(radical) side reaction forming benzopinacol. The reaction on a preparative scale, however, (with 5% excess methylmagnesium bromide) under the same reaction conditions gave almost 100% of the expected carbinol.

Reaction with pinacolone. Pinacolone (3,3-dimethyl-2-butanone) was prepared following the literature.[15] The fraction with b.p. 106.0–106.5° was free of side products (2,3-dimethyl-2-butene principally) as checked by gas-liquid chromatography. The same procedure was followed as for benzophenone and the reaction mixture was directly analyzed by gas-liquid chromatography (Griffin Mark II, silicone oil 550, temp. 130–145°) by comparing with known mixtures of pinacolone and *t*-butyldimethylcarbinol. Reaction on preparative scale gave 95% of the carbinol (b.p. 131°/760 mm.). With excess Grignard reagent no pinacolone was recovered. These facts show that only the normal addition reaction takes place, enolization and aldolization being negligible. When pinacolone was in excess the reaction constant was calculated using the equation[16]

$$k_3t = \frac{1}{a-b}\left[\frac{1}{b-x} - \frac{1}{b}\right] + \frac{203}{(a-b)^2}\,\mathrm{l.g}\,\frac{a(b-x)}{b(a-x)}$$

Acknowledgment. I thank Prof. H. Kwart for help with the presentation of this paper.

GHENT, BELGIUM

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[15] H. Gilman, *Org. Syntheses*, Coll. Vol. I, 451 (1932).

[16] J. Jungers *et al. Cinétique Chimique Appliquée* p. 84 (1958). Editions TECHNIP, Paris XVIème.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Addition of Benzylmagnesium Chloride and *p*-Chlorobenzylmagnesium Chloride to Phenyl Duryl Ketone[1]

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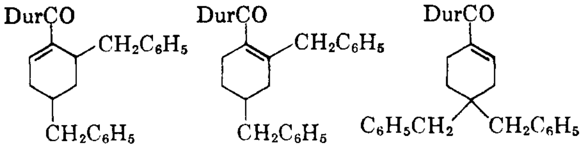
Conditions have been found under which phenyl duryl ketone reacts with two moles of benzylmagnesium chloride; the product has been shown to be duryl 2,4-dibenzyl-2,3,4,5-tetrahydrophenyl ketone. *p*-Chlorobenzylmagnesium chloride behaves in a similar way. Evidence is presented which shows that the addition of the second mole of reagent occurs before hydrolysis of the reaction mixture is begun.

Condensation of phenyl duryl ketone with benzylmagnesium chloride is known to bring about benzylation at the *para*- position of the phenyl ring.[4] If the reaction is carried out under a nitrogen atmosphere and the reaction mixture is heated under reflux for two hours, dibenzylation occurs—*i.e.*, the enolate produced by the first addition reacts with a second mole of the reagent. The dibenzyl ketone is obtained in 14% yield along with the monobenzyl ketone (15%). Chemical and spectroscopic evidence indicates that the dibenzyl ketone is a duryl dibenzyltetrahydrophenyl ketone with the double bond in conjugation with the carbonyl group. It undergoes the normal reactions of an α,β-unsaturated ketone and is reduced by lithium aluminum hydride to a duryl dibenzylcyclohexyl ketone; oxidation by alkaline hydrogen peroxide converts it into an epoxy ketone. The infrared spectrum has a carbonyl band at 1655 cm.$^{-1}$ and an olefinic band at 1638 cm.$^{-1}$ in agreement with the chemical evidence.

As the first benzyl group adds to the *para*-position of the phenyl radical, it may be assumed that one benzyl group of the dibenzyl compound is in the 4- position of the cyclohexene ring. Accordingly the most probable structures for this ketone are I, II, and III.



I II III

NMR data eliminate formula II as a possibility; the spectrum of the diaddition product (16%, carbon disulfide) has a band in the vinyl proton region at 3.66 τ that does not appear in that of the duryl dibenzylcyclohexyl ketone. This conclusion is supported by the position of the vinyl proton band in the spectrum (19%, carbon disulfide) of 1-duroylcyclohexene (3.83 τ). The ultraviolet spectrum (ethanol) has a peak at 237 mμ(ϵ 10,000) which would be expected for structures I and III but not for structure II.[5]

Dehydrogenation of the dibenzyl ketone with palladium-on-charcoal gave a diaryl dibenzyl ketone, which has been shown to have structure IV. The NMR spectrum (30%, carbon disulfide) has bands at 5.57 and 6.20 τ that can be assigned to the *ortho-* and *para*-benzylic protons, respectively.

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[2] Atomic Energy Commission Predoctoral Fellow, 1951–1953.

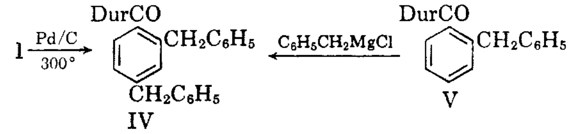
[3] Chas. Pfizer and Co. Fellow, 1960–1961.

[4] R. C. Fuson and B. C. McKusick, *J. Am. Chem. Soc.*, **65**, 60 (1943).

[5] A. E. Gillam and E. S. Stern, *Electronic Absorption Spectroscopy in Organic Chemistry*, Edward Arnold Ltd., London, 1957 (2nd ed.), p. 105.

This assignment is based on the position of the benzylic proton resonance bands in the spectra (30%, carbon disulfide) of duryl *o*-benzylphenyl ketone (5.53 τ) and duryl *p*-benzylphenyl ketone (6.05 τ). A compound having structure III would be expected to lose toluene when subjected to dehydrogenation and give duryl *p*-benzylphenyl ketone.

The same ketone (IV) has been obtained by condensing benzylmagnesium chloride with duryl *o*-benzylphenyl ketone (V). As the benzyl group in compound V is known to be in position 2 and since one benzyl group in the diaddition product is in position 4, the diaryl dibenzyl ketone is duryl 2,4-dibenzylphenyl ketone (IV). This proves that structure I is correct for the diaddition product.



Condensation of phenyl duryl ketone with *p*-chlorobenzylmagnesium chloride gave duryl 2,4-*p*-chloro benzyl-2,3,4,5-tetrahydrophenyl ketone in 14% yield; the monoaddition product, duryl *p*-(*p*-chlorobenzyl)phenyl ketone, was obtained in 10% yield.

That the addition of the second mole of Grignard reagent occurs during the hydrolysis has been suggested by the work with 1-methyl-4-bromo-4-piperidyl phenyl ketone and phenyllithium.[6] No addition during the hydrolysis has been observed in the present work. When benzylmagnesium chloride was the reagent and *p*-chlorobenzylmagnesium chloride was added to the reaction mixture just before hydrolysis, the dibenzyl ketone I was the only diaddition product formed. When the order of addition of the two Grignard reagents was reversed, only the di-*p*-chlorobenzyl ketone was isolated.

The monoaddition compound was always obtained fully aromatized, presumably because of air oxidation of the enol form of the expected dihydro compound. Under the same conditions the tetrahydro compound does not suffer dehydrogenation.

EXPERIMENTAL[7]

Condensation of benzylmagnesium chloride with phenyl duryl ketone. The directions described earlier[4] were modified so as to exclude all traces of air from the reaction mixture. The oil obtained from 0.130 mole of Grignard reagent and 6.00 g. (0.0252 mole) of ketone, when distilled under reduced pressure, gave 1.10 g. of unchanged phenyl duryl ketone. The nondistillable residue was taken up in a small amount of ether, and the solution allowed to stand at room temperature for 12 hr. The dibenzyl ketone I (0.850 g.) separated; it melted at 167–170° after recrystallization from ethanol-benzene. The ether-soluble residue was chromatographed on 200 g. of alumina. Elution with ether (5%)-cyclohexane gave 0.330 g. of product melting at 168–170°; it decolorized both bromine in carbon tetrachloride and aqueous potassium permanganate. The yield of duryl 2,4-dibenzyl-2,3,4,5-tetrahydrophenyl ketone varied from 8 to 16%. An analytical sample, crystallized from ethanol-benzene, melted at 170–171°.

Anal.[8] Calcd. for $C_{31}H_{34}O$: C, 88.10; H, 8.11; mol. wt., 422. Found: C, 88.14; H, 8.03; mol. wt. (Rast), 422.

The ether (10%)-cyclohexane fraction gave 1.04 g. (15%) of duryl *p*-benzylphenyl ketone, m.p. 127–129°. A mixed melting point with an authentic sample[4] was not depressed.

Condensation of p-chlorobenzylmagnesium chloride with phenyl duryl ketone. The procedure for the reaction of phenyl duryl ketone with benzylmagnesium chloride was used with 0.130 mole of *p*-chlorobenzylmagnesium chloride. Distillation of the oil obtained gave 0.90 g. of phenyl duryl ketone; the nondistillable oil was chromatographed on 240 g. of alumina. The ether (5%)-cyclohexane fraction gave 1.53 g. (14%) of di-*p*-chlorobenzyl ketone, m.p. 196–199°. This ketone decolorized aqueous potassium permanganate and bromine in carbon tetrachloride. The infrared spectrum shows bands for a conjugated carbonyl group (1655 cm.$^{-1}$), an olefinic double bond conjugated with a carbonyl group (1635 cm.$^{-1}$), and a 1,4-disubstituted phenyl group (805 cm.$^{-1}$). The NMR spectrum (20%, deuterochloroform) has a band in the vinyl proton region at 3.65 γ. An analytical sample, crystallized from ethanol-benzene, melted at 200–201°.

Anal. Calcd. for $C_{31}H_{32}OCl_2$: C, 75.75; H, 6.56; Cl, 14.43; mol. wt., 491. Found: C, 75.81; H, 6.48; Cl, 14.52; mol. wt., (Rast), 492.

The ether (10%)-cyclohexane fraction contained 0.815 g. (10%) of the monoaddition product, duryl *p*-(*p*-chlorobenzyl)phenyl ketone, m.p. 122–123°. The infrared spectrum shows bands for a diaryl ketone (1670 cm.$^{-1}$) and a 1,4-disubstituted phenyl group (805 cm.$^{-1}$).

Anal. Calcd. for $C_{24}H_{23}OCl$: C, 79.44; H, 6.39; Cl, 9.77. Found: C, 79.51; H, 6.40; Cl, 9.64.

Duryl 2,4-dibenzylcyclohexyl ketone. The procedure of Lutz and Hinkly for reducing α,β-unsaturated ketones was used.[9] The oil obtained by the reduction of 2.00 g. (0.00473 mole) of the dibenzyl diaddition product was taken up in methanol. The precipitate, collected on a filter, weighed 1.025 g., and melted at 110–120°. Fractional crystallization of this solid from absolute ethanol gave two ketones; the more soluble one melted at 136–137°, the less soluble at 155–156°. Only a small amount of the high-melting compound was obtained. The infrared spectra of the compounds show a band at 1690 cm.$^{-1}$ for a hindered aryl alkyl carbonyl group. Treatment of either compound with sodium ethoxide in ethanol gave a mixture melting at 110–120°, recrystallization of which from absolute ethanol yielded the low-melting compound. The low-melting ketone was submitted for analysis.

Anal. Calcd. for $C_{31}H_{30}O$: C, 87.68; H, 8.55. Found: C, 87.57; H, 8.81.

1-Duroyl-4,6-dibenzyl cyclohexene oxide. Treatment of 0.500 g. (0.00118 mole) of dibenzyl ketone I with alkaline

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(6) R. E. Lyle and H. J. Trogcianiec, *J. Org. Chem.*, **24**, 333 (1959).

(7) All melting points are uncorrected. Infrared spectra were measured with a Perkin-Elmer Model 21 B spectrophotometer by Mr. Paul E. McMahon, Mrs. Mary Verkade, and Mr. William Dalton. Nuclear magnetic resonance spectra were measured by Mr. Oliver W. Norton with a Varian high resolution spectrometer (Model V-4300 B with superstabilizer) at 60 mc. with tetramethylsilane as an internal standard.

(8) The microanalyses were carried out by Mr. Josef Nemeth, Mrs. A. S. Bay, Miss Jane Liu, and Mr. G. D. Callahan.

(9) R. E. Lutz and D. F. Hinkley, *J. Am. Chem. Soc.*, **72**, 4091 (1950).

hydrogen peroxide as described earlier[10] gave 0.479 g. (92%) of the epoxy ketone.

The infrared spectrum has a carbonyl band at 1690 cm.$^{-1}$ The analytical sample, crystallized from absolute ethanol, melted at 154–155°.

Anal. Calcd. for $C_{31}H_{34}O_2$: C, 84.89; H, 7.81. Found C, 85.09; H, 7.95.

Dehydrogenation of duryl 2,4-dibenzyl-2,3,4,5-tetrahydrophenyl ketone. A mixture of 1.00 g. (0.00237 mole) of dibenzyl ketone, I, and 0.20 g. of 10% palladium-on-charcoal was heated at 300° for 1 hr. under nitrogen. The black mass was cooled and extracted with chloroform. The solution was filtered and the solvent distilled; the colorless oil that remained was taken up in hot methanol, and water was added until the solution became cloudy. The duryl 2,4-dibenzylphenyl ketone (IV) that crystallized overnight weighed 0.436 g. (44%) and melted at 85–90°. The infrared spectrum shows bands for a hindered diaryl ketone (1668 cm.$^{-1}$), a 1,2,4-trisubstituted phenyl group (805 cm.$^{-1}$), and a monosubstituted phenyl group (695, 735 cm.$^{-1}$). The analytical sample, crystallized from methanol-water, melted at 96–97°.

Anal. Calcd. for $C_{31}H_{30}O$: C, 88.95; H, 7.22. Found: C, 88.65; H, 7.06.

Duryl o-benzylphenyl ketone. The Grignard reagent prepared from 1.89 g. (0.0150 mole) of freshly distilled benzyl chloride, 0.365 g. (0.0150 g.-atom) of ground magnesium, and 20 ml. of sodium-dried ether was added over a period of 10 min. with stirring to a solution of 3.30 g. (0.0100 mole) of duryl *o*-phenoxyphenyl ketone[11] in a mixture of 20 ml. of ether and 5 ml. of benzene. The mixture was heated under reflux for 2 hr. and decomposed in the usual way. The yellow oil obtained was dissolved in 30 ml. of cyclohexane and chromatographed on 200 g. of alumina. Elution with ether (8%)-cyclohexane gave 0.227 g. (8%) of duryl *o*-benzylphenyl ketone, m.p. 117–118°; a mixed melting point with an authentic sample[4] was not depressed.

The ether (10%)-cyclohexane fraction gave 0.500 g. of unchanged ketone followed by 0.206 g. (7%) of a ketone melting at 112–114°. The infrared spectrum shows bands for a hydrogen-bonded carbonyl group (1635 cm.$^{-1}$) and a monosubstituted phenyl group (695, 735 cm.$^{-1}$). A solution of the ketone decolorized both aqueous potassium permanganate and bromine in carbon tetrachloride. This ketone is probably the duryl 2-hydroxy-4-benzyldihydrophenyl ketone resulting from 1,6-addition of benzylmagnesium chloride and hydrolysis of the enol ether. The analytical sample, crystallized from ethanol-benzene, melted at 112–113°.

Anal. Calcd. for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 82.96; H, 7.73.

Condensation of benzylmagnesium chloride with duryl o-benzylphenyl ketone. The procedure described earlier for obtaining the fully aromatic ketone was employed.[12] The oil obtained by condensation of 0.250 mole of benzylmagnesium chloride and 1.52 g. (0.00500 mole) of duryl *o*-benzylphenyl ketone was chromatographed on 240 g. of alumina; the ether (5%)-cyclohexane fraction gave 0.365 g. of the original ketone. The second fraction (9%) contained 0.634 g. (43%) of the diaryl dibenzyl ketone, m.p. 93–95°. A mixed melting point with ketone IV was not depressed.

1-Duroylcyclohexane. The procedure is a modification of that used for the preparation of 1-benzoylcyclohexene.[13] A solution of 16.6 g. (0.0847 mole) of duroyl chloride in 50 ml. of dry methylene chloride was added, with stirring, over a 20-min. period to a suspension of 11.3 g. (0.0847 mole) of aluminum chloride in 50 ml. of dry methylene chloride. The red solution was stirred while a solution of 6.95 g. (0.0847 mole) of cyclohexene in 50 ml. of dry methylene chloride was added over a 1-hr. period. The mixture was stirred at room temperature for 12 hr. and decomposed in the usual way to give 20.6 g. of yellow solid. A 10.0-g. portion of the crude product was dissolved in 50 ml. of piperidine and allowed to stand at room temperature for 24 hr. The precipitated piperidine hydrochloride (2.22 g.) was removed by filtration. The solution was made acidic with ice cold dilute hydrochloric acid and extracted with three 100-ml. portions of ether. The ether extracts were combined, washed with two 100-ml. portions of water, and dried. Distillation of the solvent left 8.3 g. of yellow oil, which was chromatographed on 300 g. of alumina. The ether (5%)-cyclohexane fraction gave 2.25 g. (22%) of the desired ketone, m.p. 96–99°. A solution of this ketone decolorized both bromine in carbon tetrachloride and aqueous potassium permanganate. The infrared spectrum shows bands for a conjugated hindered carbonyl group (1658 cm.$^{-1}$) and a conjugated olefinic double bond (1638 cm.$^{-1}$). The ultraviolet spectrum (ethanol) has a maximum at 236 mμ (ϵ 12,100). The analytical sample, crystallized from absolute ethanol, melted at 103.1–103.5°.

Anal. Calcd. for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.34; H, 9.13.

Treatment of this ketone with 10% palladium-on-charcoal for 1 hr. at 300° under nitrogen gave phenyl duryl ketone, identified by a mixed melting point determination.

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(10) R. C. Fuson, W. R. Hatchard, R. H. Kottke, and J. L. Fedrick, *J. Am. Chem. Soc.*, **82**, 4330 (1960).

(11) R. C. Fuson and W. S. Friedlander, *J. Am. Chem. Soc.*, **76**, 4989 (1954).

(12) R. C. Fuson and B. Vittimberga, *J. Am. Chem. Soc.*, **79**, 6030 (1957).

(13) R. C. Fuson and R. E. Christ, *J. Am. Chem. Soc.*, **59**, 893 (1937).