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Abstract

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ON THE PREPARATION AND REACTIVITY OF CERTAIN ARYLATED β-IODO ETHERS

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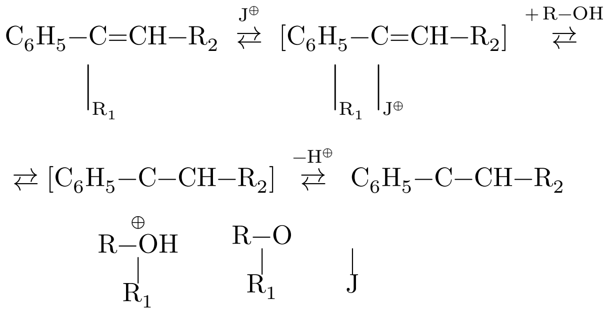
Recently we began to study the conversion of certain arylated ethylenic hydrocarbons into β-iodo ethers and their rearrangement of the pinacolone type into carbonyl compounds (^{1}, ^{2}) or into the corresponding ketals (^{2}). Only from 1,1-diphenylethane (I) was a crystalline β-iodo ether obtained—1-methoxy-2-iodo-1,1-diphenylethane (II), synthesized by the action on a methanolic solution of I of iodine in the presence of yellow mercuric oxide or iodic chloride.

In order to obtain β-iodo ethers from 1,1-diphenyl-1-propene (III) and from 1,2-diphenyl-1-propene (IV), we carried out experiments with stoichiometric quantities of hydrocarbon, iodine, and mercuric oxide. As a result, however, ketones were formed—1,2-diphenylpropanone-(1) (V) and, respectively, 1,1-diphenylpropanone-(2) (VI)—in yields above the theoretical, calculated on the mercuric oxide taken; moreover, about 30% of the starting III and, respectively, IV, was recovered. Evidently, the rearrangement of the expected β-iodo ethers proceeds at a higher rate than their formation. In the light of modern views (^{3}), their synthesis may be represented by the scheme:



$$C_6H_5-\underset{R_1}{\underset{|}{C}}=CH-R_2 \overset{J^\oplus}{\rightleftarrows} [C_6H_5-\underset{R_1}{\underset{|}{C}}=\underset{J^\oplus}{\underset{|}{CH}}-R_2] \overset{+R-OH}{\rightleftarrows}$$

$$\rightleftarrows [C_6H_5-\underset{\underset{R_1}{|}}{\underset{R-\overset{\oplus}{O}H}{C}}-CH-R_2] \overset{-H^\oplus}{\rightleftarrows} C_6H_5-\underset{\underset{R_1}{|}}{\underset{R-O}{C}}-\underset{J}{\underset{|}{CH}}-R_2 \qquad (1)$$

The exceeding of the theoretical yields of V and VI may be attributed to the formation of β-iodo ethers without the participation of mercuric oxide. Thus, for example, the acids of olive oil (^{4}) are converted quantitatively into iodomethoxy derivatives under the action of 0.2 N methanolic iodine solution. However, the addition capacity of arylalkenes is lower: an experiment with I and iodine in methanol gave a yield of only 11% of II. We therefore assumed that in the exceeding of the theoretical yields a more substantial role is played by mercuric iodide, formed in the course of the reaction: because of its tendency to form complexes of the type HgJ_3^- and HgJ_4^{2-}, it should, better than methanol (but more weakly than mercuric oxide), promote the formation of iodine cations from iodine molecules and thereby accelerate iodination. For the same reason, by binding part of the hydrogen iodide formed, mercuric iodide should suppress its reducing capacity and thus shift the equilibrium toward the formation of β-iodo ethers. Indeed, in the interaction of I with iodine and methanol in the presence of mercuric iodide, the yield of II reached almost 60% of the theoretical. The ability of mercuric iodide to cause rearrangement proved to be very low.

Next we tried to obtain a β-iodo ether from III by means of an equimolecular amount of iodic chloride, which is a very weak agent

rearrangement (1). The expected β-iodo ether proved to be unstable: in the course of its isolation iodine was split off, and from the resinified mass there were isolated 25% of the starting III, 21% of ketone V, and an insignificant amount of a hydrocarbon, $C_{30}H_{26}$, m.p. 227-228°, the structure of which has not yet been established. To determine the true yield of the intermediate β-iodo ether, in a parallel experiment silver nitrate was added to the reaction mixture, and V was formed in a yield of 89% of theory.

The extraordinary tendency toward rearrangement of the β-iodo ethers that undoubtedly are formed from III and IV under the indicated conditions is probably due to the following factors: the proximity of a methyl or phenyl group, which facilitates cleavage of the iodine atom as an iodide anion and formation of a carbonium cation; the accelerating influence of the phenyl group bonded to C_β (5); and the release of energy of steric compression (6). The relative stability of II should be ascribed to the absence of the first of these factors. Approximately the same stability was also shown by 1,1-diphenyl-1-alkoxy-2-iodoethanes VII-XI, which we synthesized from I and the corresponding alcohol (β-iodo ethers from secondary alcohols were obtained only in the form of crude oils).

For comparison, in the synthesis of VII–X we used, as iodinating agent, both a mixture of iodine with yellow mercuric oxide and iodine monochloride, which, as far as we know, had previously been used only for obtaining certain α-iodo-β-alkoxycarboxylic acids (7). Although the yields of the β-iodo ethers proved to be rather close, iodine monochloride is cheaper and gives no by-products except hydrogen chloride.

In a review that appeared in 1958 on the preparation and properties of halo ethers, the low mobility of the halogen in β-halo ethers was specially noted (β-iodo ethers are less stable and more reactive than the other β-halo ethers) (8). The strong tendency toward rearrangement of the arylated β-iodo ethers under study evidently contradicts this general characterization, which prompted us to subject the latter to several typical reactions. First of all we studied the reduction of II with hydriodic acid. At first the reaction proceeded very rapidly, but toward the end it slowed greatly. The I formed in this process dimerized under the action of iodine; this dimerization is known (9). According to the principle of microscopic reversibility, the reduction should proceed according to scheme (1)—from right to left.

The instability of 1,1-diphenyl-1-alkoxy-2-iodoethanes under illumination by sunlight* (after several days they begin to turn brown) indicates the possibility of cleavage of iodine as an iodine atom. To prove the possibility of homolytic rupture of the C—J bond, we subjected VII to the action of magnesium in an ethereal medium. As a result, a resinous mass was obtained, from which were isolated: 1,4-dimethoxy-1,1,4,4-tetraphenylbutane (yield 33% of theoretical), which is the product of a Wurtz reaction, hydrocarbon I (yield 28%), and an insignificant amount of desoxybenzoin (XII).

Only under conditions of reactions of the S_N2 type did the iodine atom prove to be truly very inert: upon 10-hour boiling of II with a 10% alcoholic solution of caustic potash or with a piperidine-ethanol mixture, as well as upon 30-hour boiling of an alcoholic solution of VII with sodium benzoate, or upon 5-hour action on IX of ethoxymagnesiomalonic ester, the starting β-iodo ether was recovered in a yield of about 90%. This extraordinarily low tendency toward direct substitutions at C_α must be due to the vicinal effect—the shortening of the C—J bond under the influence of the ether oxygen atom bonded to C_β (10), and to an even greater degree to the strong steric hindrance caused by the substituents at C_β—stronger than in neopentyl halides (11).

Experimental Part

Interaction of 1,1-diphenyl-1-propene (III) and trans-1,2-diphenyl-1-propene (IV) with iodine and yellow

mercuric oxide in the presence of methanol. a) To a mixture of 1.94 g (0.01 g-mole) of III, m.p. 48-49°, 1.08 g (0.005 g-mole) of freshly prepared dry yellow mercuric oxide, and 25 ml of absolute methanol, 2.54 g (0.02 g-atom) of iodine in 35 ml of methanol was added dropwise with stirring. On the following day the solution was concentrated by evaporation in vacuo, diluted with water, the precipitate of mercuric iodide was filtered off, and the filtrate was extracted with benzene; the extract was washed with thiosulfate solution, dried, and the benzene was distilled off. By means of the dinitrophenylhydrazine method (^{5}), 2.56 g (66% of theory) of the 2,4-dinitrophenylhydrazone (DNPH) V was isolated from the reaction mixture.

The alcoholic filtrate from the hydrazone was evaporated in vacuo, diluted with water, and extracted with petroleum ether. The dry extract was chromatographed through a layer of 10 g of alumina with activity 1.5 (according to Brockmann). This gave 0.60 g (31%) of III, m.p. 48-49°.

b) By the method described, 0.01 g-mole of IV was introduced into reaction with iodine and yellow mercuric oxide in the presence of 110 ml of methanol. A mixture of crystals and oil containing halogen was obtained.

By washing with cold methanol and recrystallization from alcohol, 0.60 g (31%) of IV, m.p. 81.5–82.5°, was obtained. From the methanolic filtrate, 2.18 g (56% of theory) of DNPH VI separated.

Interaction of 1,1-diphenylethane (I) with iodine and mercuric oxide in the presence of methanol. To a mixture of 1.08 g (0.01 g-mole) of I, 4.55 g (0.010 g-mole) of freshly prepared mercuric iodide, and 10 ml of methanol, 0.02 g-atom of iodine in 35 ml of methanol was added with stirring. The mixture was stirred for 3 hours. On the following day, 2.00 g (59% of theory) of II, m.p. 86–87° ([1]), was isolated from the mixture in the usual manner.

The experiment was repeated in the absence of mercuric iodide. By double chromatography over active alumina, 0.36 g (11% of theory) of II, m.p. 84–85.5°, and 0.74 g (41%) of I were isolated.

Interaction of 1,1-diphenylpropene (III) with iodine chloride in methanolic medium. To 0.01 g-mole of III in 40 ml of methanol, a solution of 1.79 g (0.011 g-mole) of iodine chloride in 20 ml of methanol was added with stirring. The continuously darkening mixture was stirred for 45 min; the solution was diluted with water and extracted with benzene. After removal of the solvent, iodine separated and partial resinification occurred. The decomposed product was washed with cold methanol. From the residue, by chromatography and recrystallization from glacial acetic acid and *n*-butanol, a colorless substance was isolated with m.p. 227–228°, sparingly soluble in alcohol and ether, and readily soluble in benzene and chloroform.

Found, %:	C 92.80; H 6.81
$C_{30}H_{26}$. Calculated, %:	C 93.22; H 6.78

From the methanolic filtrate, 0.83 g (21%) of DNPH V and 0.48 g (25%) of III were isolated.

To the reaction mixture obtained from 0.010 g-mole of III by the above-described method, an aqueous solution of 4.25 g of silver nitrate was added with stirring. The mixture was diluted with water, filtered, and extracted with benzene. 3.45 g of DNPH V (89% of theory) was obtained.

Preparation of 1-alkoxy-2-iodo-1,1-diphenylethanes by interaction of 1,1-diphenylethane with iodine and yellow mercuric oxide (method A) or with iodine chloride (method B) in an alcoholic medium.* The work was carried out in the usual manner, analogous to the preparation of II by methods A and B ([1]). In all cases, the structure of the β-iodo ether obtained was proved by rearrangement of it with silver nitrate into desoxybenzoin (XII). In some cases the yield of ketone (correspondingly, of the β-iodo ether) was determined more accurately from the yield of DNPH XII. Crystalline products VII–IX crystallize in very

* With the participation of M. D. Kovacheva.

well-formed colorless crystals, readily soluble in common organic solvents, less readily in alcohols. X and XI are viscous, noncrystallizing oils.

1-Ethoxy-2-iodo-1,1-diphenylethane (VII). Mp 72–74°. Yield 71% (by A and B).

Found, %: C 54.61; 54.76; H 5.09; 5.13
$C_{16}H_{17}OJ$. Calculated, %: C 54.54; H 4.87

1-(*n*-Propoxy)-2-iodo-1,1-diphenylethane (VIII). Mp 71–72°. Yield: by A 52%; by B 87% (based on the yield of DPH XII).

Found, %: C 55.83; 55.68; H 5.38; 5.46
$C_{17}H_{19}OJ$. Calculated, %: C 55.75; H 5.23

1-(*n*-Butoxy)-1-iodo-1,1-diphenylethane (IX). Mp 94–95°. Yield: by A—65%; by B—79%.

Found, %: C 56.60; 56.86; H 5.67; 5.77
$C_{18}H_{21}OJ$. Calculated, %: C 56.85; H 5.57

Unpurified 1-isopropoxy-2-iodo-1,1-diphenylethane (X). Yield: by A 63% (based on the yield of XII); by B 90% (based on the yield of DPH XII).

Unpurified 1-isobutoxy-2-iodo-1,1-diphenylethane (XI). Yield by A 71% (based on the yield of DPH XII).

Conversion of 1-methoxy-2-iodo-1,1-diphenylethane into 1,1,3,3-tetraphenyl-1-butene (XIII) with hydriodic acid. 6.76 g (0.02 g-mole) of II were treated, with vigorous stirring, in portions with 13.28 g (0.08 g-mole) of potassium iodide with an excess of hydrochloric acid in a homogeneous benzene–ether–methanol medium until the reaction for halogen became negative. Recrystallization from alcohol gave 2.58 g (72% of theory) of XIII, mp 111–113°. A mixed-melting test with XIII obtained according to ([9]) melts at the same temperature.

Reaction of 1-ethoxy-2-iodo-1,1-diphenylethane with magnesium in anhydrous ether. To 1.46 g (0.060 g-atom) of powdered magnesium, activated by addition of iodine and ethyl bromide, 7.04 g (0.02 g-mole) of VII in 25 ml of dry ether were added with stirring. The mixture was boiled and stirred for 8 hours. On the following day the mixture was decomposed with dilute hydrochloric acid, extracted with benzene, the extract was dried, and the benzene was distilled off in vacuo. The residue was a mixture of crystals, oil, and resins. With cold methanol, 2.07 g of crystalline product with mp 170–181° were washed out. From the methanolic filtrate, a small amount of XII was isolated as DPH. From the hydrazone filtrate, by the customary method, 1.00 g of I (28% of theory) was isolated.

By triple recrystallization from *n*-butanol of the product with mp 170–181°, 1.44 g (33% of theory) of 1,4-diethoxy-1,1,4,4-tetraphenylbutane (XIV) were obtained. Mp 183–185°. Colorless, needle-like crystals, poorly soluble in alcohol and ether, readily soluble in benzene.

Found, %: C 84.88; 85.05; H 7.78; 7.81
$C_{32}H_{34}O_2$. Calculated, %: C 85.29; H 7.61

XIV was converted according to (^{12}), in 70% yield, into 1,1,4,4-tetraphenyl-1,3-butadiene, mp 200–202°. A mixed-melting test with an authentic sample shows no depression.

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Note: Figure translations are in progress. See original paper for figures.