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Abstract

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A NEW METHOD FOR PREPARING 2-ARYLIDENEINDANDIONES-1,3

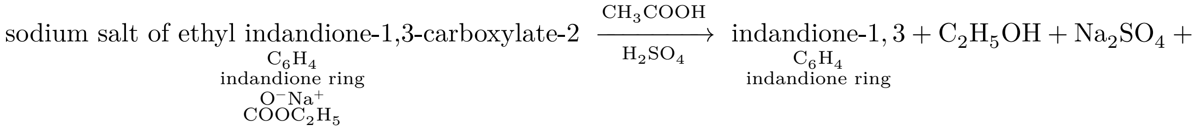
2-Arylideneindandiones-1,3 (II) are frequently used for preparing various highly complex polycyclic compounds. Thus, for example, the interaction of arylideneindandiones-1,3 with diazomethane gives furanindenones ([1]), and with ammonium acetate in glacial acetic acid gives polynuclear condensed systems containing a pyridine ring ([2]). Arylideneindandiones-1,3 are also capable of adding various nucleophilic reagents at the site of the double bond ([3–5]). Recently one of us, together with Dumpis, developed a convenient method for preparing 2-aralkylindandiones-1,3 by selective hydrogenation of the corresponding arylideneindandiones-1,3 with sodium dithionite ([6], [7]).

Arylideneindandiones-1,3 are synthesized by various methods, but all methods described in the literature are based on the condensation of indandione-1,3 with aromatic aldehydes under various conditions.

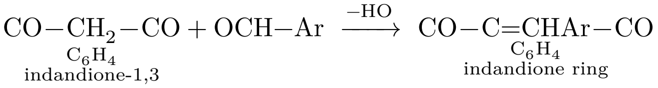
Benzalindandione-1,3 was first obtained by heating indandione-1,3 with benzaldehyde without catalysts ([8], [9]). A number of other arylideneindandiones-1,3 were also obtained by this method ([10–15]). In some cases the condensation can be carried out by heating indandione-1,3 and an aldehyde in alcoholic solution ([13], [16]) or in alcoholic solution in the presence of basic catalysts (KOH, piperidine) ([17–19]). Arylideneindandiones-1,3 are also obtained by condensing indandione-1,3 with aldehydes in a solution of glacial acetic acid in the presence of concentrated sulfuric acid ([20]). The condensation of indandione-1,3 with aldehydes often proceeds so smoothly that Ionescu ([18]) suggests using this method for the identification of aldehydes.

Our attention was drawn to the sodium salt of the ethyl ester of indandione-1,3-carboxylic-2 acid (I), which contains a readily eliminated carbethoxy group. In a solution of glacial acetic acid in the presence of conc. sulfuric acid, this salt readily loses the carbethoxy group, forming indandione-1,3. Upon addition of an aldehyde to the reaction mixture, its condensation with the indandione proceeds immediately, at the moment of formation of the latter.

(I)



$$\underset{\substack{C_6H_4\\ \text{indandione ring}\\ O^-Na^+\\ COOC_2H_5}}{\text{sodium salt of ethyl indandione-1,3-carboxylate-2}} \xrightarrow[H_2SO_4]{CH_3COOH} \underset{\substack{C_6H_4\\ \text{indandione ring}}}{\text{indandione-1,3}} + C_2H_5OH + Na_2SO_4 +$$



$$\underset{\substack{C_6H_4\\ \text{indandione-1,3}}}{CO-CH_2-CO} + OCH-Ar \xrightarrow{-HO} \underset{\substack{C_6H_4\\ \text{indandione ring}}}{CO-C{=}CHAr-CO}$$

(II)

The new method has an advantage over the above-mentioned methods for preparing arylideneindandiones-1,3 in that the process of preparing

indandione-1,3. Good yields of arylideneindandiones-1,3 under these conditions are given by aromatic aldehydes containing nitro-, dialkylamino-, methoxy-, and other groups in the molecule. It should be noted that the condensation products, for example 2-hydroxy-3-methoxybenzal- and 2-hydroxynaphthalindandiones-1,3, undergo further transformations under the reaction conditions. In this respect salicylalindandione-1,3 is also sensitive. It is possible that, under the condensation conditions, the arylideneindandiones-1,3 obtained undergo further transformation toward the formation of indenopyranols. Products of this kind are also obtained in the condensation of *o*-hydroxyaldehydes with indandione-1,3 in the presence of hydrogen chloride (17).

Vanillin (*p*-hydroxy-*m*-methoxybenzaldehyde) gives the corresponding vanillalindandione-1,3, which is stable under the condensation conditions. Condensation also proceeds smoothly with the diacetate of 5-nitrofurfural, whereas with furfural partial charring is observed. The arylideneindandiones-1,3 obtained are listed in Table 1.

Table 1

2-Arylideneindandiones-1,3, $C_6H_4(CO)_2C{=}CHAr$

Ar	Yield, %	M.p., °C	Solvent for recrystallization
phenyl	65–72	149–151150–151 (8)	Acetic acid
3,4-methylenedioxyphenyl	69	209209 (22)	Dioxane
methoxyphenyl	82	155–156155–157 (22)	Dioxane + methanol
dimethoxyphenyl	96	205205 (22)	Same
hydroxy-methoxyphenyl	91	212212 (22)	Dioxane + water
dimethylaminophenyl	96	199–200	Dioxane

Ar	Yield, %	M.p., °C	Solvent for recrystallization
diethylaminophenyl	95	150–152145 (1)	Alcohol
nitro-dimethylaminophenyl	97	220–221221 (22)	Dioxane
dinitrophenyl	84	228–229228–230 (22)	Dioxane + water
nitrophenyl	88	246–248246–247 (22)	Acetic acid
nitrophenyl	83	182–183183 (22)	Same
furyl	32	202–203203 (22)	Dioxane + methanol
nitrofuryl	91	213–214214 (21)	Acetic acid
hydroxyphenyl	21	194–196196 (22)	Dioxane + water

The condensation is carried out as follows: 5 g of the recrystallized Na salt of the ethyl ester of indandione-1,3-carboxylic-2 acid is poured over with a mixture of 15 ml of glacial acetic acid and 2.5 ml of conc. sulfuric acid and heated with stirring. At ~ 50° decomposition of the ethyl ester of indandione-1,3-carboxylic-2 acid begins, as indicated by the evolution-

evolution of carbon dioxide. At this moment the corresponding aldehyde is added. Condensation begins at once with self-heating. To complete the reaction, after the evolution of carbon dioxide has ceased, the mixture is heated further. After cooling, the arylideneindandiones formed are filtered off, washed first with small portions of methanol, then thoroughly washed with water, and recrystallized.

When carrying out the condensation of the Na salt I with dialkylaminobenzaldehydes, sulfuric acid is added in a twofold amount, since in the reaction sulfates of the corresponding arylideneindandiones-1,3 are formed. The initial condensation product obtained is washed with water, then with a solution of soda.

In the condensation of the Na salt I with furfural, as well as with salicylaldehyde, sulfuric acid, on the contrary, was taken in half the amount.

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