

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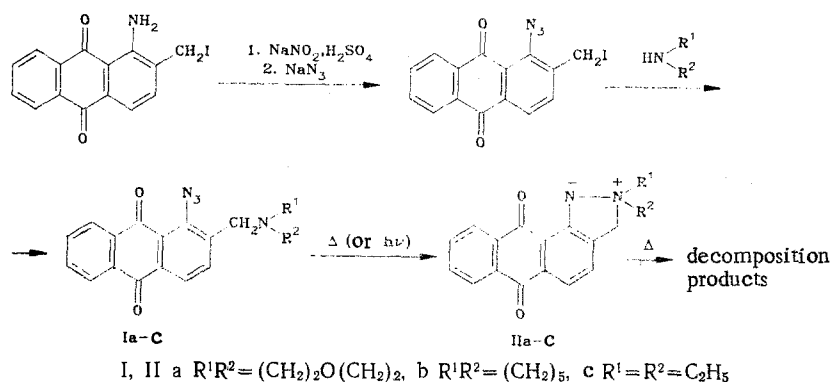
The photolysis of 1-azido-2-dialkylaminomethyl-9,10-anthraquinones leads to 2,2-dialkyl-6H,11H,6,11-dioxanthra[1,2-d]pyrazoline-1,2-amide(I)imides. The same products are formed in the thermolysis of the initial compounds; however, they decompose under the reaction conditions.

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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The azides Ia-c are stable when heated in low-boiling solvents (methanol, benzene) and react only very slowly when refluxed in toluene; in boiling m-xylene they decompose in 0.5 h. By following spectrophotometrically the thermolysis of compound Ia in m-xylene we have found that initially the optical density increases noticeably in the region 605 nm in which the initial substance does not absorb; after this, simultaneously with the consumption of the initial azide Ia ( $\lambda_{\max}$  370 nm) and an intermediate product ( $\lambda_{\max}$  605 nm) increases the optical density at 476 nm, where finally the absorption maximum of the new substance appears. It must be pointed out that in the course of the decomposition of the azide Ia the UV spectrum of the reaction mixture does not contain the characteristic intensive absorption band in the region 440-460 nm which corresponds to anthra[1,9-cd]-6-isoxazolines that do not contain strong electron donor substituents. It is known [6] that the appearance of long-wave absorption maxima in derivatives of 9,10-anthraquinone is related to the presence of strong electron donor substituents in these compounds. By taking into account this fact and the ability of nitrenes or their precursors [7] to catch the electron pair of nucleophiles, we have assumed that the azides Ia-c are transformed during refluxing in xylene mainly according to the scheme proposed above.

The 2,2-dialkyl-6H,11H,6,11-dioxoanthra[1,2-d]pyrazoline-1,2-amine(I)imides are formed more clearly by the short illumination of solutions of compounds Ia-c with natural light. In the photolytic conversion Ia-c  $\rightarrow$  IIa-c in nonpolar solvents (benzene, hexane) the solution quickly achieves a blue coloration, followed by spontaneous crystallization of the products IIa-c. No intermediate products have been detected by TLC.

We have followed the conversion Ia  $\rightarrow$  IIa spectrophotometrically. The set of spectral curves passes through an isobestic point. The relationship between the optical densities of the reaction mixtures at two wavelengths (307 and 605 nm) is linear, which indicates that no intermediate or side products are present in the reaction mixture in detectable concentrations. This is an argument in favor of the direct interaction of the azidogroup of compounds Ia-c or of the nitrene derived from it with the dialkylamino group during photo- or thermal excitation. Thus the character of the substituent of 1-azidoanthraquinones in position 2 has an influence on the course of the conversions of these substances.

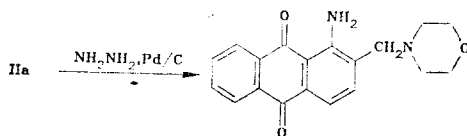
TABLE 1. Characteristics of 1-Azido-2-dialkylaminomethyl-9,10-anthraquinones (Ia-c) and 2,2-Dialkyl-6H,11H,6,11-dioxoanthra[1,2-d]pyrazoline-1,2-amine(I)imides (IIa-c)

| Compound | mp, °C  | Electron spectrum<br>$\lambda_{\max}$ , nm<br>(log $\epsilon$ ) | IR spectrum, <sup>2)</sup><br>cm <sup>-1</sup> |                  | Found<br>N, % | Empirical<br>formula  | Theory<br>N, % | Yield,<br>% |
|----------|---------|---|--|------------------|---------------|---|----------------|-------------|
|          |         |   | C=O  | N <sub>(3)</sub> |               |   |                |             |
| Ia       | 124-126 | —   | 1675   | 2120             | 16,2          | C <sub>19</sub> H <sub>16</sub> N <sub>4</sub> O <sub>3</sub> | 16,1           | 70          |
| Ib       | 117-119 | —   | 1675   | 2120             | 15,4          | C <sub>20</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub> | 16,2           | 81          |
| Ic       | 91-93   | —   | 1675   | 2120             | 16,8          | C <sub>19</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub> | 16,8           | 86          |
| IIa      | 181-183 | 605 (3,91)  | 1645   | —                | 8,8           | C <sub>19</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> | 8,8            | 72          |
| IIb      | 158-160 | 605 (3,88)  | 1645   | —                | 8,7           | C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> | 8,8            | 60          |
| IIc      | 128-130 | 605 (3,82)  | 1645   | —                | 9,6           | C <sub>19</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub> | 9,2            | 67          |

\* I, II a R<sup>1</sup>R<sup>2</sup> = (CH<sub>2</sub>)<sub>2</sub>O(CH<sub>2</sub>)<sub>2</sub>, b R<sup>1</sup>R<sup>2</sup> = (CH<sub>2</sub>)<sub>5</sub>, c R<sup>1</sup> = R<sup>2</sup> = C<sub>2</sub>H<sub>5</sub>.

The structure of the compounds IIa-c is in accordance with their IR and PMR spectra (Table 1). The band of the valence oscillations of the C=O bond of compounds IIa-c is shifted toward shorter wavelengths in comparison with the corresponding band of the azides Ia-c and is located in the region 1650-1640  $\text{cm}^{-1}$ . This is attributed to the presence of a strong donor in the substances IIa-c, conjugated with the carbonyl group. A comparison of the PMR spectra of compounds Ic and IIc shows that the signals of the protons of the methylene groups of the diethylamino fragment (3.3 ppm, qu, 4H) and the signal of the protons of the methylene group linked with the aromatic ring (4.5 ppm, s, 2H) of compound IIc are shifted approximately by 0.8 ppm toward the weaker field. The signals of the aromatic protons of compound IIc are shifted toward the strong field approximately by 0.5 ppm as compared with the product Ic; this is attributed to the appearance of the electron donor nitrogen atom in position 1 of compound IIc. Similar regularities have been observed also in the PMR spectra of compounds Ia,b and IIa,b, which is in agreement with the proposed structure of compounds IIa-c.

The proposed structure of compounds IIa-c is also supported by the ease of reduction of product IIa to 1-amino-2-morpholinomethyl-9,10-anthraquinone.



The compounds IIa-c are the first representatives of cyclic ylides in the 9,10-anthraquinone series.

#### EXPERIMENTAL

The UV spectra were recorded on a Specord UV-vis spectrometer (in ethanol), the IR spectra on a Specord IR-75 spectrometer (in liquid petrolatum), and the PMR spectra on a Tesla BS-467 (60 MHz) spectrometer in  $\text{CD}_3\text{OD}$  and  $\text{CCl}_4$ . The melting points were determined on a Boetius heated microstage. TLC on Silufol foils (acetone-toluene, 1:5) was used to follow the course of the reactions and to establish the purity of the compounds.

1-Azido-2-iodomethyl-9,10-anthraquinone. A sample of 1.82 g (5 mmole) 1-amino-2-iodomethyl-9,10-anthraquinone is added to 250 ml acetic acid. The suspension obtained is treated under stirring at 15° by a solution of nitrosylsulfuric acid prepared from 0.69 g (10 mmole)  $\text{NaNO}_2$  and 5 ml concentrated  $\text{H}_2\text{SO}_4$ . The reaction mixture is kept under these conditions for 20 min and then added during 10 min under stirring into a mixture consisting of 500 ml water, 500 g ice, 100 g sodium acetate, and 0.65 g (10 mmole)  $\text{NaN}_3$ . The precipitate formed is filtered off, dried, dissolved in benzene, and chromatographed on silica gel (100 × 250) by eluting the first yellow zone with benzene ( $R_f$  0.86 in a mixture of acetone-toluene, 1:7). After evaporation of the benzene, the precipitate is washed with hexane, yield 1 g (51%) 1-azido-2-iodomethyl-9,10-anthraquinone; mp 179-181°. IR spectrum: 2120 ( $\text{N}_3$ ), 1670  $\text{cm}^{-1}$  (C=O). Found, %: N 10.4.  $\text{C}_{15}\text{H}_8\text{IN}_3\text{O}_2$ . Calculated, %: N 10.8.

1-Azido-2-dialkylaminomethyl-9,10-anthraquinones (Ia-c). 1.94 g (5 mmole) 1-azido-2-iodomethyl-9,10-anthraquinone and 25 mmole dialkylamine are added to 50 ml dioxane at 25° and kept in the dark for 6 h. The reaction mixture is then poured into a mixture of 200 ml water and 100 g ice, saturated with NaCl. After keeping at 0° the products are filtered off, dried, and chromatographed on silica gel foils (100 × 250) protected from light with a mixture of chloroform-acetone 5:1. After evaporation of the eluent the products are recrystallized from methanol.

2,2-Dialkyl-6H,11H,6,11-dioxoanthra[1,2-d]pyrazoline-1,2-amine(I)imides (IIa,b). A solution of 0.1 g of azides Ia,b in 80 ml absolute ether is kept at 25° in a glass vessel under natural light. After 6 h the contents are concentrated to 10 ml and the blue products IIa,b filtered off.

2,2-Diethyl-6H,11H,6,11-dioxoanthra[1,2-d]pyrazoline-1,2-amine(I)imide (IIc) is prepared in the same way as the compounds IIa,b; a solution of 0.1 g azide in a mixture of 120 ml hexane and 60 ml acetone is then subjected to photolysis for 6 h. IIc is isolated in the same way as IIa,b.

Reduction of the Ylide IIa. A solution of 0.05 g (0.16 mmole) of compound IIa in 10 ml ethanol with 0.2 ml hydrazine hydrate is refluxed for 5 min in the presence of 0.05 g of 0.2% Pd on carbon. After hot filtration dilution of the filtrate with water gives 0.037 g (74%) 1-amino-2-morpholinomethyl-9,10-anthraquinone, identified by comparison with a sample prepared according to [9].

The photolytic conversion Ia  $\rightarrow$  IIa is followed spectrophotometrically by recording the UV spectra of the solution of compound Ia ( $5 \cdot 10^{-5}$  M) in toluene at given time intervals after irradiation with an OI-18 lamp in a 1-cm cell through a WK-38 light filter ( $\lambda_{\text{pass}} > 370$  nm). Under these conditions full conversion Ia  $\rightarrow$  IIa is achieved after 0.5 h.

The thermolysis of the azide Ia is followed spectrophotometrically by taking samples from the boiling solution of Ia in m-xylene, with a final concentration of the product Ia of  $5 \cdot 10^{-5}$  M. The decomposition of the azide Ia is completed after 0.5 h.

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#### CYCLIZATION OF N-ALKYLAMMONIUM CATIONS WITH BIFUNCTIONAL NUCLEOPHILES.

#### 17.\* ANNELATION OF IMIDAZOLE AND 1,2,4-TRIAZINE RINGS WITH PYRAZINES

#### VIA THE REACTIONS OF THIOSEMICARBAZIDES WITH PYRAZINIUM SALTS

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1- and 4-mono- as well as 1,4-disubstituted thiosemicarbazides undergo cyclization reactions upon treatment with N-alkylpyrazinium and quinoxalinium salts to give N-aminosubstituted imidazo[4,5-b]pyrazines and imidazo[4,5-b]quinoxalines, respectively. Thiosemicarbazides containing substituents in the 2-position react with N-alkylquinoxaline salts to give 1,2,4-triazino[5,6-b]quinoxalines after cyclization.

In previous papers [2-4] we have reported that cyclization of quaternary N-alkylquinoxalinium salts with bifunctional nucleophiles containing a thioamide functional group, R-C(=S)-NH<sub>2</sub>, results in the formation of a variety of heterocyclic derivatives, depending on the nature of the substituents and on the reaction conditions. For example, treatment of salts of the N-alkylquinoxalinium ions I with thiobenz- and thioacetamides gives thiazolo[4,5-b]quinoxalines [2]; in the same way, reaction with phenylthioureas produces imidazo[4,5-b]quinoxalines [3]. The course of these types of cyclization reactions are governed not only by

\*For communication No. 16, see [1].

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