenyl)alkanes[5,6] and that benzyl alcohol will benzylate indene at both the 1 and 3 positions.[4] Douris and Mathieu,[7] however, isolated only a mixture of 1,3-dibenzylindene and 1-benzyl-3-benzalindene from treatment of indene with benzyl alcohol in the presence of sodium alkoxide or potassium hydroxide, although methanol, ethanol, and 2-propanol gave only the corresponding monoalkylated derivatives under the same conditions. Fritz et al.,[6] using less than molar equivalents of potassium hydroxide, were able to obtain a 74% yield of the dialkylated product with 2-ethylhexanol and indene and 26% yield of dialkylated product with cyclohexanol; however, only a monoalkylate derivative was obtained with 2-propanol.

It was desirable, therefore, to increase the applicability of the reaction to "multifunctional" cyclopentadienes (i.e., cyclopentadienes possessing more than one potentially active methylene group) to provide groundwork for the possible synthesis of a new class of all-hydrocarbon condensation polymers, some of which would be expected to possess a high order of thermal stability. It was further of interest to determine whether amines (which are considerably more basic than alcohols) could be similarly employed. Such a reaction would make possible alkylation by a similar route of methylene or methyl groups much less acidic than those present in cyclopentadienes.

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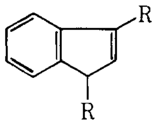
Results and Discussion

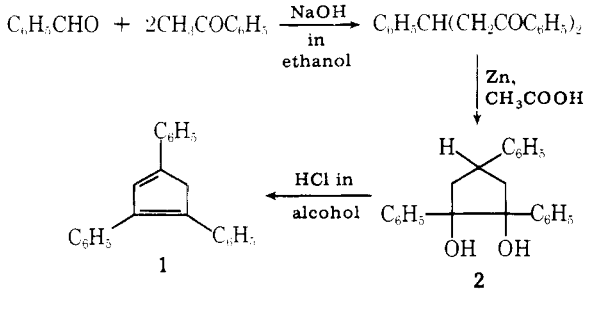
1,3-Dialkylindenes. In contrast to the work just cited[6,7] the reaction of indene with a large excess of alcohol (ethanol, 1-propanol, 2-propanol, and benzyl alcohol in separate experiments) in the presence of the corresponding sodium alkoxide in a heated pressure vessel afforded good yields of 1,3-dialkylindenes. What had previously been an isolated example of hydrocarbon difunctionality in this reaction[4] has now been shown to be quite general. Since in earlier work[4] care was taken to prove conclusively that indene was benzylated in the 1 and 3 positions but not elsewhere, it was only necessary at this time to consider the elemental analyses, boiling temperatures in relation to indene and the reported[8] 1,3-dimethylindene, and the boiling point order (diethyl < diisopropyl < di-*n*-propyl) to be reasonably certain of the structures.



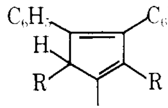
An interesting exception to the dialkylation of indene was the attempt made with methanol. Although 1,3-dimethylindene is a known stable compound,[8] bp 212 °C, none whatever could be isolated by the present method; in fact, no material boiling above 208 °C was present in the reaction product from indene, methanol, and sodium methoxide. Two fractions boiling in the range 202–208 °C were collected, however. Gas chromatographic analysis revealed the presence of two partially resolved peaks. Elemental analyses of these products afforded values corresponding to $C_{11}H_{14}$, identified as a mixture of *cis*- and *trans*-1,3-dimethylindane. Since the basic alcoholic mixture is known to reduce carbon–carbon double bonds,[3] it appears that under the conditions used methanol is capable of reducing any 1,3-dimethylindene formed to a mixture of *cis*- and *trans*-1,3-dimethylindane [reported[9] bp 202.3 °C (740.5 mm)], which would account for the two partially resolved peaks upon gas chromatography.

1,2,4-Triphenylcyclopenta-1,3-diene and the 3,5-Dialkyl-1,2,4-triphenylcyclopenta-1,3-dienes. The dialkyltriphenylcyclopentadienes were prepared by reaction of 1,2,4-triphenylcyclopenta-1,3-diene with appropriate alcohols and corresponding sodium alkoxides. The chemistry of the starting material contains much that is of interest. 1,2,4-Triphenylcyclopenta-1,3-diene (1) was prepared by the series of reported reactions[10-12] depicted in Scheme I. The first two steps are straightforward, but the conversion of the pinacol 2 to the hydrocarbon merits some discussion. Dehydration is preferred over a pinacol rearrangement, a fact contrary to many typical cases. Although the 1,2 migration would not be favored because of the attendant formation of a cyclobutane ring from a cyclopentane moiety, phenyl migration could be expected to give a stable triphenylcyclopentanone. Two possible explanations for the direction of the reaction may be proposed. First, dehydration gives the resonance-stabilized conjugated diene,[13] which would provide a driving force for this manner of reaction. A second explanation is on steric grounds. It is known that the pinacol rearrangement on ring systems is favorable only if the migrating and leaving groups lie trans to each other.[12,13] Thus, if the glycol is principally the trans isomer (that is, if the phenyl migrating group is *not* opposite the OH group), rearrangement would not be favored. It is possible that there is some 2,2,4-triphenylcyclopentan-1-one resulting from a pinacol–pinacolone rearrangement in the small amount of byproduct having a wide melting range.

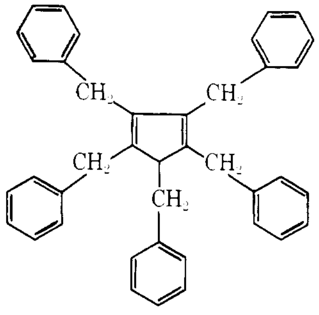
Scheme I



The 3,5-dimethyl and 3,5-di-*n*-propyl derivatives were prepared in 35 and 63% yields, respectively, from the corresponding alcohols and their alkoxides by heating with the trisubstituted cyclopentadiene 1 in a steel reaction vessel as described for the preparation of the dialkylindenes. That the compounds possess the claimed structure is indicated by the presence in the UV spectra of the longer wavelength band demonstrated in the starting material. In the alkylated products, the band suffers a slight hypsochromic shift and is decreased somewhat in intensity, presumably due to steric interference with planarity. It should be noted that in this more highly conjugated system, methanol is a suitable alkylating alcohol, in contrast to the reaction with indene.



1,2,3,4,5-Pentabenzylcyclopenta-1,3-diene. The reaction of cyclopentadiene dimer with a large excess of benzyl alcohol and sodium benzyloxide in diisopropylbenzene solvent under reflux afforded a 19% yield of pentabenzylcyclopentadiene (4).



4

The structure of this hitherto unreported hydrocarbon was established by ultimate analysis, molecular weight determination, and NMR spectroscopy. The NMR spectrum obtained in deuteriochloroform was consistent with the pentabenzylcyclopentadiene structure. Peaks at τ 2.80 (relative area = 20) and τ 3.21 (relative area = 5) were assigned to aromatic protons. The unique aromatic ring is almost assuredly the one linked ultimately to the 5-carbon atom of the five-membered ring. Its relatively high-field position suggests that it is held essentially above (or below) the planes of the nearby aromatic rings. Moreover, peaks in the range τ 5.91–6.82 had a total relative area of approximately 11, consistent with the nature and number of the nonaromatic protons in the molecule. In connection with the nonplanarity of the structure, Pauson has determined that in the related multiphenylcyclopentadienes, the aromatic rings are twisted out of plane.[16]

When similar reactions with ethanol or 1-propanol as the alkylating alcohol were attempted, only mixtures of products could be obtained. Evidence points to varying degrees of reaction, with termination prior to pentaalkylation likely due to reduction of the double bonds of the cyclopentadiene ring (see the above discussion of the attempted preparation of 1,3-dimethylindene). Such an occurrence would account for the low yield of the pentabenzyl compound as well. It should be noted that reduction of the double bonds in cyclopentadiene itself due to diminished opportunity for resonance stabilization would be favored over such a process in the other compounds of this class which have been subjected to the reaction.

9-Benzylfluorene from Fluorene and Benzylamine. During the course of this work it became of interest to determine whether amines could split out ammonia when heated with one of the acidic hydrocarbons and base, just as the alcohols lose a molecule of water. Such a process would result in similar alkylations, but since an amine plus sodium amide is much more basic a mixture than is an alcohol and its alkoxide, the former mixture should be able to alkylate much more weakly acidic molecules. It was felt that the first step in testing such a hypothesis should be alkylation by this method of one of the hydrocarbons known to be alkylated by alcohols. Accordingly, when fluorene was heated with an excess of benzylamine and some sodium amide in diisopropylbenzene solvent, ammonia was evolved and a 67% yield of 9-benzylfluorene was obtained. Although there is no conclusive evidence, it is very probable that the mechanism of this reaction is similar to that with alcohols.

Experimental Section[17,18]

1,3-Diethylindene. To a solution of 7.7 g (0.33 g-atom) of sodium metal in 150 mL of absolute ethanol[19] in a 300-mL steel reaction vessel was added 13.2 g (0.114 mol) of indene (Neville Chemical Co., 97.5% minimum purity). After the mixture was heated and rocked at 205 °C for 8 h, the reaction product was removed with the aid of 400 mL of water and 150 mL of benzene added alternately in small portions. The resulting mixture was acidified with a small amount of hydrochloric acid, and the layers were separated. After the aqueous layer was shaken with 50 mL of benzene, the extract was combined with the original organic layer. The combined organic solutions were washed with two 400-mL portions of water and then dried over potassium carbonate. After the benzene had been removed by distillation through a 6-in. Vigreux column, the residue was vacuum distilled through a 1/3 × 12-in., helix-packed column to give 12.5 g (65%) of 1,3-diethylindene: bp 136 (26 mm), 140 °C (28.5 mm); $n^{26}{}_{D}$ 1.5385. A purity of at least 95% was indicated by gas chromatography.

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.80; H, 9.54.

1,3-Di-*n*-propylindene. A mixture of 11 g (0.095 mol) of indene and a solution of 6 g (0.026 g-atom) of sodium metal reacted with 150 mL of 1-propanol[19] was treated as described for the preparation of diethylindene to give 13.5 g (72%) of 1,3-di-*n*-propylindene, bp 159.8–161.7 °C (20.5 mm), $n^{26}{}_{D}$ 1.5270, which showed a single peak when examined by gas chromatography.

Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 90.03; H, 9.89.

1,3-Diisopropylindene. This reaction was a duplicate of that for di-*n*-propylindene with the same quantities of reagents, but with 2-propanol replacing 1-propanol. Because the solubility of sodium isopropoxide in 2-propanol is fairly low, the hot alcoholic solution solidified when an attempt was made to pour it into the reaction vessel. For this reason the sodium metal was allowed to react with the alcohol in the vessel under reflux and the indene was then added. Fractionation gave 14.0 g (74%) of 1,3-diisopropylindene, bp 144.9–148.8 °C (20 mm), $n^{26}{}_{D}$ 1.5234, which likewise gave a single peak when examined by gas chromatography.

Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 90.20; H, 10.10.

1,3-Dibenzylindene. A mixture of 7.0 g (0.06 mol) of indene and a solution of 4.0 g (0.17 g-atom) of sodium metal reacted with 150 mL of benzyl alcohol[19] was treated exactly as for the diethylation of indene, except that during the workup, after acidification, the organic layer was extracted with three portions of a sodium bicarbonate solution to remove precipitated benzoic acid. Fractionation gave 7.6 g (43%) of 1,3-dibenzylindene, bp 166–173 °C (0.05–0.08 mm) [reported[4] bp 240–247 °C (5 mm)].

Reaction of Indene with Sodium Methoxide and Methanol. A mixture of 13.2 g (0.114 mol) of indene and a solution of 7.7 g (0.33 g-atom) of metallic sodium reacted with 150 mL of methanol[19] contained in a 300-mL reaction vessel was heated and rocked for 16 h at 220 °C. The workup to the distillation was exactly as described for diethylindene. Distillation without a column was carried out at atmospheric pressure to give one fraction, bp 200–205 °C, and a second fraction, bp 205–208 °C. No material was collected that distilled above 208 °C, even though the bath temperature was taken as high as 280 °C and a small amount of liquid remained in the flask (reported[6] for 1,3-dimethylindene, bp 212–214 °C). The fractions were combined and redistilled through a 1/3 × 12-in., helix-packed column at atmospheric pressure to give 2.5 g of a mixture of *cis*- and *trans*-1,3-dimethylindane, bp 202–203 °C [reported[9] bp 202.3 °C (740.5 mm)], and 1 g of residue that was collected by flash distillation. On examination by gas chromatography on a 1:6 silicone grease on Chromosorb P column at 220 °C, cut 1 gave a partially resolved doublet while cut 2 corresponded mainly to the second peak found for cut 1.

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.57; H, 9.80.

1,3,5-Triphenyl-1,5-pentanedione (Benzaldiacetophenone). To a mixture of 60.0 g (0.57 mol) of benzaldehyde and 180 g (1.50 mol) of acetophenone dissolved in 600 g of ethanol was added 150 g of 40% aqueous sodium hydroxide. After the mixture was heated under reflux for 15 min, the solution was cooled to room temperature and 600 mL of water was added, whereupon a deep orange oil settled to the bottom of the vessel. To a solution of this oil in hot ethanol was added just enough water to approach but not reach the precipitation point. When the mixture was allowed to stand, oil but not solid was deposited. The mixture was then poured with stirring into 1.5 L of water and allowed to stand overnight to produce a mass of light yellow crystals. These crystals were collected, crushed, and stirred with 250 mL of cold methanol to obtain 122 g of white product, mp 82–84 °C (reported[11] mp 85 °C). The mother liquor was evaporated to 25% of its volume, cooled, and allowed to crystallize to provide an additional 15 g (for a total 73% yield) of 1,3,5-triphenyl-1,5-pentanedione, mp 81.5–83.5 °C.

1,2,4-Triphenyl-1,2-cyclopentanediol. To a solution of 80.0 g (0.24 mol) of 1,3,5-triphenyl-1,5-pentanedione in 4000 mL of glacial acetic acid at 95 °C contained in a 5-L, three-neck flask equipped with a mercury sealed stirrer, a reflux condenser, and a thermometer dipping into the liquid, a fivefold excess of zinc dust was added periodically with stirring during 5 h. Considerable unreacted zinc remained at the end of this time. The hot mixture was filtered and the filtrate was poured into 4 gal of cold water to give a voluminous light yellow precipitate. After the solid was collected on a filter with suction and air dried, the material was dissolved in hot ethanol and reprecipitated by pouring the solution into 4 gal of cold water. The precipitate was recrystallized from 90–100 °C petroleum ether to afford 42 g (53%) of white solid 1,2,4-triphenyl-1,2-cyclopentanediol, mp 140.5–144.5 °C (reported[11] mp 142 °C).

1,2,4-Triphenylcyclopenta-1,3-diene. When a mixture of 75 mL of concentrated hydrochloric acid, 400 mL of ethanol, and 42 g (0.13 mol) of 1,2,4-triphenyl-1,2-cyclopentanediol was heated under reflux for 3 h, the precipitate (which formed after the first few minutes of boiling) was separated by filtration from the cooled mixture to give a yellow solid, mp 147.8–150.2 °C. One crystallization from the minimum quantity of boiling ethanol afforded 26.6 g (70%) of yellow crystals, mp 151.6–152.9 °C (reported[11] mp 149 °C).

Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.88; H, 6.24.

The ultraviolet spectrum taken on a solution of 1.236 ± 0.004 mg of the diene in 100 mL of isooctane gave the following results.

λ, nm	absorbance	log ε
229	0.817	4.290
244	0.746	4.250
256	0.778	4.267
338	0.723	4.236

An NMR spectrum on a saturated solution of the compound in carbon tetrachloride showed that the ratio vinyl/allylic hydrogen atoms was 2:1. A second portion of impure crystals (6.5 g, 100 °C melting range) was deposited from the mother liquor of the recrystallization step after being allowed to stand at −20 °.

3,5-Dimethyl-1,2,4-triphenylcyclopenta-1,3-diene. A mixture of 2.94 g (0.01 mol) of 1,2,4-triphenylcyclopentadiene and a solution of 4.5 g (0.20 g-atom) of metallic sodium reacted with 80 mL of methanol was heated and rocked in a steel reaction vessel at 215 °C for 17 h. After the vessel was allowed to cool and the mixture was removed with the aid of several alternate portions of benzene and water, the resulting mixture was neutralized with dilute hydrochloric acid. After the aqueous layer was extracted with three small portions of benzene, the combined extracts and benzene layer were washed with three portions of a dilute calcium chloride solution and then dried over potassium carbonate. Most of the solvent was gradually removed with a rotary evaporator (the solution became quite cold) until an appreciable amount of solid was deposited. Rapid filtering and drying gave 1.26 g of light yellow powder. (Only tar was deposited upon removal of additional solvent from the mother liquor in the same manner.) The powder was recrystallized in 83% recovery from methanol to give 1.05 g (35%) of 3,5-dimethyl-1,2,4-triphenylcyclopenta-1,3-diene, mp 122–124 °C. Recrystallization from ethanol plus a few drops of chloroform gave an analytical sample, mp 125.7–126.7 °C.

Anal. Calcd for $C_{25}H_{22}$: C, 93.12; H, 6.88. Found: C, 93.28; H, 7.05.

An ultraviolet spectrum on a solution of 1.025 ± 0.004 mg of the methylated diene in 100 mL of isooctane gave λ_{max} 230 (log ϵ 4.253) and 322 nm (log ϵ 4.220) with a slight shoulder at 253 nm.

3,5-Di-*n*-propyl-1,2,4-triphenylcyclopenta-1,3-diene. The same method described for the dimethyl derivative was followed, with an equal volume of 1-propanol instead of the methanol and heating and rocking at 210 °C for 17 h. After the solvent was removed in a rotary evaporator, 2.38 g (63%) of the light yellow powder was obtained. This material was recrystallized first from methanol, then from 1:1 methanol–ethanol and finally from methanol plus 10% ethanol to give an analytical sample of 3,5-di-*n*-propyl-1,2,4-triphenylcyclopenta-1,3-diene, mp 93.7–94.7 °C.

Anal. Calcd for $C_{29}H_{30}$: C, 92.01; H, 7.99. Found: C, 91.74; H, 7.79.

An ultraviolet spectrum on a solution of 1.015 ± 0.004 mg of the dipropyl derivative in 100 mL of isooctane gave λ_{max} 257 (log ϵ 4.230) and 315 nm (log ϵ 4.152).

1,2,3,4,5-Pentabenzylcyclopenta-1,3-diene. After 324 g (3 mol) of benzyl alcohol and 23 g (1 g-atom) of metallic sodium cut into small pieces had been reacted under a flow of prepurified nitrogen, the mixture was allowed to cool and 300 mL of diisopropylbenzene (mixed isomers) plus 6.6 g (0.05 mol) of cyclopentadiene dimer (Carbide and Carbon Chemicals Co.) was added. While the mixture was stirred under reflux for 16 h in an atmosphere of nitrogen, the liquid temperature increased from 182 °C at the commencement of boiling to a maximum of 203 °C 6 h later, during which time 8 mL of aqueous layer had collected in a Dean Stark trap filled with benzyl alcohol. The temperature did not change with further reflux. As the reaction mixture was allowed to cool, a gel of sodium benzoate deposited. The semisolid mixture was dissolved in a mixture of benzene and water. After the organic layer was washed with three portions of water and dried with sodium sulfate, the solvent was removed by distillation at atmospheric pressure until 90 mL of liquid remained in the flask. After the liquid was cooled, the pressure was lowered to 16 mm with a water aspirator and solvent was removed until no more would come over at a bath temperature of 165 °C. The residue was distilled from a Claisen flask (no column) in an oil bath at a pressure of 0.8 mm to give a forerun, fraction A, bp 250–255 °C, and fraction B, bp 255–275 °C. These two fractions could not be poured when cool. Each of these two fractions was dissolved separately in hot methanol and allowed to stand for 4 days at 2 °C. From fraction A was obtained 4 g of white solid, mp 64–71 °C, while fraction B gave 6 g of yellowish crystals, mp 67.5–74.0 °C. The total amount represented 19% of the theoretical yield based on cyclopentadiene dimer. Each sample was recrystallized from methanol to give from solid A a material with mp 69.2–75.7 °C, and from solid B a material with mp 68.5–75.7 °C. These two samples were recrystallized again from the methanol to give crystals, mp 73.5–75.5 and mp 73.2–76.0 °C, respectively. A mixture melting point of the two samples gave a value of 72.8–75.5 °C. The combined samples were recrystallized three times from methanol plus a small amount of chloroform to obtain an analytical sample, mp 74.0–74.7 °C.

Anal. Calcd for $C_{40}H_{36}$: C, 92.97; H, 7.02, mol wt, 517. Found: C, 92.96; H, 6.80; mol wt, 494.

Molecular weight determination was cryoscopic in benzene. The ultraviolet spectrum in isooctane gave a single peak with λ_{max} 276 nm (log ϵ 3.92), while the infrared spectrum confirmed that the material was a hydrocarbon.

9-Benzylfluorene from Fluorene and Benzylamine. Into a 250-mL, three-neck flask equipped with a mercury sealed stirrer, a reflux condenser, a tube for admitting prepurified nitrogen, and a thermometer extending through the condenser far enough to dip into the liquid were placed 4.15 g (0.025 mol) of fluorene (Eastman Organic Chemicals, recrystallized from acetone), 10 g (0.093 mol) of benzylamine, 1.4 g (0.035 mol) of sodium amide, and 100 mL of diisopropylbenzene. Heat was gradually applied until boiling commenced at 199 °C (flask temperature). As the reflux was continued, the color became progressively darker and the temperature attained a maximum of 204 °C 8 h later, but refluxing was continued for an additional 2 h. The copious flow of ammonia which first was liberated gradually dwindled until after 10 h only a trace was evident as indicated by moist red litmus paper held at the exit tube. After the mixture was allowed to cool overnight under the nitrogen stream, the solution was decanted and the remaining solid was dissolved by rinsing alternately with benzene and ethanol. After the combined extracts and main solution were washed with three portions of water, the brown organic layer was dried with sodium sulfate and calcium chloride. When the solvent was removed by distillation until the residue amounted to 10 mL, green crystals were deposited from the cold solution. Removal of additional solvent by distillation afforded a second crop of brown crystals. The combined samples (4.31 g, 67%) were recrystallized from hexane with the aid of decolorizing carbon to give 3.5 g of cream-colored crystals, mp 133.7–135.0 ° C. The crystallization was repeated from a small amount of toluene together with the hexane to give 3.12 g of almost white crystals, mp 134.5–136.0 °C. A mixture melting point with authentic sample of 9-benzylfluorene, mp 135.7–136.0 °C, prepared by the method of Sprinzak,[20] melted at 135.5–136.4 °C.

Registry No.—**1**, 5074-28-2; **2**, 67209-28-3; **4**, 67209-29-4; 1,3-diethylindene, 67209-30-7; ethanol, 64-17-5; sodium ethoxide, 141-52-6; indene, 95-13-6; 1,3-di-*n*-propylindene, 67209-31-8; 1-propanol, 71-23-8; sodium propoxide, 6819-41-6; 1,3-diisopropylindene, 67209-32-9; 2-propanol, 67-63-0; sodium isopropoxide, 683-60-3; 1,3-dibenzylindene, 40241-58-5; benzyl alcohol, 100-51-6; sodium benzyloxide, 20194-18-7; methanol, 67-56-1; sodium methoxide, 124-41-4; *cis*-1,3-dimethylindane, 26561-33-1; *trans*-1,3-dimethylindane, 40324-83-2; benzaldiacetophenone, 6263-84-9; benzaldehyde, 100-52-7; acetophenone, 98-86-2; 3,5-dimethyl-1,2,4-triphenylcyclopenta-1,3-diene, 67209-33-0; 3,5-di-*n*-propyl-1,2,4-triphenylcyclopenta-1,3-diene, 67209-34-1; cyclopentadiene dimer, 7313-32-8; 9-benzylfluorene, 1572-46-9; fluorene, 86-73-7; benzylamine, 100-46-9.

References and Notes

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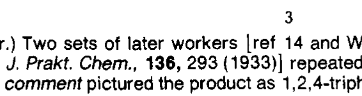
(13) Granted that dehydration occurs, there is still an unanswered question concerning the structure of the product. Newmann[12] clearly pictures (without proof) that water is split out from the diol in the "conventional" manner to give 2,3,5-triphenylcyclopenta-1,3-diene (**3**). (The original article used a different numbering system for the ring to obfuscate the situation



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even further.) Two sets of later workers [ref 14 and W. Dilthey and W. Schommer, *J. Prakt. Chem.*, **136**, 293 (1933)] repeated this preparation and *without comment* pictured the product as 1,2,4-triphenylcyclopenta-1,3-diene (**1**). It seemed logical to the present authors that the structure **1**, possessing both the conjugated stilbene and 1,4-diphenylbutadiene systems, would be favored over **3**, which merely can claim styrene contributions. To prove this contention, ultraviolet and NMR spectra were obtained. In the ultraviolet the compound showed, in addition to several other bands, a strong absorption maximum at 338 nm (log ϵ 4.236). This can be rationalized only in terms of the more highly conjugated structure **1**. Nuclear magnetic resonance, however, was the ideal tool for distinguishing between structures **1** and **3**. Formula **3** possesses (in addition to aromatic protons) two vinyl protons and one nonvinyl type. The reverse is true of structure **1**. The spectrum clearly showed that the vinyl peak was half the size of the allylic one. Thus, water is split out from the glycol to give as the final product the thermodynamically favored isomer, not the most "straightforward" one.

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(17) The authors are grateful to Drs. Leon Petrakis and Byron Arison for obtaining and interpreting NMR spectra and to Dr. Franz Kasler for obtaining the microanalyses.
(18) All melting points, boiling points, and refractive indices are corrected. The melting points were determined with a micro Kofler hot stage and a polarizing microscope. Ultraviolet spectra were taken on a model 14 Cary spectrometer at 25 °C and NMR spectra were obtained with a Varian Associates Model DP-60 nuclear magnetic resonance spectrometer.
(19) After sodium metal was dissolved in the appropriate alcohols, the resulting solutions were deliberately exposed to the atmosphere for about 1 min before further use. The reason for this step is that the mechanism (see ref 3) requires that a trace of aldehyde be present for reaction to occur.
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Stereoselective Alkylation of Cyclic Ketones by Dialkylamino- and Aryloxy(methyl)magnesium Compounds

E. C. Ashby* and G. Fred Willard

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

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Reactions of dialkylamino(methyl)magnesium compounds, CH_3MgNR_2 (where NR_2 = N-i-Pr_2, NPh_2, and $NC_5H_8Me_2$), and aryloxy(methyl)magnesium compounds, CH_3MgOR (where OR = O-2,6-i-$Pr_2C_6H_3$ and O-2,6-t-Bu_2-4-MeC_6H_2), with cyclic ketones such as 4-*tert*-butylcyclohexanone and 2,2,6,6-tetramethyl-4-*tert*-butylcyclohexanone have been studied. These reagents exhibit excellent stereoselectivity in the alkylation of these model compounds. The selectivity of the amide or aryloxy reagent has been shown to depend on the steric requirement of the aryloxy group, the steric requirement of the ketone, and the nature of the solvent.

A recent review[1] concerning the stereochemistry of organometallic compound addition to ketones points out the paucity of stereoselective alkylating agents, especially for the case of methylation of unhindered ketones. The reaction of methyllithium, in the presence of a lithium salt such as $LiClO_4$, with 4-*tert*-butylcyclohexanone to give a 94:6 axial/equatorial alcohol ratio is probably the best example of stereoselective methylation hitherto reported.[2]

Our success with the stereoselective reduction of cyclic and bicyclic ketones with dialkylaminomagnesium hydrides[3] prompted us to apply similar reasoning to the problem of stereoselective alkylation. Namely, if such hydrides are good stereoselective reducing agents by virtue of their bulky dialkylamino groups, then similar bulkiness in an alkylating agent should produce a similar effect.

We would now like to report on the reactions of dialkylamino- and aryloxy(methyl)magnesium compounds with cyclic ketones, showing their unusual stereoselective behavior as alkylating reagents.

Experimental Section

Apparatus. Reactions were performed under nitrogen at the bench using Schlenk tube techniques.[4] GLC analyses were performed on an F and M Model 720 gas chromatograph. NMR spectra were recorded on a Jeol 100 MHz Fourier transform NMR spectrometer.

Analyses. Gas analyses were carried out by hydrolyzing samples with hydrochloric acid or methanol on a standard vacuum line equipped with a Toepler pump. Magnesium was determined by EDTA titration at pH 10 using Eriochrome Black T as an indicator.

Materials. Diisopropylamine (Aldrich), 2,6-dimethylpiperidine (Aldrich), and 2,6-diisopropylphenol (Ethyl Corp.) were dried over NaOH and fractionally distilled prior to use. Diphenylamine (Fisher), *tert*-amyl alcohol (Mallinckrodt), 2,6-di-*tert*-butyl-*p*-cresol (Eastman), and triphenylphosphine (Fisher) were used without further purification. 4-*tert*-Butylcyclohexanone (Frinton) was sublimed under vacuum prior to use.

Diethyl ether and benzene were distilled from $LiAlH_4$ and $NaAlH_4$, respectively. Diphenyl ether was fractionally distilled under vacuum. Dimethylmagnesium was prepared by the reaction of dimethylmercury with excess magnesium metal (Ventron chips) at 25 °C.[5] A solution in diethyl ether was standardized by magnesium and methane analyses (Mg/CH_4 ratio was 1.00:1.98).

Preparation of 2,2,6,6-Tetramethyl-4-*tert*-butylcyclohexanone. To a 1-L three-neck flask equipped with a reflux condenser and nitrogen bubbler was added 34.5 g of sodium (1.50 mol) and 178 mL of *tert*-amyl alcohol (excess). The mixture was stirred for 24 h under reflux until no sodium remained. Then 38.8 g of 4-*tert*-butylcyclohexanone (0.252 mol) in 158.4 g of methyl iodide (excess) was added dropwise, and the refluxing was continued for 1 week. The reaction mixture was then quenched with water and extracted with diethyl ether. The ether extract was dried over $MgSO_4$ and reduced under vacuum to give 49.6 g of an oil (93.7% crude yield). The material was crystallized twice from pentane to give 8.2 g (15.5% yield), mp 77.0–78.0 °C. The solid was sublimed at 65–85 °C at 2 mmHg. The yield was 7.1 g (mp 92.0–93.0 °C). The 2,2,6,6-tetramethyl-4-*tert*-butylcyclohexanone thus prepared was hygroscopic and was handled in a glovebox: NMR ($CDCl_3$) δ 0.95 (s, 9 H), 1.10 (s, 6 H), 1.18 (s, 6 H), 1.62 (m, 5 H); IR (Nujol) 1715 cm^{-1} (C=O); MS *m/e* 210 (M^+), 153 ($M^+ - C_4H_9$). Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 79.69; H, 12.40.

Characterization of *cis*- and *trans*-1,2,2,6,6-Pentamethyl-4-*tert*-butylcyclohexanol (Axial and Equatorial). The methylation products from the reaction of 2,2,6,6-tetramethyl-4-*tert*-butylcyclohexanone and methylmagnesium bromide were collected via GLC on a 4 ft × 0.5 in 5% Carbowax 20M on Chromosorb W column. The equatorial alcohol eluted first, as will be shown later.

***trans*-1,2,2,6,6-Pentamethyl-4-*tert*-butycyclohexanol (Equatorial).** The first material collected by GLC gave the following data: mp 44.0–45.0 °C; NMR ($CDCl_3$) δ 0.85 (s, 9 H), 0.98 (s, 3 H), 1.05 (s, 6 H), 1.13 (s, 6 H), 1.26 (m, 4 H), 1.61 (m, 1 H); IR (as melt) 3620, 3500 cm^{-1} (OH); MS *m/e* 226 (M^+), 169 ($M^+ - C_4H_9$). Anal. Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.35. Found: C, 79.39; H, 13.39.

***cis*-1,2,2,6,6-Pentamethyl-4-*tert*-butylcyclohexan-1-ol (Axial).** The second material collected by glc gave the following data: mp 35.5–36.0 °C; NMR ($CDCl_3$) δ 0.85 (s, 9 H), 0.95 (s, 3 H), 1.10 (s, 6 H), 1.15 (s, 6 H), 1.20 (m, 4 H), 1.32 (m, 1 H); IR (as melt) 3620, 3500 cm^{-1} (OH); MS *m/e* 169 ($M^+ - C_4H_9$). Anal. Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.35. Found: C, 79.40; H, 13.34.

Assignment of Stereochemistry. Preliminary assignment of stereochemistry for the isomeric alcohols was based on melting point and NMR data. The axial alcohol is expected to have a lower melting point because of less steric hindrance from association due to hydrogen bonding. Also, the α-methyl group of the axial alcohol (δ 0.95) was found at a higher field in the NMR spectrum than the corresponding signal of the α-methyl group in the equatorial alcohol (δ 0.98) since the α-methyl group is shielded more by the β-methyl groups in the axial alcohol.

In order to verify the assignment of stereochemistry, a shift reagent study was conducted. NMR samples were prepared from standard solutions of pure axial and equatorial alcohols in $CDCl_3$. Small aliquots of a standard solution of Eu(fod)$_3$ (Bio-Rad) in $CDCl_3$ were added using a microliter syringe. The NMR spectra were recorded for various shift reagent/alcohol ratios, and chemical shifts due to the

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