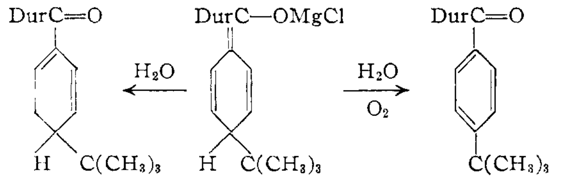
the dihydroaromatic type but are fully aromatized ketones that the present study is concerned.

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[5] 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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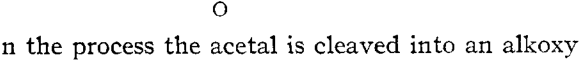
The only record of interaction of an acetal and an olefin oxide reports that 1,3-dioxolane and ethylene oxide at elevated pressure and temperature yield a useful but little characterized copolymer.[1] It is now found that in the presence of boron trifluoride, acetals and olefin oxides yield alkyl β-alkoxyalkyl acetals



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

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 $\mathrm{RCH(OR')(O\overset{|}{\underset{|}{C}}\!-\!\overset{|}{\underset{|}{C}})_nOR'}$. 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).

molecules of olefin oxide added are in fact immediately adjacent to each other and not non-adjacent, as in $RCH(O\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}OR')_2$, for example, was proved by identification of hydrolysis products. As would be expected, the 1:1 addition was favored by maintaining a considerable excess of the acetal during reaction. All the products were liquids miscible with water and common alcohols, ethers, esters and hydrocarbons.

Experimental

Methylal and Ethylene Oxide.—A solution of 12 g. of boron trifluoride in 500 g. (6.6 moles) of methylal was prepared at 0° with stirring. An ice-cooled condenser was attached and 200 g. (4.5 moles) of liquid ethylene oxide was gradually introduced under the same conditions. The mixture was added to an aqueous slurry of potassium carbonate and allowed to stand for separation of layers. The lower layer upon brief steam distillation and saturation of the distillate with potassium carbonate gave 6 g. of an organic liquid identified as *p*-dioxane by its boiling point (101°) and its formation of an insoluble complex with mercuric chloride.[2] The upper layer was rapidly distilled at atmospheric pressure up to 140°, where noticeable decomposition began, and thereafter under reduced pressure. Refractionation in a Todd column gave considerable unreacted methylal, b.p. 40–55°, *p*-dioxane (3 g.), and the following other products.

1-Methoxymethoxy-2-methoxyethane (I), b.p. 130–131.5° (750 mm.), 97 g. (18%). This compound had n^{25}_D 1.3913 and d^{25}_4 0.9465.

Anal. Calcd. for $C_5H_{12}O_3$: C, 49.98; H, 10.07; mol. wt., 120; *MR*, 30.07. Found: C, 49.56; H, 9.87; mol. wt.,[3] 119, 121; *MR*, 30.12.

I was characterized by its non-reaction with metallic sodium and by hydrolysis in 5% aqueous hydrochloric acid to (a) methanol, characterized as the 3,5-dinitrobenzoate (b) 2-methoxyethanol, characterized as the *p*-nitrobenzoate, m.p. 49°, and (c) formaldehyde, identified as the 2,4-dinitrophenylhydrazone. As might be surmised from its structure, this new acetal is a solvent in which the addition of sodium to naphthalene[4] can be effected.

1-(2-Methoxyethoxy)-2-methoxymethoxyethane (II), b.p. 185° (748 mm.) or 139–140.5° (98 mm.), was obtained in 14% yield (47 g.). It has n^{27}_D 1.4089 and d^{27}_4 0.9896.

Anal. Calcd. for $C_7H_{16}O_4$: C, 51.20; H, 9.82; mol. wt., 164; *MR*, 41.10. Found: C, 51.20; H, 9.74; mol. wt.,[3] 166, 167; *MR*, 41.16.

Hydrolysis gave methanol, formaldehyde and a liquid boiling at 190–193°, but no 2-methoxyethanol. Since 2-(2-methoxyethoxy)-ethanol boils at 194°, the parent structure must have been that of II rather than the isomeric bis-(2-methoxyethoxy)-methane.

A series of fractions boiling higher than II was obtained, but there was no distinct plateau on the boiling point curve to signify isolation of a higher analog of I and II.

A preparative run in which the molar ratio of methylal to ethylene oxide was 3:1 gave a 53% yield of I and only 5% of II.

Anhydrous aluminum chloride, zinc chloride, calcium chloride and mercuric chloride were all insoluble in methylal and failed to catalyze its reaction with ethylene oxide. Methylal and ethylene oxide also yielded no adduct upon being heated overnight in sealed tubes at temperatures up to 200°.

Methylal and Propylene Oxide.—Methylal (912 g., 12 moles), boron trifluoride (17 g.) and propylene oxide (232 g., 4 moles) were caused to react as before. The major products comprised about 20 g. of material which was assumed to be dimethyldioxanes, a large fraction (III) boiling at 135–143° (744 mm.), and 195 g. of residue boiling above 195°. III, obtained in 330-g. (61%) yield, n^{32}_D 1.3902, d^{32}_4 0.9182, was considered to be the expected mixture of 1-methoxymethoxy-2-methoxypropane and 1-methoxy-2-methoxymethoxypropane. No attempt was made to separate the isomers.

Anal. Calcd. for $C_6H_{14}O_3$: C, 53.71; H, 10.52; mol. wt., 134; *MR*, 34.84. Found: C, 53.73; H, 10.45; mol. wt.,[3] 131, 132; *MR*, 34.64.

Ethylal and Ethylene Oxide.—By the same method, 1560 g. (15 moles) of ethylal, 15 g. of boron trifluoride and 220 g. (5 moles) of ethylene oxide gave 364 g. (49%) of 1-(ethoxymethoxy)-2-ethoxyethane, b.p. 163–164° (746 mm.), n^{32}_D 1.3940, d^{32}_4 0.8974.

Anal. Calcd. for $C_7H_{16}O_3$: C, 56.73; H, 10.88; mol. wt., 148; *MR*, 39.46. Found: C, 56.80; H, 10.78; mol. wt.,[3] 149, 150; *MR*, 39.37.

Dimethyl Acetal and Ethylene Oxide.—Dimethyl acetal (900 g., 10 moles), boron trifluoride (20 g.) and ethylene oxide (88 g., 2 moles) did not react so smoothly as usual, and the crude product fractions all contained hydroxyl compounds, presumably from hydrolysis. Treatment of the 130–155° fraction with excess metallic sodium and refractionation gave 69 g. (22%) of 1-(1-methoxyethoxy)-2-methoxyethane, b.p. 141° (746 mm.), n^{32}_D 1.3930, d^{32}_4 0.9218.

Anal. Calcd. for $C_6H_{14}O_3$: C, 53.73; H, 10.52; mol. wt., 134; *MR*, 34.84. Found: C, 53.70; H, 10.41; mol. wt.,[3] 135, 136; *MR*, 34.75.

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(2) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3d ed., John Wiley and Sons, Inc., New York, N. Y., 1948.

(3) J. J. Hawkins and P. Arthur, *Anal. Chem.*, **23**, 533 (1951).

(4) N. D. Scott, J. F. Walker and V. L. Hansley, THIS JOURNAL, **58**, 2442 (1936).

Effect of Structure on the Polarographic Reduction of Iodo Compounds

BY EUGENE L. COLICHMAN[1] AND SHIH KUNG LIU[2]

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The presently reported investigation deals with the polarographic properties of twenty-nine different iodo compounds. Polarographic data have not appeared in the literature[3] on the majority of these compounds. Results are considered in terms of Hammett's[4] linear free-energy relationship between structure and reactivity. The abnormal and unique polarographic properties noted in some cases are appraised and compared with normal behavior. The criterion of normalcy is the quantitative relationship found between structure and susceptibility to polarographic reduction. Hammett's rho–sigma function[4] serves well in establishing this quantitative relationship.

Results and Discussion

Ortho or Proximity Effect.—It is apparent (Table I) that most substituents in the ortho position to the iodo group lead to abnormal half-wave potentials. The *proximity* phenomenon seems to facilitate the polarographic reduction of the iodo group whether the ortho substituent is *electropositive* or *electronegative*. *Ortho* or *proximity* effects are well known[4] in

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(1) North American Aviation, Inc., Atomic Energy Research Department, Downey, California.

(2) In partial fulfillment of the requirements for the Degree of Master of Science from the University of Portland.

(3) E. Gergely and T. Iredale, *J. Chem. Soc.*, **13**, 3502 (1951), have reported half-wave potential values for some of the iodo compounds under conditions different from those here.

(4) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940, 1st Ed., Chap. VII, pp. 184–228.