their crystals as being truncated octahedra with the main interfacial angle of 142°. This description corresponds with the shape and face angle of the pure pentahydrate crystals, prepared by Hebert and Lister[12] and ourselves.

The data on which our belief is based that the material of this analysis is primarily pentahydrate, with an admixture of some hydrolyzed material and possibly some mother liquor, is essentially the following. All of the material crystallized at room temperature and subjected to X-ray diffraction analysis has shown the pattern of the pure pentahydrate, which indicates a low content of other material. In at least one case, large clear crystals have been obtained, for which the thoria analysis gives 46.24%, and nitrogen analysis gives a nitrate/Th ratio of 3.98, obviously pentahydrate. In cases where cloudy crystals are obtained, small crystals, etc., the analysis approaches the typical values for the usual product from water. If the crystallization is performed at 100° or at 80°, the thoria runs very high (47.2%, 47.5%) without the water content showing appreciable reduction (17.8%, 16.0%) so that material balances calculated on the assumption that the thorium is all present as nitrate run appreciably over 100%. Crystallizations at 25° fail to show this effect definitely, other than that the water values run higher than for the pentahydrate. In view of the fact that second crops of crystals from the same mother liquor tend to give higher thoria values and higher material balances than first crops (presumably by loss of nitric acid through evaporative concentration of the solution), and with the other facts mentioned in this paragraph, some hydrolysis must be assumed. The nitrogen–thorium ratios, however, in the cases where they have been measured, do not deviate significantly from 4. The tendency for large crystals to be cloudy suggests that part of the effect may be due to greater inclusion of mother liquor in the absence of added acid. Typical material crystallized from water and then desiccated at reduced pressure over sulfuric acid gave analyses of 46.64% thoria and 16.28% water, and at a still later time, 46.89% thoria. The thoria values are much too high even for pentahydrate, and the hypothesis of partial hydrolysis seems justifiable. When pentahydrate is allowed to stand over aqueous sulfuric acid, or even water, to raise its water content, and then desiccated over concentrated acid, with a short time over phosphorus pentoxide, the terminal analysis is only 46.23% thoria, 16.28% water, corresponding to a slightly damp pentahydrate. In any case, the addition of only 1% nitric acid to the system gives clean pentahydrate as the solid phase separating.

In the attempt to prepare higher hydrates comparable to those in the older European literature,[4–6] crystallization at 4° was used as being more comparable to the winter temperatures of those laboratories than the 25° temperature customary here. From water, solids with approximately 6 molecules of water per thorium were obtained, which had no well-defined crystalline shape and appeared wet. Gentle drying of the solids by pressing between filter paper sheets lowered the water content, and the analyses approached the compositions of the solids isolated from aqueous solutions at 25°. From 1% nitric acid solutions at 4° poorly characterized solids with as much as 10 molecules of water per thorium were obtained, but these also lost water, as visible droplets, when brought to room temperature.

Possible Lower Hydrates.—Although Marshall, Gill and Secoy[10] reported a transition from tetrahydrate to a lower hydrate at 151°, Templeton[11] on studying the system to 160° failed to identify a lower hydrate. Kolb[14] reported isolating a dihydrate from fuming nitric acid solutions at 105–110°. The solids we isolated under these conditions were always highly decomposed and contained water approximating four molecules per thorium. No indications of a dihydrate were found in our ternary phase studies, though it is conceivable that such a hydrate might have a stability region too short to be resolved in this system.

Grateful acknowledgment is made to the following members of the Argonne National Laboratory staff for occasional assistance: to Stanley Siegel for the taking and interpretation of the X-ray powder diagrams of the solids studied in this paper; to L. H. Fuchs for assistance in the crystallographic characterization of the pentahydrate; and to Miss Mary Lou Sjoholm for assistance with the nitrogen analyses.

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Alkylation of Duryl Phenyl Ketone with the Grignard Reagent

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Conjugate addition of a Grignard reagent to an aromatic ketone in such a way as to involve an aromatic ring has been realized by a number of workers among whom Kohler and Nygaard[2] were the first to appreciate the nature of the reaction. From the recent work of Mosher and Huber[3] it is apparent that Schmidlin and Wohl accomplished a change of this type in 1910.[4]

Although the products of such reactions normally are dihydroaromatic compounds, fully aromatic derivatives have been obtained by the action of certain alkylmagnesium halides on duryl phenyl ketone, *i.e.*, this ketone appears to undergo direct alkylation.[5] This alkylation is unusual also in that it proceeds without resort to "forcing" conditions. Moreover, it leads to the formation of *p*-alkylated derivatives whereas in other reactions an ortho-position usually is involved. In other words, this type of alkylation corresponds to 1,6-addition, which rarely occurs with Grignard reagents. It is with the observation that the products are not of

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

[2] E. P. Kohler and E. M. Nygaard, THIS JOURNAL, **52**, 4128 (1930).

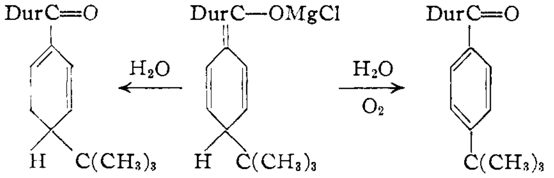
[3] W. A. Mosher and M. L. Huber, *ibid.*, **75**, 4604 (1953).

[4] J. Schmidlin and J. Wohl, *Ber.*, **43**, 1145 (1910).

[5] R. C. Fuson and B. C. McKusick, THIS JOURNAL, **65**, 60 (1943).

the dihydroaromatic type but are fully aromatized ketones that the present study is concerned.

The problem was brought into sharp focus when, at the outset, it was found that the earlier work with the *t*-butyl agent apparently could not be repeated. The reaction product proved to be the dihydroaromatic ketone I rather than the fully aromatic compound III prepared earlier. Examination of the reaction conditions,[5,6] indicated that adventitious access of air to the reaction mixture might be responsible for the aromatization of the initial adduct. Experiment has confirmed this suggestion. If the reaction is conducted in the absence of air, the product is always dihydroaromatic. It has been established also that the 1,6-addition product is oxidized by the air while still in the salt form II.



I II III

Parallel results have been obtained with the *sec*-butyl and cyclohexyl reagents. The recent report[7] that the reaction of duryl phenyl ketone with *sec*-butylmagnesium chloride affords the *p*-alkylation product in only 10% yield (previously reported 62%[6]) when it is conducted at 60° in a mixture of benzene and dimethoxybutane serves to emphasize the dependence of the nature and yield of the product upon the reaction conditions employed.

The position assigned to the double bonds in the hydroaromatic rings of the dihydro compounds is consistent with the infrared data but has not been proved conclusively.

Experimental[8]

Condensation of Duryl Phenyl Ketone with *t*-Butylmagnesium Chloride.—Twenty grams of the solid ketone[6] was added in portions to a Grignard reagent prepared from 12 g. of magnesium, 56 ml. of *t*-butyl chloride and 250 ml. of ether. Heat was evolved and the mixture developed a deep orange color, which at the end of 30 minutes of stirring had changed to a light yellow. The mixture, which had become thick, was then heated under reflux for 2 hours and decomposed with ice and dilute hydrochloric acid. The dihydro compound I, which was extracted with ether, solidified when the solvent was evaporated. It crystallized from ethanol and benzene as shiny white platelets; yield 10 g. (39%). After repeated recrystallization it melted at 150–151°.

Anal. Calcd. for $C_{21}H_{26}O$: C, 85.08; H, 9.52. Found: C, 85.04; H, 9.43.

The compound decolorized solutions of bromine and permanganate. Its infrared spectrum has a band at 1650 cm.$^{-1}$ attributable to a conjugated carbonyl group, and a weak band at 1630 cm.,$^{-1}$ which may indicate the presence of an ethylenic double bond. The infrared spectrum of authentic duryl *p*-*t*-butylphenyl ketone has the band attributable to the carbonyl group at 1668 cm.$^{-1}$.

***p*-*t*-Butylphenyl Duryl Ketone.**—The dihydro compound (2 g.) was heated at 310–350° for 45 minutes with 0.5 g. of 10% palladium-on-charcoal. The product was dissolved in benzene and the solution, after filtration, was evaporated. The residue was recrystallized from ethanol; m.p. 125–127°. A mixed melting point with an authentic specimen of *p*-*t*-butylphenyl duryl ketone[6] showed no lowering.

This ketone also was made by a modification of the method used for the preparation of the dihydroketone. The reaction was run in the manner described above except that a stream of air was passed into the reaction vessel for the final half-hour of the reaction. The product was recrystallized from ethanol; yield 47%.

Condensation of Duryl Phenyl Ketone with *sec*-Butylmagnesium Bromide.—The original directions[6] were modified to the extent that the reaction mixture was stirred at reflux for 2 hours instead of at room temperature. The product, isolated in the usual manner, was a yellow oil that failed to crystallize. It was dissolved in hot methanol and the solution was cooled; white crystals were deposited; yield 4.4 g. (44%). Several recrystallizations from methanol gave a product melting at 92–94°.

Anal. Calcd. for $C_{21}H_{26}O$: C, 85.08; H, 9.52. Found: C, 84.65; H, 9.44.

Attempts to purify this material further seemed to lead to partial oxidation to the fully aromatic compound. The dihydroketone decolorized bromine and permanganate, and its infrared spectrum had a band attributable to a non-aromatic, conjugated carbonyl group (1650 cm.$^{-1}$). Dehydrogenation with palladized charcoal converted it to a compound melting at 68–70° after one recrystallization from methanol. A mixed melting point with authentic *p*-*sec*-butylphenyl duryl ketone showed no depression.

Condensation of Duryl Phenyl Ketone with Cyclohexylmagnesium Chloride.—The methods used for the preparation, isolation and recrystallization were those employed with the *sec*-butyl adduct. The dihydro ketone melted at 107–108°; yield 30%.

Anal. Calcd. for $C_{23}H_{28}O$: C, 85.66; H, 9.38. Found: C, 85.91; H, 9.10.

The infrared spectrum of the compound had the same carbonyl band at 1650 cm.$^{-1}$ as the other dihydroketones described. Dehydrogenation over palladized charcoal yielded a compound identical with authentic *p*-cyclohexylphenyl duryl ketone.[6] The aromatic ketone was also produced when the air oxidation scheme, outlined for *p*-*t*-butylphenyl duryl ketone, was used.

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Addition of Acetals to Olefin Oxides

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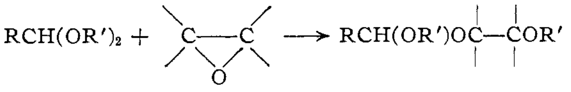
The only record of interaction of an acetal and an olefin oxide reports that 1,3-dioxolane and ethylene oxide at elevated pressure and temperature yield a useful but little characterized copolymer.[1] It is now found that in the presence of boron trifluoride, acetals and olefin oxides yield alkyl β-alkoxyalkyl acetals



$$RCH(OR')_2 + \underset{O}{>C\!-\!C<} \longrightarrow RCH(OR')O\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}OR'$$

In the process the acetal is cleaved into an alkoxy and an alkoxyalkyl fragment, evidently by a carbonium ion mechanism. Since the product is still an acetal, it can add to an additional molecule of olefin oxide; the general formula for products is thus $RCH(OR')(O\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}})_nOR'$. That successive

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(6) R. C. Fuson and R. Tull, THIS JOURNAL **71**, 2543 (1949).

(7) H. L. Cohen and G. F Wright, *J. Org. Chem.*, **18**, 432 (1953).

(8) The infrared spectra were determined and interpreted by Miss Helen Miklas. The microanalyses are by Mrs. Katherine Pih, Miss Emily Davis, Mrs. Jeanne Fortney, Mrs. Esther Fett and Mr. Joseph Nemeth.

(1) W. F. Gresham, U. S. Patent 2,394,910 (1946); *C. A.*, **40**, 3022 (1946).