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REACTION OF ISOPROPYLIDENE MALONATE WITH N-ARYLIDENE-1(OR 2)-NAPHTHYLAMINES

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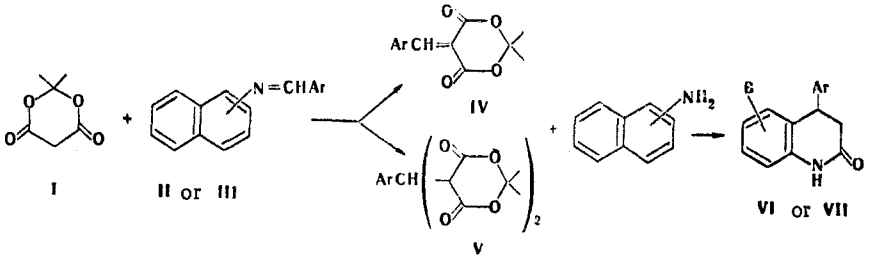
The initial step in the reaction of isopropylidene malonate with N-arylidene-1(or 2)-naphthylamines is cleavage of the latter. The reaction gives isopropylidene 2-arylidene malonates, which subsequently react with α(or β)-naphthylamines to give 4-aryl-2-oxo-1,2,3,4-tetrahydro-7,8(or 5,6)-benzoquinolines. The latter are also obtained in the reaction of arylbis(isopropylidenemalonatyl)methanes with α(or β)-naphthylamines. Indane-1,3-dione and dimedone also cleave N-arylidene-1(or 2)-naphthylamines, and 2-arylideneindane-1,3-diones or arylbis(dimedonyl)methanes are obtained.

The reaction of isopropylidene malonate (I) with N-arylidene-1(or 2)-naphthylamines (II or III) gives [1, 2] 4-aryl-2-oxo-1,2,3,4-tetrahydro-7,8(or 5,6)-benzoquinolines (VI or VII).

When a mixture of isopropylidene malonate (I) was refluxed with arylidenenaphthylamines IIa or IIIa in ethanol for 1 h, the reaction product was unexpectedly isopropylidene 2-(4-N,N-dimethylaminobenzylidene)malonate (IVa). An increase in the reaction time to 12 h led to benzoquinolines VIa or VIIa. The latter were also obtained by reaction of isopropylidene arylidenemalonate IVa with α(or β)-naphthylamines. This indicates that the initial step is cleavage of amines IIa or IIIa to give IVa, which subsequently reacts with naphthylamines to give VIa or VIIa. It was felt that it was necessary to ascertain whether this sort of reaction occurs in all of the investigated cases.



II = α-$C_{10}H_7$; III = β-$C_{10}H_7$; VI B = 7,8-benzo; VII B = 5,6-benzo; a Ar = 4-$(CH_3)_2NC_6H_4$; b Ar = 4-$(C_2H_5)_2NC_6H_4$; c Ar = 3,4-$(CH_3O)_2C_6H_3$; d Ar = 4-$CH_3OC_6H_4$; e Ar = 4-$O_2NC_6H_4$; f Ar = C_6H_5; g Ar = H

Cleavage products IV are isolated in good yields in the reaction of arylidenenaphthylamines II or III with electron-donor substituents. The absorption of arylidenenaphthylamine IId vanishes in the UV spectrum of the reaction mixture of isopropylidene malonate (I) with N-(4-methoxybenzylidene)-1(or 2)-naphthylamine (IId), and absorption characteristic for isopropylidene arylidenemalonate IVd appears; the spectrum contains two isobestic points (255 and 330 nm) in which the sum of the extinction coefficients of starting I and IId is equal to the sum of the extinction coefficients of products IVd and α-naphthylamine. This indicates that the cleavage reaction takes place exclusively. The UV spectrum of the reaction mixture of I and IIId does not contain isobestic points, but a decrease in the intensity of the absorption of product IVd is observed, and this indicates the occurrence of a subsequent reaction. Overlapping of the absorption bands of the starting compounds and the cleavage products is observed for the reaction mixtures of other arylidenenaphthylamines II or III

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with isopropylidene malonate (I), and they were therefore not subjected to spectroscopic study.

When the aryl residue of arylidenenaphthylamines II or III contains electron-acceptor substituents, isopropylidene arylidenemalonates IV cannot always be isolated because of subsequent reaction. Isopropylidene arylidenemalonate IVe was obtained from the reaction mixture of isopropylidene malonate (I) with arylidenenaphthylamine IIIe (it should be noted that the results are difficult to reproduce), whereas we were unable to isolate cleavage product IVe in the case of arylidenenaphthylamine IIe.

Benzoquinolones VIc, e, f or VIIc, e, f were also synthesized by reaction of isopropylidene arylidenemalonates IVc, e, f with α(or β)-naphthylamines. The yields of the corresponding products are approximately the same as in the reaction of isopropylidene malonate (I) with arylidenenaphthylamines IIb, e, f or IIIb, e, f. This may constitute evidence that the course of the reaction is determined precisely by the reaction of cleavage products IV with α(or β)-naphthylamines. Benzoquinolones VIf, g or VIIf, g are obtained in the reaction of arylbis(isopropylidenemalonatyl)methanes Vf, g with α(or β)-naphthylamines [the formation of V is possible in the reaction of arylidenenaphthylamines II or III with isopropylidene malonate (I)]. The yield of the product in the case of Vf is considerably lower than in the reaction of arylidenenaphthylamines IIf or IIIf with isopropylidene malonate (I). However, in the case of Vg benzoquinolones VIg or VIIg are formed in good yields. We were unable to obtain benzoquinolone VIg by reaction of isopropylidene malonate (I) with a mixture of paraformaldehyde and α-naphthylamine.

Thus the first step in the reaction of isopropylidene malonate (I) with arylidenenaphthylamines II or III is cleavage of the latter, and the products are isopropylidene arylidenemalonates IV or arylbis(isopropylidenemalonatyl)methanes V, which in turn react with α(or β)-naphthylamines to give benzoquinolones VI or VII.

It has been shown [3, 4] that cyclic 1,3-diketones such as indane-1,3-dione (VIII) and dimedone (X) react readily with arylidenenaphthylamines II or III to give benzoquinoline derivatives. Since VIII and X, like isopropylidene malonate (I), are strong C—H acids, it was possible that cleavage of arylidenenaphthylamines II or III would also occur in the reaction with VIII and X. We therefore studied the reactions of indane-1,3-dione (VIII) with arylidenenaphthylamines IId or IIId and of dimedone (X) with arylidenenaphthylamines IIa or IIIa.

The absorption bands of arylidenenaphthylamines IId or IIId vanish in the UV spectra of the reaction mixture of indane-1,3-dione VIII with arylidenenaphthylamine IId or IIId, and absorption of the product of cleavage of the latter — 2-(4'-methoxybenzylidene)indane-1,3-dione (IX) — appears. The spectrum of the reaction mixture contains two isobestic points. This constitutes evidence that only cleavage of the latter occurs initially in the reaction of indane-1,3-dione (VIII) with arylidenenaphthylamine II (or III).

Cleavage product 4-dimethylaminophenylbis(dimedonyl)methane (XI) was isolated from the mixture in the reaction of dimedone (X) with arylidenenaphthylamine IIa or IIIa. The results were difficult to reproduce because of the formation of the corresponding benzoquinoline derivatives. It is possible that the more reactive 2-(4-N,N-dimethylaminobenzylidene)-dimedone, which readily reacts with α(or β)-naphthylamines to give the final products, is also formed in addition to XI in this reaction.

Thus strong C—H acids cleave arylidenenaphthylamines II or III, as a consequence of which aldehyde derivatives or cyclic 1,3-diketones — arylidene-1,3-diketones or arylbis-(1,3-diketonyl)methanes — are formed. The subsequent trend of the reaction depends on the properties of the latter and the amine.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil (1500-1800 cm^{-1}) and hexachlorobutadiene (2900-3600 cm^{-1}) were recorded with an IK-14A spectrometer. The UV spectra of 10^{-4} M solutions of the compounds were recorded with a Specord UV-vis spectrophotometer.

Isorpopylidene 2-Arylidenemalonates (IVa-c) (Table 1). A 5-mmole sample of isopropylidene malonate (I) was added to a hot solution of 5 mmole of arylidenenaphthylamine (IIa-c or IIIa-c) in 10 ml of ethanol, and the mixture was refluxed. Compounds IVa-c, which precipi-

TABLE 1. Isopropylidene 2-Arylidenemalonates, 4-Aryl-2-oxo-1,2,3,4-tetrahydro-7,8(or 5,6)-Benzoquinolines, and 4-Dimethylaminophenylbis(dimedonyl)methane

Compound	Reaction time, h	mp, °C	IR spectra		Yield, %
			1800—1500 cm^{-1}	3600—2900 cm^{-1}	
IVa	1	173—174	1740 (sh), 1717 (74), 1618 (55)	—	58[a], 72[b]
IVb	1	124—125	1736 (22), 1710 (40), 1620 (30)	—	52[a], 78[b]
IVc	0,1	169—170	1755 (sh), 1720 (62), 1610 (37)	—	41[a], 55[b]
IVe	0,2	216—217	1758 (65), 1726 (79), 1629 (62)	—	1[b]
VIa	10	215—216	1667 (79), 1609 (52)	3307, 3204, 3169, 3103	50
VIc	8	169—170	1671 (69), 1640 (sh), 1627 (sh)	3323, 3219, 3120, 3086	41
VIe	0,5	222—223	1689 (91), 1646 (sh), 1597 (53)	3343, 3221, 3195, 3125	66
VIf	1,6[c]	199—200	1676 (72), 1605 (30)	3339, 3218, 3186, 3120	62, 14[c]
VIg[d]	16	192—193	1680 (58), 1573 (33)	3338, 3222, 3194, 3123	85
VIIa	10	274—275	1677 (86), 1611 (69), 1560 (40)	3333, 3200, 3186, 3073	40
VIIc	8	214—215	1681 (53), 1624 (42), 1587 (41)	3345, 3219, 3203, 3170	52
VIIe	0,5	265—266	1679 (80), 1625 (59), 1601 (54)	3205, 3109, 3083	83
VIIf	1,2[c]	263—264	1681 (84), 1624 (65), 1610 (61)	3345, 3199, 3128, 3106	60, 27[c]
VIIg	0,5	237—239	1705 (55), 1625 (22), 1600 (18)	3320, 3199, 3164, 3122	66
XI	0,2	194—195	1600 (74), 1585 (76), 1524 (51)		—

[a]From I and II. [b]From I and III. [c]From V and α(or β)-naphthylamine. [d]Found: C 79.5; H 5.7; N 7.3%. $C_{13}H_{11}NO$. Calculated: C 79.2; H 5.6; N 7.1%.

tated when the mixtures were cooled, were removed by filtration, washed with a small amount of ethanol, and crystallized from ethanol.

Isopropylidene 2-(4-Nitrobenzylidene)malonate (IVe) (Table 1). A 3-mmole sample of isopropylidene malonate (I) was added at room temperature to a solution of 3 mmole of arylidenenaphthylamine IIIe in 5 ml of chloroform. After 15 min, the resulting precipitate was removed by filtration, washed with a small amount of chloroform, and dissolved in 7 ml of chloroform. The chloroform solution was filtered to remove the undissolved impurities, and IVe crystallized from the filtrate.

The isopropylidene 2-arylidenemalonates IVa-c, e were identical to the compounds obtained by the methods in [5, 6].

4-Aryl-2-oxo-1,2,3,4-tetrahydro-7,8(or 5,6)-benzoquinolines (VIa, c, e-g or VIIa, c, e-g) (Table 1). A) From Isopropylidene 2-Arylidenemalonates (IVa, c, e, f) and α(or β)-Naphthylamine. A 0.01-mole sample of α(or β)-naphthylamine was added to a hot solution of 0.01 mole of isopropylidene arylidenemalonate IVa, c, e or IVf in 10 ml of ethanol, and the mixture was refluxed. Benzoquinolones VIa, c, e, f or VIIa, c, e, f, which precipitated during the refluxing period or after the reaction mixtures were cooled, were removed by filtration, washed with ethanol, and crystallized from dioxane and water (VIa, c and VIIa, c, f), acetic acid and water (VIe and VIIe), and benzene (VIf).

B) From Arylbis(isopropylidenemalonatyl)methanes (Vf, g) and α(or β)-Naphthylamine. A 0.01-mole sample of α(or β)-naphthylamine was added to a hot solution of 0.01 mole of Vf, g in 10 ml of ethanol, and the mixture was refluxed. The mixture was then worked up as indicated above, and the product was crystallized from dioxane.

Benzoquinolones VIa, c, e-g and VIIa, c, e-g were identical to the compounds obtained by the methods in [1, 2].

4-N,N-Dimethylaminophenylbis(dimedonyl)methane (XI) (Table 1). A 0.01-mole sample of dimedone X was added at room temperature to a solution of 0.01 mole of arylidenenaphthylamine IIa or IIIa in 10 ml of ethanol, during which the bulk of IIa or IIIa dissolved to give a red solution. Compound XI precipitated. After 10 min, the precipitate was removed by filtration, washed with ethanol, and crystallized from ethanol to give a small amount of XI, which was identical to the preparation obtained by the method in [7].

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ACIDITIES OF ANTHRAQUINONE AND ITS HYDROXY DERIVATIVES*

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The acidities of anthraquinone and its 1- and 6-hydroxy derivatives were studied. It is shown that the anthrone ring in the anthrapyridone molecule displays a strong electron-acceptor effect that stabilizes the anion during the development in the pyridone ring of a negative charge as a result of ionization; as a consequence of this, anthrapyridone and 1-hydroxyanthrapyridone are considerably stronger acids than 2-pyridone and 3-hydroxy-2-pyridone, respectively.

It has been previously shown on the basis of quantum-chemical calculations of the π charges on the atoms and the bond orders that anthrapyridone, which is the basis of a valuable series of dyes, to a certain extent retains the properties of pyridone and anthraquinone [2, 3]. This conclusion is to some extent confirmed by the IR spectra of anthrapyridone and its derivatives [2], according to which the overall intensity of the bands of the CO groups of anthrapyridone in the IR spectra is close to the arithmatic sum of the intensities of the CO groups of 2-pyridone and anthrone; this may constitute evidence for the similarity in the amide and ketone CO groups and the anthrapyridone CO groups of the corresponding model compounds.

To ascertain the degree of probability of the redistribution of the electron density between the 2-pyridone and anthrone rings in the anthrapyridone molecule as compared with model compounds in the ground state, we studied the acidities of anthrapyridone and its 1- and 6-hydroxy derivatives and some model compounds (Table 1). The ionization constants corresponding to the detachment of a proton were measured spectrophotometrically in solutions in aqueous ethanol (1:1).

It has been established [2, 3] that anthrapyridone exists in the lactam form. The 2-pyridone $\rightleftharpoons$ 2-hydroxypyridine tautomeric equilibrium is also shifted to favor the lactam form [4]. A comparison of the NH acidities of anthrapyridone (I) and 2-pyridone (II) therefore gives information regarding the character of the effect of a condensed anthrone fragment on the heteroring in the anthrapyridone molecule. It follows from the pK_a values presented in Table 1 that the anthrone fragment has a substantial electron-acceptor effect on the pyridone ring in anthrapyridone, as a result of which the acidity of anthrapyridone is 2.66 pK_a units higher than the acidity of 2-pyridone. The ionization of anthrapyridone I is accompanied by a bathochromic shift of the long-wave absorption band, which in the nonionized form is expressed in the form of a shoulder (Fig. 1).

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