Chemistry

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Abstract

Full Text

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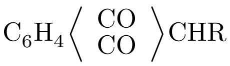
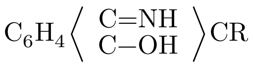
IMINATION OF 2-SUBSTITUTED INDANDIONES-1,3

In previous works we proved that 2-phenyl- (1) and 2-methylindandione-1,3 (2) (Ia and b) with ammonium acetate in glacial acetic acid form imines of structure II (a, b). It remained to determine whether the reaction described would be general for 2-aryl- and 2-alkylindandiones-1,3.



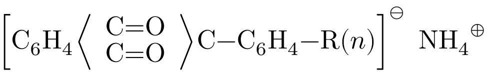
$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle CHR$$

(I)



$$C_6H_4\left\langle\begin{matrix}C{=}NH\\C{-}OH\end{matrix}\right\rangle CR$$

(II)



$$\left[C_6H_4\left\langle\begin{matrix}C{=}O\\C{=}O\end{matrix}\right\rangle C{-}C_6H_4{-}R(n)\right]^{\ominus}\ NH_4^{\oplus}$$

(III)

In I or II, R: a = C_6H_5; b = CH_3; c = C_2H_5; d = $CH(C_6H_5)_2$; e = 9-xanthyl; f = n-$CH_3OC_6H_4$; g = n-$NO_2{-}C_6H_4$; z = α-$C_{10}H_7$.

Six new imino derivatives of 2-substituted indandiones have been prepared (II c—z). The imines of 2-alkylindandiones (II b—d) are more readily soluble in organic solvents than their analogues with a phenyl group in position 2 (II a, f—g) (cf. (1,2)). Imines (II b, c) are somewhat soluble also in hot water. The imine of 2-xanthylindandione (II e) is close in its properties to the imines of 2-arylindandiones; compounds (II a, e—g) have relatively higher melting points and are poorly soluble in low-polarity solvents. The imine of 2-α-naphthylindandione (II z), in its physical properties, occupies an intermediate position between the two mentioned groups of imines.

All imines, on boiling in alcohol acidified with hydrochloric acid, are hydrolyzed to the corresponding 2-substituted indandiones. Only in the case of the imine of 2-xanthylindandione, together with hydrolysis, partial dexanthylation of the diketone also proceeds.

From a theoretical point of view, the imination of 2-n-nitrophenylindandione (I g), which differs somewhat in its acidity and other properties from the other 2-arylindandiones (3), proved to be of interest. On imination this compound at first forms only the ammonium salt of 2-nitrophenylindandione (III, R = NO_2), which is stable in an acetic-acid medium in the presence of a sufficient excess of ammonium acetate. However, at elevated temperature (ammonium propionate in propionic acid), the expected imine (II g) is slowly formed. The ammonium salt of 2-phenylindandione (III, R = H), prepared by another method, does not precipitate in acetic acid in the presence of an excess of ammonium acetate; the solution obtained, on boiling, gives the imine of phenylindandione. In this connection it is assumed that the imination reaction of 2-*n*-nitrophenylindandione proceeds insofar as the salt (III, R = NO_2) has time to thermally dissociate into the starting β-diketone and ammonia. Then nucleophilic attack of the molecule of 2-*n*-nitrophenylindandione by a molecule of ammonia occurs, with formation of the corresponding imine. Incidentally, the formation of an ammonium salt of a β-diketone as a by-product in the preparation of β-aminovinyl ketones has also been noted earlier $^{(4)}$.

The imine of 2-*p*-nitrophenylindandione (II) already has weak acidic properties. In aqueous alkalis, upon heating, it dissolves slightly with a bright-red coloration (upon addition of a little alcohol to this mixture, dissolution improves).

Table 1 gives some information on the newly obtained compounds.

Table 1

Imines of 2-substituted indandiones-1,3

Compound	M.p., °C	Color	Solvent for crystallization	Yield, %
II	168–169	Red	CH_3OH; CH_3OH + H_2O (1 : 1)	68
II	205.5–206.5	Orange-red	C_2H_5OH	65
II	265–266	Orange-yellow	Butylcellosolve; CH_3COOH	96
II	260–265	Red	CH_3COOH	88
II	289	Brick-red	CH_3COOH	90
II	202.5–203.5	Brick-red	$C_6H_5CH_3$	Negligible
III R = NO_2	258–260	Dark brown	–	75
III R = H	–	Dark brown	–	93

Experimental Part*

Imine of ethylindandione (II). 2 g of ethylindandione (I)$^{(5)}$ in 6 ml of glacial CH_3COOH and 6 g of ammonium acetate are heated to boiling. To the cooled mixture, 24 ml of water are gradually added, rubbing the walls of the flask with a rod. The next day the imine (II), 1.37 g, is separated; it is soluble in ordinary organic solvents and less soluble in hot water.

Found, %: N 8.31

$C_{11}H_{11}ON$. Calculated, %: N 8.09

Imine of benzhydrylindandione (II). 1 g of benzhydrylindandione (I)$^{(6)}$ in 10 ml of glacial CH_3COOH is boiled with 6 g of ammonium acetate for half an hour. Add 1 ml of water and cool, rubbing the walls of the flask with a rod. The next day the imine (II), 0.65 g, is separated; it is moderately soluble in alcohols and other polar solvents.

Found, %: N 4.58
$C_{22}H_{17}ON$. Calculated, %: N 4.50

Imine of xanthylindandione (II). 0.5 g of xanthylindandione (I)$^{(7)}$ in 5 ml of glacial CH_3COOH is boiled with 3 g of ammonium acetate for several minutes. The mixture is cooled and the imine (II), 0.48 g, is separated. The substance is almost insoluble in low-boiling solvents, except acetic acid; it dissolves better in decalin, in glycol ethers or diethylene glycol ethers.

Found, %: N 4.27
$C_{22}H_{15}O_2N$. Calculated, %: N 4.31

Imine of α-naphthylindandione (II). 1 g of α-naphthylindandione (I)$^{(8)}$ in 5 ml of glacial CH_3COOH is boiled with 10 g of ammonium acetate for 10 min. On cooling, a red resin separates. It is dissolved in alcohol and poured into water. The imine is filtered off (II). This compound, better than the other imines of 2-arylindandiones, is soluble in nonpolar and slightly polar solvents.

Found, %: N 5.27
$C_{19}H_{13}ON$. Calculated, %: N 5.16

Imine of *p*-methoxyphenylindandione (II). 1.5 g of *p*-methoxyphenylindandione (I) (9) in 20 ml of glacial CH_3COOH and 4.5 g of ammonium acetate are boiled for 10 min. The mixture is cooled and the imine (II) is separated, 1.33 g; it is sparingly soluble in alcohols, somewhat better in acetic acid.

Found, %: N 5.38
$C_{16}H_{13}O_2N$. Calculated, %: N 5.58

Ammonium salt of 2-phenylindandione (III, R = H). Dry ammonia is passed for 1 hour through a solution, heated to 100–110°, of 3 g of phenylindandione in 30 ml of xylene. The mixture is cooled under a weak stream of ammonia, and the salt is filtered off (III, R = H), 3 g. The salt is readily soluble in water and alcohols, and is insoluble in hydrocarbons and slightly polar solvents. On heating in air, the dry salt decomposes into phenylindandione and ammonia; when the salt is heated in a sealed ampoule (or a solution of the salt in ethylene glycol at 150–170°), the imine of phenylindandione (II) is formed. With acetic acid, phenylindandione and ammonium acetate are first formed; on heating this solution, the imine (II) is obtained.

* Some physical properties and yields of the substances are given in Table 1.

Found, %: N 5.91
$C_{15}H_{13}O_2N$. Calculated, %: N 5.85

Ammonium salt of *p*-nitrophenylindandione (III, R = NO_2). 0.5 g of *p*-nitrophenylindandione (I) (10) is dissolved with boiling in 20 ml of glacial CH_3COOH, and about 1.5 g of ammonium acetate is gradually added. After several minutes, the whole crystallizes into a dense felt-like mass. Yield of salt (III, R = NO_2), 0.4 g. The salt dissolves readily in water and alcohols. Hot acetic acid decomposes the salt to *p*-nitrophenylindandione; a hot solution with an excess of ammonium acetate again precipitates the ammonium salt of the diketone. Mineral acids decompose the salt completely.

Found, %: N 9.68
$C_{15}H_{12}O_4N_2$. Calculated, %: N 9.86

Imine of *p*-nitrophenylindandione (II). 0.5 g of *p*-nitrophenylindandione (I) in 3 ml of propionic acid is boiled for 27 h with 3 ml of ammonium propionate. The dark-brown ammonium salt of the starting diketone gradually dissolves. The mixture is cooled, and the imine (II) is filtered off, 0.45 g. The substance is almost insoluble in hydrocarbons, ether, and other slightly polar solvents; better soluble in alcohols and acetic acid, and readily soluble in dimethylformamide.

Found, %: N 10.27
$C_{15}H_{10}O_3N_2$. Calculated, %: N 10.52

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