SYNTHESIS OF N,N'-DIALKYLQUINACRIDONES UNDER THE CONDITIONS OF HETEROGENEOUS CATALYSIS

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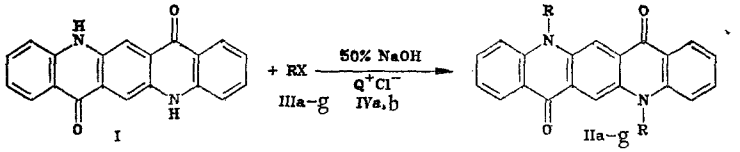
UDC 547.835'831.7:542.97

Alkylation of quinacridone in a heterogeneous medium in the presence of catalytic amounts of quaternary ammonium salts was used to synthesize N,N'-dialkyl derivatives with yields of 80-92%. Performance of the reaction with phase transfer catalysts allows the use of alkylsulfates and alkylsulfonates besides alkyl halides. The use of a branched alkylating agent (isopropyl iodide) increases, due to steric factors, the reaction time, and reduces the yield of the product of alkylation.

The derivatives of the linear trans-quinacridone (7,14-dioxo-5,7,12,14-tetrahydroquinolino[2,3-b]acridine) (I), in particular the N,N'-dialkylquinacridones, are of practical interest as pigments and polymer-soluble dyes. They are obtained by the alkylation of quinacridone I with alkyl iodides in bipolar solvents in the presence of an aqueous alkali solution [1]. However, alkylation in a homogeneous medium limits the number of alkylating agents, since alkylsulfates and alkylsulfonates are hydrolyzed in the presence of aqueous alkali. However, during the last years heterogeneous catalysis [2, 3] has been introduced in the N-alkylation of nitrogen-containing heterocycles (pyridone, acridone) which are readily soluble in nonpolar solvents which are used as the organic phase.

The essential difference between compound I and the earlier investigated heterocycles [2, 3] is that it is insoluble in the organic and aqueous phases. We have studied the alkylation of insoluble substrates under the condition of heterogeneous catalysis on the example of N-alkylation of the diimide of perylenetetracarboxylic acid [4].

In the present work we have alkylated quinacridone I in a heterogeneous system consisting of a 50% aqueous solution of NaOH and toluene, xylene, or chlorobenzene in the presence of catalytic amounts of hexadecyltrimethylammonium chloride (IVa) or triethylbenzylammonium chloride (IVb) as phase transfer catalysis.



II, III a $R=C_2H_5$; b $R=i\text{-}C_3H_7$; c $R=C_4H_9$; d $R=C_6H_5CH_2$; e $R=o\text{-}ClC_6H_4CH_2$; f $R=p\text{-}ClC_6H_4CH_2$; g $R=p\text{-}CH_3C_6H_4CH_2$; IV a $Q=C_{16}H_{33}\overset{+}{N}(CH_3)_3$; b $Q=C_6H_5CH_2\overset{+}{N}(C_2H_5)_3$

In the reaction of quinacridone I with the ethyl ester of benzenesulfonic acid we have studied the influence of the degree of dispersion of the substrate, the concentration of the catalyst, and the ratio of the phase volumes on the yield of N,N'-diethylquinacridone IIa. The yield of the product IIa was determined spectrophotometrically in concentrated H_2SO_4 with the use of calibration graphs, plotted on the basis of synthetic binary mixtures of compounds I and IIa. The conversion of compound I was determined at λ_{max} 600 nm and the formation of compound IIa at λ_{max} 628 nm.

The influence of the degree of dispersion on the degree of alkylation after 10 h was investigated by using compound I with a particle size of 0.1, 0.1-0.3, 0.3-0.5, and 0.5 mm. The yields of compound IIa, determined spectrophotometrically, were equal to 99, 99, 47, and 28%, respectively. Consequently, for the alkylation of an insoluble substrate the particle

Rubezhnoe Branch, Scientific-Research Institute of Organic Intermediates and Dyestuffs, Rubezhnoe 349870. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 952-955, July, 1985. Original article submitted July 10, 1984.

 0009-3122/85/2107-0792$09.50

TABLE 1. Yield of N,N'-Diethylquinacridone IIa as Function of the NaOH:Quinacridone I Ratio

Moles NaOH per mole quinacridone I	Yield of IIa, % (spectrophotometrically), after				
	1 h	2 h	3 h	4 h	5 h
2	9	13	16	21	26
4	12	17	22	29	41
6	19	28	35	43	50
8	27	43	55	65	74
10	35	45	60	72	86
15	37	46	61	74	87
20	36	45	62	73	86

TABLE 2. Spectral Characteristics and Appearance of Quinacridone I and N,N'-Dialkylquinacrodines IIa-g

Compound	Appearance	IR spectrum, cm^{-1} (C=O)	UV spectrum, λ_{max}, nm (log ε)	
			DMFA	conc. H_2SO_4
I	Blue-red crystals	1590, 1635	480 (4,9), 510 (4,98)	512 (4,79), 552 (4,99), 600 (5,02)
IIa	Orange needles	1608, 1630	490 (4,35), 523 (4,53)	530 (4,60), 570 (4,92), 628 (5,01)
IIb	Dark-red crystals	1609, 1630	484 (4,25), 515 (4,85)	515 (4,59), 557 (4,89), 600 (4,97)
IIc	Red crystals	1607, 1623	484 (4,95), 523 (5,15)	530 (4,64), 572 (4,95), 622 (5,07)
IId	Orange-red prism	1605, 1625	480 (4,45), 510 (4,61)	514 (4,63), 552 (4,86), 598 (4,94)
IIe	Dark-orange needles	1609, 1633	478 (4,35), 508 (4,96)	515 (4,49), 554 (4,82), 600 (4,90)
IIf	Brown needles	1609, 1634	480 (4,80), 512 (4,98)	512 (4,70), 552 (4,98), 597 (5,06)
IIg	Yellow-orange needles	1608, 1632	480 (4,94), 510 (5,22)	514 (4,58), 555 (4,91), 600 (5,00)

size must be reduced to 0.1-0.3 mm. At a particle size larger than 0.3 mm a complete conversion of quinacridone I is not achieved. Variation of the concentration of the catalyst IVa from 2 to 20 moles has practically no effect on the yield of compound IIa.

The yield of N,N'-diethylquinacridone IIa as function of the ratio NaOH—quinacridone I was investigated by using in the reaction a 50% aqueous solution of NaOH containing from 2 to 20 moles NaOH per mole of substrate I. The yield of the compound IIa is at the optimum at a NaOH—quinacridone ratio of I $\leq$ 10:1 (Table 1).

The influence of the degree of dispersion and the NaOH:quinacridone ratio on the yield of the alkylation product IIa indicates that deprotonation of quinacridone I takes place at the interface between the phases, i.e., according to a mechanism which has been proposed earlier in [5, 6] for the alkylation of phenylacetonitrile and its derivatives, not in the organic phase based on the transfer of the hydroxyl ion by the catalyst [7]. In fact, when the transfer of the hydroxyl ion into the organic phase would take place, the duration of the reaction would be proportional to the concentration of the catalyst.

The formation of the compound IIa was used to investigate the efficiency of ethylating agents of different nature: ethyl iodide, diethyl sulfate, and ethyl esters of benzene- and toluenesulfonic acids. Table 2 shows that all ethylating agents are efficient under the conditions of heterogeneous catalysis. The best results were obtained in the alkylation of quinacridone I with diethyl sulfate. A preparative yield of 90% is reached in a shorter time, requiring an excess of the alkylating agent which is smaller by a factor of 1.5-3 (4 moles per mole of compound I instead of 6-12 moles of ethyl sulfonates or ethyl iodide). This is evidently due to the less lipophilic character of the outgoing $C_2H_5SO_4^-$ group in comparison with $ArSO_3^-$ and I^- so that the catalyst maintains a high activity; this is in agreement with the results obtained in [8] on the influence of the lipophilic character of anions.

TABLE 3. N,N-Dialkylquinacridones IIa-g

Compound	RX	Amount of RX, mole/mole I	Duration of reaction, h	mp, °C	Found, %			Empirical formula	Theory, %			Yield, %
					C	H	N (Cl)		C	H	N (Cl)	
IIa	$C_2H_5SO_3C_6H_5$	6	10	360	77,5	5,5	7,2	$C_{24}H_{20}N_2O_2$	78,2	5,4	7,6	92
	$(C_2H_5)_2SO_4$	4	7	360								90
	$C_2H_5SO_3C_6H_4CH_3$-*p*	6	12	360								91
	C_2H_5I	12	13	360								89
IIb	*i*-C_3H_7I	20	32	125—127	78,4	6,5	7,4	$C_{26}H_{24}N_2O_2$	78,4	6,5	7,0	50
IIc	*n*-C_4H_9Br	4	12	262—265	78,6	6,6	6,6	$C_{28}H_{28}N_2O_2$	79,0	6,6	6,6	87
IId	$C_6H_5CH_2Cl$	6	11	360	82,7	4,7	5,7	$C_{34}H_{24}N_2O_2$	82,9	4,9	5,7	85
IIe	*o*-$ClC_6H_4CH_2Cl$	4	12	343—345	72,1	3,7	4,9 (12,3)	$C_{34}H_{22}Cl_2N_2O_2$	72,7	3,9	4,9 (12,7)	82
IIf	*p*-$ClC_6H_4CH_2Cl$	6	9	360	72,0	4,1	4,9 (12,1)	$C_{34}H_{22}Cl_2N_2O_2$	72,7	3,9	4,9 (12,7)	81
IIg	*p*-$CH_3C_6H_4CH_2Cl$	4	10	353—355	82,7	5,4	5,3	$C_{36}H_{28}N_2O_2$	83,1	5,4	5,4	80

The change in the color of the quinacridone allows us to follow the course of the reaction visually. When the 50% aqueous alkali solution is added to the suspension of quinacridone I in the aromatic hydrocarbon, the color of the solid phase changes from blue-red to violet, while the aqueous-alkali and the organic phases remain colorless. The alkali salt of the quinacridone is formed which is insoluble in the aqueous-alkali and organic phases. The addition of catalytic amounts of hexadecyltrimethylammonium chloride IVa or triethylbenzylammonium chloride IVb makes the organic phase turn blue, due to the formation of the bis-ammonium salt of quinacridone which is soluble in nonpolar solvents. After addition of the alkylating agent the organic phase becomes colorless and a precipitate of N,N'-dialkylquinacridone II is formed (with a color ranging from yellow-orange to red-brown; Table 2). The role of the interface transfer catalyst is to transport the dianion of quinacridone from the interface between the phases into the organic phase in which the alkylation then takes place.

The only reaction products are the compounds IIa-g; products of monoalkylation and alkylation at the oxygen atom have not been observed. The composition and structure of compounds IIa-g were established by elemental analysis and on the basis of their electron and IR spectra (Tables 2 and 3). The IR spectra of compounds IIa-g retain two bands at 1590-1609 and 1623-1635 cm^{-1} (C=O); the band at 2900-3200 cm^{-1} disappears (N–H), which is characteristic for the unsubstituted quinacridone I. The electron spectra of compounds IIa-g in DMFA and of the protonated forms in concentrated H_2SO_4 are analogous to the corresponding spectra of the unsubstituted quinacridone I (Table 2). This indicates that the nature of the heterocyclic system has been retained.

The introduction of a branched alkylating agent (isopropyl iodide) increases the reaction time by a factor of 2.5-4.5 (to 32 h instead of 7-13 h in the case of the n-alkyl derivatives) and requires stoichiometric quantities of the catalyst IVb in order to obtain the product IIb with a yield of only 50%.

EXPERIMENTAL

The IR spectra were taken on an UR-20 spectrophotometer (in KBr tablets), the electron spectra on an SF-14 spectrophotometer (in DMFA and concentrated H_2SO_4); the concentration of compound I was $1.3 \cdot 10^{-3}$, of compound II, $1.2 \cdot 10^{-3}$ mole/liter. The initial 7,14-dioxo-5,7,12,14-tetrahydroquinolino[2,3-b]acridine (I) was synthesized according to [9]. The characteristics of the synthesized compounds are shown in Tables 2 and 3.

N,N'-Diethylquinacridone (IIa). A suspension of 3.12 g (10 mmole) of quinacridone I, ground to a particle size 0.1-0.3 mm, and 0.27 g (1 mmole) of compound IVa in 50 ml chlorobenzene, is treated under stirring with 5.25 ml of a 50% aqueous NaOH solution (100 mmole NaOH). The mixture is stirred for 30 min, treated with 11.6 g (60 mmole) ethyl ester of benzene-sulfonic acid, heated at 80° for 10 h, and poured into 100 ml water. The mixture is filtered, the precipitate washed with 30 ml methanol and water, and dried. Yield of compound IIa was 3.39 g (92%); after recrystallization from nitrobenzene, mp above 360°.

N,N'-Diisopropylquinacridone (IIb). A suspension of 3.12 g (10 mmole) quinacridone I and 4.46 g (20 mmole) of compound IVb in 50 ml toluene is treated under stirring with 5.25 ml of 50% aqueous NaOH solution. Stirring is continued at 80° for 32 h, adding 8.5 g (50 mmole) isopropyl iodide every 8 h. The mixture is poured into 100 ml water, the precipitate filtered and washed with 30 ml methanol. In order to remove the unreacted quinacridone I, the reaction product is treated with 50 ml of a mixture of 10% aqueous NaOH and DMFA 1:1, washed, and dried. Yield of compound IIb, 1.8 g (50%). Recrystallization from o-dichlorobenzene, mp 125-127°. The filtrate is diluted with 200 ml water, filtered, washed, and dried to separate 1.15 g of compound I (48%).

Compounds IIc-g are prepared in the same way as compound IIa. The completion of the reaction is determined by the disappearance of the initial compound I: the absence of a blue coloration of the solution when a mixture of 10% aqueous NaOH and DMFA 1:1 is added to the reaction mixture.

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SYNTHESIS OF DIOXOANTHRA[1,2-d]PYRAZOLINE-1,2-AMINE(I)IMIDES BY THE PHOTOLYSIS OF 1-AZIDO-2-DIALKYLAMINOMETHYL-9,10-ANTHRAQUINONES

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UDC 547.673.5:541.144.8

The photolysis of 1-azido-2-dialkylaminomethyl-9,10-anthraquinones leads to 2,2-dialkyl-6H,11H,6,11-dioxanthra[1,2-d]pyrazoline-1,2-amide(I)imides. The same products are formed in the thermolysis of the initial compounds; however, they decompose under the reaction conditions.

When heated [1] or irradiated [2], 1-azido-9,10-anthraquinones are converted to anthra-[1,9-cd]-6-isoxazolones. In the presence of substituents in position 3 which are conjugated with the aromatic ring and are inclined to an intramolecular reaction with the nitrene, the latter isomerize when heated or irradiated into derivatives of 9,10-anthraquinone, condensed in the positions 1,2 with a five- or six-membered heterocycle [3-5]. It was of interest to investigate the behavior of such 1-azido-9,10-anthraquinones which in position 2 contain a strongly nucleophilic group which is not conjugated with the anthraquinone nucleus, and which is capable of reacting with the nitrene or its precursor (see scheme below).

The scheme was used to synthesize the 1-azido-2-dialkylaminomethyl-9,10-anthraquinones Ia-c (Table 1).

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 956-959, July, 1985. Original article submitted July 20, 1984.

0009-3122/85/2107-0795$09.50