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Abstract

Full Text

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CLEAVAGE OF IODONIUM DERIVATIVES OF DIMEDONE

We have reported (1,2) that the product of the reaction of dimedone with iodobenzene—phenyldimedonyliodonium (I)—readily decomposes at elevated temperature with formation of iodobenzene and the phenyl ether of iododimedone (II), while in the presence of pyridine and silver nitrate the decomposition products are phenol and the silver salt of iododimedone. In connection with the preparation of iodonium salts of enol ethers of dimedone (III), it was of interest to investigate the direction of their decomposition and to compare it with the direction of decomposition of phenyldimedonyliodonium, as well as to study the possibility of obtaining new dimedone derivatives. At present, cleavage of iodonium salts is used for obtaining arylonium (3,4) and organometallic (5–10) compounds.

(I) (II) (III)

Both phenyldimedonyliodonium and phenyl-(alkoxydimedonyl)-iodonium salts are typical unsymmetrical iodonium derivatives and can undergo cleavage with rupture of the iodine—carbon bond in two directions and by two mechanisms —heterolytic and homolytic (3,4). The mechanism of the cleavage reaction of iodonium salts depends on the nature of the reagent present, the salt-forming anion, and the solvent. Thus, it is known that cleavage of borofluorides in the presence of tertiary derivatives of nitrogen, phosphorus, etc., proceeds heterolytically according to the scheme (3):

$$\begin{array}{ccc} \mathrm{R{-}J^{\oplus}{-}R} + \,:\mathrm{A} & \longrightarrow & \mathrm{R{-}A^{\oplus}} + \mathrm{RJ} \\ \mathrm{BF_4^{\ominus}} & & \mathrm{BF_4^{\ominus}} \end{array}$$

Cleavage in various solvents in the presence of anions may have either a homolytic or a heterolytic character, depending on a number of conditions (nucleophilicity of the anion, catalyst, solvent), and determination of the true mechanism is difficult (11–13).

In the presence of certain metals the cleavage reaction proceeds homolytically, but is strongly influenced by the polar factors of the substituents (5,7,8,10). Reutov also discusses a possible heterolytic mechanism (8).

The cleavage of phenyldimedonyliodonium was investigated in dioxane, pyridine, and water solutions. In all cases, rupture of the iodine—carbon bond in two directions was observed, with formation of a mixture of the phenyl ether of iododimedone and iodobenzene (Table 1).

The yield of the silver salt of iododimedone in the cleavage of phenyldimedonyliodonium in aqueous solutions in the presence of pyridine and silver nitrate depends both on the amount of pyridine and on the amount of silver nitrate (see Table 2). Iodobenzene is not formed in appreciable amounts in this reaction.

Table 1

Cleavage of phenyldimedonyliodonium

Solvent	Duration of boiling	Amount of products isolated, %: iodobenzene*	Amount of products isolated, %: II	Ratio iodobenzene : II
Water	2 h	32	10	3.2
Dioxane	30 min	41	30	1.36
Toluene (1)	1 h	40	47	0.85
Pyridine	15 min	14.5	54	0.27

* Iodobenzene was distilled off and converted into phenyliodosyl chloride, which was weighed.

Cleavage of the bromide and borofluoride of phenyl-(O-ethyldimedonyl)-iodonium (III, $R = C_2H_5$, $X = Br^-$ or BF_4^-) was studied in aqueous solutions

Table 2

Cleavage of phenyldimedonyliodonium in the presence of pyridine and silver nitrate
(in moles per 1 mole of iodonium) (Reaction conditions: five-minute boiling in aqueous methanol medium, cooling, filtration)

Silver nitrate	1	2	4	1	1	2	4
Pyridine	1	1	1	2	4	2	4
Yield of silver salt, %	54	59	64.5	41	0	58	79

in the presence of certain anions (Br^-, NO_2^-, S^{2-}, OH^-). The bromide of phenyl-(O-ethyldimedonyl)-iodonium was also cleaved in the presence of mercury, and the borofluoride—in pyridine solution. In all cases iodobenzene was isolated, and in some cases derivatives of dimedone could also be detected. The results are shown in Table 3.

Table 3

Cleavage of salts of phenyl-(O-ethyldimedonyl)-iodonium

Substance	Solvent	Reaction conditions	Yield of iodobenzene* in %	Other products
Bromide (III, $R = C_2H_5,\ X = Br^-$)	–	Decomposition at 160°	36	Oily mass. Bromobenzene (detected qualitatively)
Bromide (III, $R = C_2H_5,\ X = Br^-$)	Water	Boiling for 30 min	56	2-Bromodimedone 30%. M.p. 175–176°; lit. (^{15}) 175°
Bromide (III, $R = C_2H_5,\ X = Br^-$)	Acetone	Stirring for 2 h in the presence of mercury	32	Oily mass containing mercury
Borofluoride (III, $R = C_2H_5,\ X = BF_4^-$)	Water	Addition of nitrite solution at 90°	52	Oily mass containing nitrogen
Borofluoride (III, $R = C_2H_5,\ X = BF_4^-$)	Water	Addition of sulfide solution at 0°	29	Ethyl ether of ioddimedone 13%. M.p. 129–131°. Sulfidobis-dimedone 8%. M.p. 231°; lit. (^{14}) 234°
Borofluoride (III, $R = C_2H_5,\ X = BF_4^-$)	Water	Addition of alkali solution at 0°	50	Oily mass

Substance	Solvent	Reaction conditions	Yield of iodobenzene* in %	Other products
Borofluoride (III, $R = C_2H_5,\ X = BF_4^-$)	Pyridine	Stirring at 10–20° for 10 h	62	Borofluoride of *o*-ethyldimedonylpyridinium (IV). M.p. 120–122°; 70%

* Iodobenzene was distilled off with steam or in vacuo, converted into phenyliodosyl chloride, and weighed.

From the foregoing it is evident that the direction of cleavage of the iodine—carbon bond depends on structural factors and on the reagent present. Thus, an interesting difference is observed between the direction of cleavage of phenyldimedonyliodone (I) and of phenyl-(alkoxydimedonyl)-iodonium salts (III). It is especially useful to compare the cleavage in the presence of pyridine. If, in the case of phenyldimedonyliodone, the iodine—phenyl bond is cleaved predominantly, then in alkoxy salts (III) the iodine—dimedonyl bond is cleaved. Since it may be assumed that the bond with the lower electron density will be cleaved ([8]), it follows that in the present case, from the nature of the bond cleavage, we can judge the relative electron density on the carbon atom of the active methylene group as a function of structure. Since in phenyldimedonyliodone the dimedone residue presumably exists in the enolate-anion form, consequently the enolate-anion form is capable of creating a greater electron density on the carbon atom of the active methylene group than phenyl- or alkoxydimedonyl. This is explained by the greater mobility of the electron system of the enolate anion. Exactly the same conclusion follows from the known fact that 2-halo derivatives of dimedone are difficult to saponify ([15]).

If the enolate-anion structure is disrupted, then the iodine—dimedonyl bond is weakened in comparison with the iodine—phenyl bond, and on cleavage iodobenzene is formed predominantly. Already in aqueous solution the yield of the phenyl ether of iododimedone decreases, and in the presence of hydrochloric acid the iodine—dimedonyl bond is cleaved completely ([16]). This is evidently connected with addition of a proton and formation of a system of the non-ionized enol. Conversely, the presence of silver ions apparently stabilizes the enolate-anion system. Evidently, the low solubility of the silver salt of iododimedone plays an important role. In compounds with a fixed enol form (phenylalkoxydimedonyliodonium salts) the enolate-anion system is also disrupted, and they cleave with predominant formation of iodobenzene, provided only that the reaction does not have a clearly radical (homolytic) character (decomposition at 160°, decomposition in the presence of mercury, sulfide ion). The radical character of the cleavage is manifested especially clearly upon attack by sulfide structural formulas IV and V

Figure 1: structural formulas IV and V

ion: cleavage of the iodine—carbon bond depends little on polar factors and proceeds in two directions. In contrast to this, the typical heterolytic cleavage reaction proceeds in pyridine solution with formation of the pyridinium derivative of dimedone (IV). On saponification of the latter, as was reported ([17]), the pyridine enolate betaine (V) is obtained. Borofluoride (IV) is characterized by very distinctive properties. First, in microdetermination of nitrogen, greatly elevated results are always obtained. Therefore the substance was characterized by determination of BF_4' (as KBF_4, by precipitation in absolute alcohol) and by infrared spectra. Second, the substance is capable of existing in two modifications with melting points 120—122° and 140°.

The extraordinary ease with which cleavage reactions occur in the presence of pyridine in all the cases considered above indicates some influence of pyridine on the heterolytic cleavage reaction. Most probably, pyridine solvates the attacked carbon atom, thereby facilitating bond cleavage and nucleophilic attack by the corresponding reagent ([18]).

Such reactions may have important preparative significance for obtaining other, hitherto inaccessible, onium derivatives of dimedone.

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