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Abstract

Full Text

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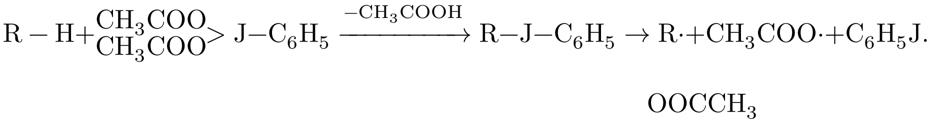
ON THE MECHANISM OF THE INTERACTION OF PHENYLIODOSO COMPOUNDS WITH CERTAIN β-DIKETONES

Iodosobenzene (I) and its derivatives (acetate, fluoride, benzoate) (II, $X = CH_3COO, C_6H_5COO, F$) are known in organic chemistry as rather strong oxidizing agents ($^{1-3}$) and as starting substances for the preparation of aryliodonium salts ($^{4-7}$). Phenyliodoso acetate (II, $X = CH_3COO$) is used most often. The reactions of phenyliodoso acetate are divided into two subtypes. First, on interaction with alcohols, α-glycols, and amines, its oxidizing properties are manifested and the corresponding ketones, azo compounds, and other products are formed ($^{1-3}$). In such reactions phenyliodoso acetate fully corresponds to lead tetraacetate, and to explain the course of the reaction Posaker and coworkers proposed a radical mechanism (^{8,9}). The first stage of the reaction is the elimination of an acetic acid molecule; the second is the decomposition of the intermediate product according to the following scheme:



$$R-H+\begin{matrix}CH_3COO\\CH_3COO\end{matrix}\!>J{-}C_6H_5\xrightarrow{-CH_3COOH}R{-}J{-}C_6H_5\to R\cdot+CH_3COO\cdot+C_6H_5J.$$
$$OOCCH_3$$

Second, phenyliodoso acetate in the presence of strong acids is capable of reacting with aromatic hydrocarbons, forming iodonium salts.

In fact, both types of reaction are based on a general scheme, which consists of the following: a) abstraction of a labile proton and formation of the corresponding derivative of divalent iodine, b) decomposition or stabilization of the intermediate product, which depends on the nature of the new iodine–element bond (C, N, O) and of the anion present. The reactions investigated of phenyliodoso acetate with certain β-diketones are in complete agreement with the mechanism indicated above.

We have already reported earlier that dimedone reacts with iodosobenzene and phenyliodoso fluoride (II, $R = F$), forming an internal iodonium salt of the enolate-betaine type (III, $R_1 = R_2 = CH_3$) (^{10}).

Structural formulas IV, V, and VI

Figure 1: Structural formulas IV, V, and VI

Reaction scheme leading to iodonium salt VII

Figure 2: Reaction scheme leading to iodonium salt VII

(I) (II) (III)

In the same way 5-phenylcyclohexanedione-1,3 reacts, forming the corresponding iodonium derivative (III, $R_1 = H$; $R_2 = C_6H_5$) (^{11}). On extending this reaction to other β-diketones, it turned out that iodonium compounds could not be isolated. Acetylacetone, dibenzoylmethane, indandione-1,3, 2-phenylindandione-1,3, as well as acetoacetic ester and malonic ester as representatives of β-keto esters, were investigated. Depending on the mobility of the protons of the compounds studied, the reaction with phenyliodoso-

acetate proceeds with a greater or lesser thermal effect, and in all cases iodobenzene is formed. The second reaction product in the case of dibenzoylmethane and phenylindandione proved to be the 2-acetoxy derivatives (IV and V).

2-Acetoxydibenzoylmethane is known in the literature (^{12}), and the structure of our product was additionally confirmed by IR spectra. 2-Acetoxyphenylindandione was obtained by counter synthesis from 2-bromophenylindandione and potassium acetate, and its structure was confirmed by an IR spectrum. Indandione gave products that could not be identified. Special experiments on the acetoxylation of acetylacetone and acetoacetic ester were not carried out, while the reaction of acetoacetic ester, acetylacetone, and also dibenzoylmethane with phenyliodosoacetate was carried out in the presence of pyridine. It was found that, from the reaction products, enolate betaines of pyridinium β-dicarbonyl compounds (VI) can be isolated.

Such compounds could be formed as products of the heterolytic decomposition of the corresponding iodonium compounds. Consequently, it may be assumed with high probability that, in the first phase of the reaction of phenyliodosoacetate with β-dicarbonyl compounds, a C-iodonium derivative is formed. It may be assumed that those β-dicarbonyl compounds which are capable of existing in the enol form react through it, with subsequent electrophilic attack on the carbon atom of the active methylene group. It is presumed that the attacking agent is the cation $C_6H_5-\overset{+}{J}-OOCCH_3$, for whose formation a labile proton is required. If salts of β-diketones are taken, or the reaction is carried out in the presence of proton acceptors (triethylamine, pyridine), the reaction rate decreases markedly.

As a result of the reaction, an iodonium salt (VII) is formed, which may either be stabilized in the form of an inner salt or decompose. In the presence of pyridine, typical heterolytic decomposition takes place. The formation of acetoxy derivatives could occur either heterolytically or homolytically.

Consequently, the reaction of phenyliodosoacetate with β-dicarbonyl compounds is a new confirmation of the dual reactivity of the latter and once again reveals the profound difference between the properties of β-diketones of the cyclohexanedione-1,3 series and those of the other groups studied. The former, even in the presence of pyridine, form only an inner iodonium salt, whereas β-diketones of the acyclic and indandione series give cleavage products. This difference can be explained by particular structural factors of cyclohexanediones-1,3, for which extremely rapid secondary enolization is possible. This has been repeatedly noted in titration of the latter with bromine (196% enol is obtained) (13). One may also point to the great similarity of the properties of cyclohexanediones-1,3 to phenols (14).

Table 1

Characteristics of the substances obtained

Substance	Color; m.p., °C; yield, %	Found, %	Calculated, %	UV absorption maxima, CH_3OH, mμ	IR absorption maxima, solid, cm^{-1}	IR absorption maxima, solution, $CHCl_3$, cm^{-1}
2-Acetoxydibenzoylmethane	Colorless 93–94° 94° (12) 80%	C 72.63 H 4.85	$C_{17}H_{14}O_4$ C 72.32 H 4.96		1582 (56) 1598 (70) 1691 (95) 1753 (92)	
2-Acetoxy-2-phenylindandione-1,3	Colorless 164–165° 47%	C 72.08 H 4.29	$C_{17}H_{12}O_4$ C 71.33 H 4.20		1592 (50) 1724 (90) 1741 (89)	
Enolate betaine of pyridinium dibenzoylmethane	Dark yellow 212–214° 220° (15) 67%	N 4.62	$C_{20}H_{15}O_2N$ N 4.65	222 (14400)* 312 (9240)	1465–1480 (100) 1545 (80) 1581 (53) 1628 (52)	1497 (100) 1553 (44) 1626 (20)

Substance	Color; m.p., °C; yield, %	Found, %	Calculated, %	UV absorption maxima, CH_3OH, mμ	IR absorption maxima, solid, cm^{-1}	IR absorption maxima, solution, $CHCl_3$, cm^{-1}
Enolate betaine of pyridinium acetylacetone	Dark yellow172—174°17%	N 8.03	$C_{10}H_{11}O_2N$ 7.91	274 (19300)312 (760)In acidic medium256 (12600)	1544 (100)1583 (84)1627 (69)	1512 (89)1582 (28)1628 (21)
Enolate betaine of pyridinium acetoacetic ester	Dark yellow114—119°24%	N 6.33	$C_{11}H_{13}O_3N$ 6.76	257 (18500)376 (850)In acidic medium231 (8700)	1511 (80)1627 (57)1670 (84)1704 (66)	1533 (65)1624 (41)1654 (43)1718 (43)

* In the literature (^{18}) ~ 250 (10500) and ~ 320 (10500), without indication of the solvent. In parentheses are given: for UV spectra—the values of ϵ, for IR spectra—the percentages of absorption.

The pyridinium enolate betaines (VI) obtained are yellow crystalline substances. The dibenzoylmethane derivative (VI, $R_1 = R_2 = C_6H_5$) is known in the literature (^{15}). The derivatives of acetylacetone (VI, $R_1 = R_2 = CH_3$) and of acetoacetic ester (VI, $R_1 = CH_3$; $R_2 = OC_2H_5$) rapidly absorb moisture from the air, thereby greatly lowering the melting point. The melting point of these compounds is unsuitable for their precise characterization.

The enolate betaines were characterized by ultraviolet and infrared absorption spectra. The UV spectra were recorded in neutral and acidic media and show an interesting pattern in comparison with the absorption of the β-dicarbonyl compounds themselves. A considerable hypsochromic shift of the K band of the enolatanion system is observed, by approximately 20 mμ, which is explained by a change in the electronic structure of the enolatanion in these enolate betaines (^{11}). In acidic medium the enolate betaines show a strong shift of the absorption maximum, which is associated with formation of the nonionized form. It is interesting that the absorption maximum of the nonionized form of the enolate betaine is lower by 10 mμ in comparison with the absorption of the enol form of the β-dicarbonyl compounds themselves and coincides with the absorption of trans-enol esters (^{16}). Consequently, the absorption of the enols of acetoacetic ester and acetylacetone indicates the cis form, whereas the absorption of the nonionized forms of the pyridinium enolate betaines indicates the trans configuration of the latter. An exception is the enolate betaine of dibenzoylmethylpyridinium, whose absorption spectrum in acidic medium is charac-

is characterized by only one absorption maximum in the range of 250 mμ. This indicates decomposition of the substance, since all derivatives of dibenzoylmethane are characterized by two absorption maxima (^{17}).

The IR absorption spectra of the investigated enolatobetaines in the region of double bonds show a complex picture, as yet difficult to interpret. Nevertheless, it is interesting to note the typical absorption behavior of the carbonyl groups of the systems investigated. The pyridinium enolatobetaines of acetylacetone and dibenzoylmethane are not characterized by absorption in the usual region of carbonyl groups. By contrast, the acetoacetic ester derivative is characterized by absorption at 1718 and 1654 cm^{-1}, which indicates a significant concentration of charge on the carbon atom of the active methylene group. Consequently, the absorption spectra of the investigated enolatobetaines confirm that the localization of charge in enolate-anion systems depends to a strong degree on structural factors.

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