Acid-catalysed, Nucleophile-catalysed and Thermal Decomposition of 2-Amino-3-(2',2'-dimethylaziridino)-1,4-naphthoquinone (1,2)

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The course of the thermal, acid-catalysed and iodide-catalysed decomposition of 2-amino-3-(2',2'-dimethylaziridino)-1,4-naphthoquinone (III) was investigated. Thermal and iodide-catalysed decompositions gave mainly 2,3-diamino-1,4-naphthoquinone (VI) and 2-amino-3-(2'-methylallylamino)-1,4-naphthoquinone (V) together with low amounts of 2,2-dimethyl-1,2,3,4,5,10-hexahydrobenzo[*g*]quinoxaline (IV) and 2-isopropyl-1*H*-naphthoimidazole-4,9-dione (VII). The acid catalysed isomerization of the aziridinonaphthoquinone III with halohydric acids or with acetic acid readily gave the opening of the aziridine ring; the corresponding salts of 2-amino-3-(2'-haloisobutylamino)-1,4-naphthoquinones (VIIIa-c) and 2-amino-3-(2'-acetoxyisobutylamino)-1,4-naphthoquinone (X) were formed by cleavage of the carbon-nitrogen bond at the substituted carbon atom. Hypotheses on the mechanism of these reactions are given.

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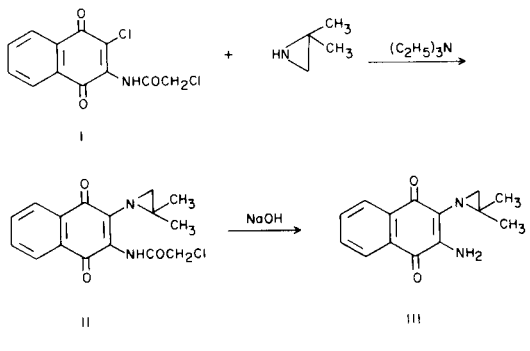
It is well known that 1-acylaziridines and other activated aziridines give easy opening of the aziridine ring; these isomerizations can be carried out either by acids or nucleophiles or by heat, and normally lead to isomeric linear chain or ring expanded compounds (3-6). In previous papers it was reported (7,8) the hydriodic acid-catalysed and iodide-catalysed isomerizations of several 2-amino-3-aziridino-1,4-naphthoquinones, unsubstituted, monosubstituted and symmetrically disubstituted with alkyl groups at the aziridine ring. It seemed interesting to extend this investigation to the isomerization of 2-amino-3-(2',2'-dimethylaziridino)-1,4-naphthoquinone (III) as a model of vinylogous activated aziridines not symmetrically substituted with alkyl groups. In fact, this aziridine can be regarded as an activated aziridine since the naphthoquinone moiety in some measure, could be related to an α,β-unsaturated carbonyl system. Compound III was prepared by selective hydrolysis of the corresponding 2-chloroacetamido-3-(2',2'-dimethylaziridino)-1,4-naphthoquinone (II), which in turn was prepared from 2-chloroacetamido-3-chloro-1,4-naphthoquinone (I) (9) and 2,2-dimethylaziridine (10) (Scheme I).

The isomerization of III was carried out in three different ways: in acidic medium with halohydric acids in ethanol and with acetic acid alone, with sodium iodide in refluxing acetone, and xylene at different temperatures.

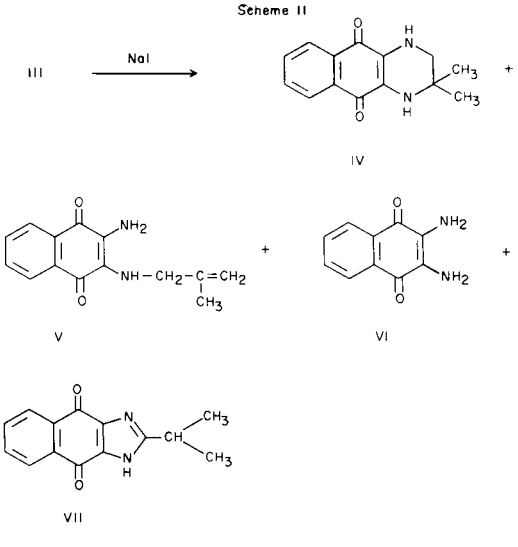
Nucleophile-catalysed Decomposition.

The aminoaziridine III was isomerized with sodium iodide in refluxing acetone in neutral medium. Compound III readily reacted at a higher rate than that observed in the isomerization of monoalkyl-substituted aminoaziridinonaphthoquinones under the same conditions. The complex reaction mixture obtained in the isomerization was chromatographed on a silica gel column; the main components separated are listed in Scheme II.

Scheme I



Scheme II



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In previously observed isomerizations of monosubstituted and *trans*-symmetrically disubstituted aminoaziridinonaphthoquinones (8), benzo[*g*]quinoxalines of type IV were formed as main products. On the contrary, by isomerization, III gave IV in very low yields, the main products formed being 2,3-diamino-1,4-naphthoquinone (VI) and 2-amino-3-(2′-methylallylamino)-1,4-naphthoquinone (V). From the reaction mixture was also isolated in low yields (see Table I), 2-isopropyl-1*H*-naphthoimidazole-4,9-dione (VII). The structure of compounds IV and V was established on the basis of the elemental analysis and of ir and nmr spectra, whereas that of compounds VI and VII was confirmed also by comparison with authentical samples (11,12) (see Experimental).

Table I

Relative Yields of Compounds Obtained in the Decomposition of III under Several Different Conditions

	IV	V	VI	VII
Nucleophilic decomposition (NaI in refluxing acetone)	4	22	69	4
Thermal decomposition:				
xylene refluxing	7	26	66	2
xylene at 120°	2	39	54	2
xylene at 100°	4	46	48	2

Thermal Decomposition.

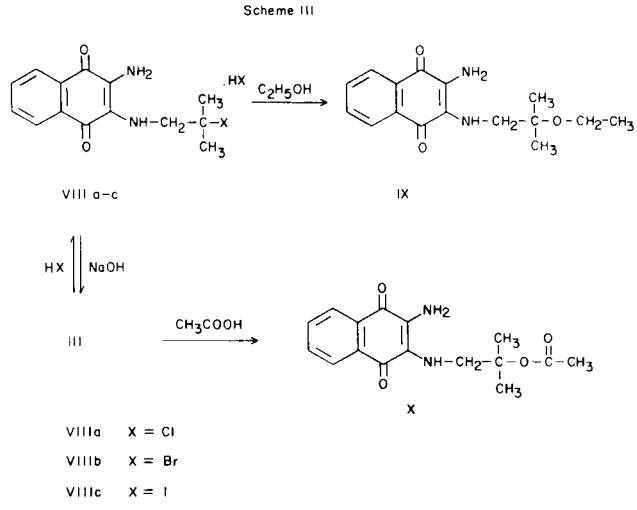
Thermal decomposition of III was carried out using xylene as the solvent at three different temperatures; refluxing, 120° and 100°. Under all conditions the same complex reaction mixture was obtained: in all cases the main components were the same as those found in the isomerization with sodium iodide as presented in scheme II. The only difference was in yields; in fact, as illustrated in Table I, VI was always the main product, V being the other significant product obtained. By isomerization of III with sodium iodide in refluxing acetone or by thermal decomposition in refluxing xylene V and VI were formed in almost identical yields, whereas compounds IV and VII were always formed in very low yields. In the thermal decomposition lower temperatures reduced the formation of VI and increased that of IV and V.

Acid-catalysed Decomposition.

The acid-catalysed decomposition of III was carried out with hydrochloric, hydrobromic, hydriodic and acetic acids. Compound III dissolved in glacial acetic acid readily gave opening of the aziridine ring with formation of 2-amino-3-(2′-acetoxyisobutylamino-1,4-naphthoquinone (X) (Scheme III).

The structure of X was assigned on the basis of the elemental analysis and of ir and nmr spectra. Compound X was formed in nearly quantitative yields; the isomeric acetoxy derivative, which could have been generated in the opening of the aziridine ring by cleavage of the carbon-nitrogen bond at the unsubstituted carbon atom, was not formed.

Scheme III



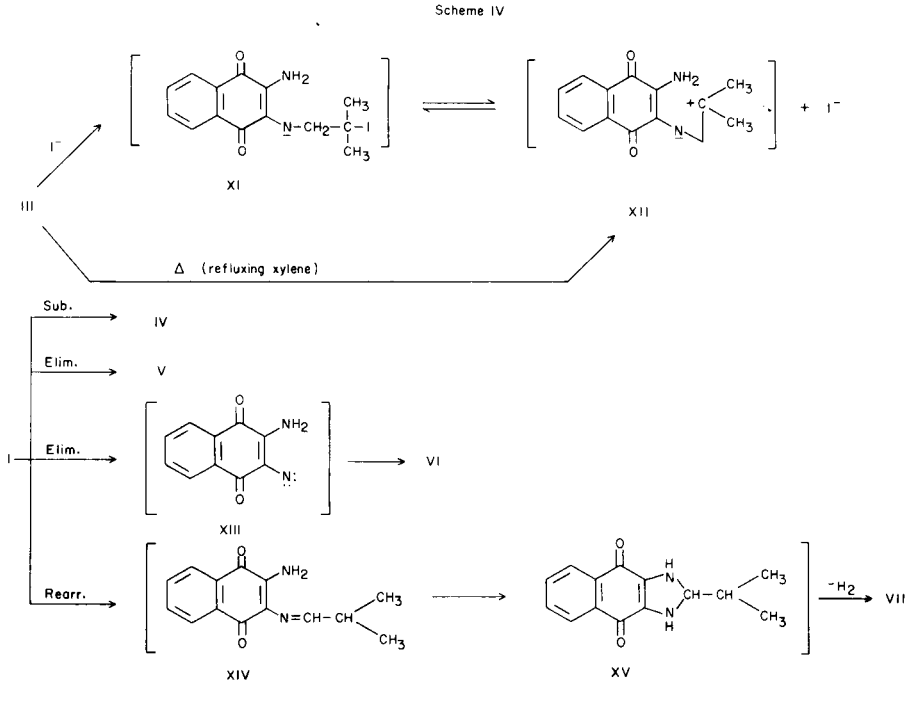
By adding at room temperature to an ethanolic or benzene solution of III a slight excess of 57% hydriodic acid or gaseous hydrogen bromide and hydrogen chloride, the opening of the aziridine ring was readily observed and, in a few minutes, 2-amino-3-(2′-haloisobutylamino)-1,4-naphthoquinone halohydrates (VIIIa,b,c) precipitated. Because of hydrolysis, these salts were unstable and uncrystallizable; their structures were assigned on the basis of their elemental analysis and nmr spectra. As in the case of the opening with acetic acid, the presence of the isomeric 2-amino-3-(2′-haloterbutylamino)-1,4-naphthoquinone halohydrates was excluded. The structures of VIIIb and VIIIc were confirmed by their transformation, when dissolved in ethanol at room temperature, into 2-amino-3-(2′-ethoxyisobutylamino)-1,4-naphthoquinone IX in one day and in less than thirty minutes, respectively. Moreover, in the ethanolysis of VIIIb and VIIIc, the formation of the isomeric 2-amino-3-(2′-ethoxyterbutylamino)-1,4-naphthoquinone was excluded; instead, very low amounts of IV, V and VI were detected. On the contrary, under the same conditions hydrochloride VIIIa was stable to ethanolysis. In fact, by neutralization after one day of an ethanolic solution of VIIIa was obtained a very small trace of IX and a violet compound which was the free base of VIIIa.

By adding an hydroalcoholic solution of sodium hydroxide to an alcoholic solution of VIIIc at room temperature, III was obtained almost instantaneously and quantitatively by closure of the aziridine ring. Under the same conditions, VIIIb gave III almost completely in a few minutes. Compound VIIIa reacted slowly and, after one day at room temperature, it was transformed into III in about 50% yields.

Discussion.

It is generally accepted that acid- and nucleophile-catalysed isomerizations of aziridine derivatives proceed by two consecutive S_N^2 processes (5,13-15). However, for more reactive aziridines there is the possibility that the reaction could have, to some extent, an S_N^1 character. The results obtained in the acid-catalysed, nucleophile-catalysed and thermal isomerization of the aziridine III seems to confirm this hypothesis. In fact, in the opening of activated aziridines with acids, especially in 2,2-dialkyl substituted aziridines, the proof supporting an S_N^1 mechanism is the formation of products derived from cleavage on the carbon-nitrogen bond at the more highly substituted carbon atom (5). In the acid-catalysed opening of III with acids of different strength and different nucleophilicity of their anions, the direction of opening of the aziridine ring is always observed on the substituted carbon atom; only one halo derivative isomer was always obtained. This seems good evidence that the mechanism of opening of III in acidic medium is of type S_N^1. The stability of halo derivatives VIIIa,b,c is in agreement with the reactivity of tertiary alkyl halides. The formation of the ethoxy derivative IX can proceed by an S_N^1 mechanism; the presence in the ethanolic solution of traces of IV, V and VI, which can be generated by a dissociative process from VIII, support this hypothesis. Also the results obtained in the isomerization of III with sodium iodide in acetone or by heating in xylene, lead us to believe that both decompositions proceed with the same mechanism. In fact, in both cases, isomerization gives the same products, although the properties of solvents are different. The formation of products IV, V and VI and VII can be explained supposing an intermediate carbonium ion which reacts as illustrated in Scheme IV. In the isomerization with sodium iodide, iodide ion could give a nucleophilic attack on the aziridine ring forming an unstable iodo derivative intermediate XI; it rapidly, and probably also anchimerically assisted by the aziridine nitrogen, could dissociate giving the ion-pair XII. A tight ion pair of type XII could have its origin in xylene in the thermal isomerization by heterolytic cleavage of the carbon-nitrogen bond of the aziridine ring. The formation of the allylamine V could occur by a β-elimination reaction of an hydrogen ion from XI. The diamino derivative VI could occur from a nitrene intermediate XIII which in turn could be generated from XII by a β-elimination process. The formation of the imidazole derivative VII could be explained by a rearrangement process of XII into the imino derivative intermediate XIV. By attack of the amino group in position 2, XIV could give the naphthoimidazoline intermediate XV; a dehydrogenation process could transform XV into VII. The formation of VII seems like good evidence of the dissociative process proposed; the yields of VII obtained in the isomerization with sodium iodide in acetone, higher than those obtained in thermal isomerization, seem to confirm that in xylene the dissociative process could proceed with difficulty as largely expected. The yields of V and VI change with temperature, but the sum of their yields is constant; this seems to confirm that V and VI could have origin from the

Scheme IV



same intermediate through two competitive elimination reactions. In fact, V is stable in refluxing xylene, and it is not transformed into VI under the conditions used in the isomerization reaction. The formation of IV may be due to the attack of the amino group in position 2 on the ion-pair XII or, in the isomerization with sodium iodide, directly on the iodo derivative XI. However, in the thermal isomerization in xylene, higher reaction temperatures increase yields of IV; this could mean that the transition state leading to IV has a higher activation energy than that required in the elimination reaction. As regards V, it could be formed also by a synchronous cyclic mechanism: by a seven membered cyclic transition state, a hydrogen atom could be transferred from a methyl group to the amino group in position 2 or to the quinonic oxygen in position 4. In fact, in literature there are examples of thermal isomerization of 1-acyl-2,2-dimethylaziridine (16), 1-benzenesulfonyl-2,2-dimethylaziridines (17), 1-azaspiro-[2.4]heptanes and 1-azaspiro[2.5]octanes (18) in which the formation of unsaturated amides was explained with an intramolecular cyclic transition state similar to the Chugaev reaction. In our case, III would react as a vinylogous acylaziridine. However, the fact that V was detected, although as a trace, in the ethanolic solutions of VIII leads us to exclude this cyclic concerted mechanism at least in the acid and in the nucleophile-catalysed isomerizations.

EXPERIMENTAL

The melting points were determined with a Büchi apparatus and are uncorrected. The nmr spectra were recorded in deuteriochloroform and DMSO solutions with a Jeol JNM C 60 HL and a Varian EM-390 90 MHz spectrometers, using TMS (tetramethylsilane) and sodium 3-(trimethylsilyl)propansulfonate as internal standards. The ir spectra were recorded on a Perkin Elmer model 257 spectrophotometer. The uv spectra were recorded on a Perkin Elmer model 575 spectrophotometer. Tlc was carried out on tlc plates prepared with silica gel GF 254 Merck. For column chromatography silica gel 60 Merck was used.

2-Chloroacetamido-3-(2,2'-dimethylaziridino)-1,4-naphthoquinone (II).

Anhydrous triethylamine (8 ml.) and 0.03 mole of 2,2-dimethylaziridine (10) were added to a suspension of 0.015 mole of 2-chloroacetamido-3-chloro-1,4-naphthoquinone (9) in 100 ml. of anhydrous benzene with stirring. The reaction mixture was stirred at room temperature for 15 hours. The yellow solid formed was filtered and recrystallized from ethanol, m.p. 160-161° dec. (yield 62%); uv λ max (ethanol): nm (log ε) 248 (4.20); 254 (4.21); 287 (3.96); 340 (3.39); ir ν max (cm^{-1}): 3260 (NH stretching); 1685, 1660 (C=O stretching).

Anal. Calcd. for $C_{16}H_{15}ClN_2O_3$: C, 60.29; H, 4.74; N, 8.79. Found: C, 60.41; H, 4.45; N, 8.91.

2-Amino-3-(2',2'-dimethylaziridino)-1,4-naphthoquinone (III).

A suspension of 0.01 mole of 2-chloroacetamido-3-(2',2'-dimethylaziridino)-1,4-naphthoquinone in 100 ml. of ethanol and 100 ml. of 2*N* sodium hydroxide was stirred at room temperature for 12 hours. The reaction mixture was poured in 300 ml. of water and extracted with 300 ml. of methylene chloride in three portions. Evaporation of the solvent under *vacuo* at room temperature gave a residue which was recrystallized from ethyl ether-*n*-hexane, m.p. 88-89° (yield 65%); uv λ max (ethanol): nm (log ε) 238 (4.10); 245 (4.11); 289 (4.25); 520 (3.28). Ir ν max (cm^{-1}): 3450-3340 (NH stretching); 1665 (C=O stretching).

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.83; N, 11.56. Found: C, 69.74; H, 6.03; N, 11.25.

Isomerization of III with Acetic Acid.

Compound III (0.001 mole) was dissolved in 25 ml. of glacial acetic acid. In a few minutes the opening reaction was complete and the formation of a blue coloured compound was observed; then, in time, the solution changed to a yellow-green colour. After ten minutes, the solution was poured into water and extracted with chloroform. The chloroform solution, washed with sodium bicarbonate and then with water was dried. By evaporation, there was obtained a residue which was purified by column chromatography on silica gel eluted with a mixture benzene-ethyl acetate 80:20. Evaporation of the solvent gave 0.25 g. of X as oily compound; uv λ max (ethanol): nm (log ε) 235 (3.93); 257 (3.89); 296 (4.07); 545 (3.03); ir ν max (cm^{-1}): 3450, 3340 (NH stretching); 1740, 1630 (C=O stretching); nmr (deuteriochloroform): δ 1.51 (6H, s, NH-CH_2-C(CH_3)$_2$-O-); δ 4.75 (broad 3H, N-H; vanishes on addition of deuterium oxide); δ 7.10-7.95 (4H, m, aromatics).

Isomerization of III with Hydrohalic Acids.

a) Hydrogen Chloride.

Compound III (0.003 mole) was dissolved in 30 ml. of benzene and gaseous hyrogen chloride was bubbled at room temperature into the solution; after a few minutes the colour of the solution changed to yellow. The introduction of hydrogen chloride was stopped and the solution stirred at room temperature for several minutes. A yellow precipitate was recovered and washed with benzene. Compound VIIIa (0.82 g.) was obtained m.p. 165-167°; nmr (DMSO): δ 1.70 (6H, s, NH-CH_2-C-(CH_3)$_2$-Cl); δ 3.74 (2H, s, NH-CH_2-C(CH_3)$_2$-Cl); δ 7.55-8.33 (8H, m, NH and aromatics, partially vanishes on addition of deuterium oxide).

Anal. Calcd. for $C_{14}H_{16}Cl_2N_2O_2$: C, 53.35; H, 5.12; N, 8.89. Found: C, 52.98; H, 4.97; N, 8.66.

The free base of VIIIa was obtained by dissolving VIIIa in ethanol. The ethanolic solution was poured into water and the aqueous solution extracted with chloroform. The chloroform solution was washed with sodium bicarbonate and then with water, dried over sodium sulphate and gave, after evaporation, 2-amino-3-(2'-chloroisobutylamino)-1,4-naphthoquinone (XI) as an oily compound; nmr (deuteriochloroform): δ 1.62 (6H, s, NH-CH_2-C(CH_3)$_2$-Cl); δ 3.30 (2H, s, NH-CH_2-C(CH_3)$_2$-Cl; δ 4.40-5.00 (3H, broad, vanishes on addition of deuterium oxide NH); δ 7.12-8.50 (4H, m, aromatics).

b) Hydrogen Bromide.

Compound III (0.003 mole) was dissolved in 30 ml. of benzene and gaseous hydrogen bromide was bubbled into the solution at room temperature; after a few minutes the colour of the solution changed to yellow. The introduction of hydrogen bromide was stopped and the solution stirred at room temperature for several minutes. A yellow precipitate was recovered and washed with benzene; 1.05 g. of VIIIb was obtained m.p. 162-164°; nmr (DMSO): δ 1.81 (6H, s, NH-CH_2-C(CH_3)$_2$Br); δ 3.79 (2H, s, NH-CH_2-C(CH_3)$_2$-Br); δ 7.55-8.21 (8H, m, partially vanishes on addition of deuterium oxide, NH and aromatics).

Anal. Calcd. for $C_{14}H_{16}Br_2N_2O_2$: C, 41.61; H, 3.99; N, 6.93. Found: C, 41.34; H, 3.80; N, 6.64.

c) Hydriodic Acid.

To 0.003 mole of III dissolved in 25 ml. of ethanol was added, with stirring at room temperature, 1.2 ml. of 57% hydriodic acid. The colour of the solution changed to yellow. By stirring at room temperature for several minutes there was obtained a yellow precipitate which was recovered and washed with ether; 1.2 g. of VIIIc was obtained m.p. 210-212° dec.; nmr (DMSO): δ 1.28 (6H, s, NH-CH_2-C(CH_3)$_2$-J); δ 3.35 (2H, s, NH-CH_2-C(CH_3)$_2$-J); δ 6.5-7.1 (4H broad, NH); 7.65-8.15 (4H, m, aromatics).

Anal. Calcd. for $C_{14}H_{16}I_2N_2O_2$: C, 33.76; H, 3.24; N, 5.62. Found: C, 33.47; H, 3.16; N, 5.44.

Alcholysis of Hydrohalides VIIIb and VIIIc.

Compounds VIIIb or VIIIc (0.001 mole) were dissolved in 30 ml. of absolute ethanol. The solution was left at room temperature for 30 minutes in the case of VIIIc and for one day in the case of VIIIb. The ethanolic solution, after addition of 100 ml. of water, was made neutral with sodium bicarbonate and extracted with chloroform. The organic layer was washed with water and dried. By evaporation there was obtained a residue which was purified by column chromatography on silica gel eluting with a mixture of benzene-ethyl acetate 90:10. The fractions containing the pure blue compound, after evaporation gave IX as a residue which was crystallized from benzene, m.p. 103-104°; nmr (deuteriochloroform): δ 1.23 (9H, s, and t, NH-CH_2-C(CH_3)$_2$-O-CH_2-CH_3); δ 3.12 (2H, s, NH-CH_2-C(CH_3)$_2$-); δ 3.44 (2H, q, O-CH_2-CH_3), δ 5.32 (3H, broad s, vanishes with deuterium oxide NH), δ 7.20-7.98 (4H, m, aromatics).

Anal. Calcd. for $C_{16}H_{20}N_2O_3$: C, 66.64; H, 6.99; N, 9.72. Found: C, 66.72; H, 6.91; N, 9.83.

Isomerization of III with Sodium Iodide.

To 0.003 mole of III dissolved in 100 ml. of acetone was added 1.8 g. of sodium iodide and the resulting solution was refluxed for one hour. Compound III was completely reacted and the reaction mixture after evaporation of the solvent gave a residue which was dissolved in ethyl acetate and extracted with water. By evaporation of the organic layer, a residue was obtained which was chromatographed on silica gel column eluted with a mixture ethyl acetate-cyclohexane 50:50. Four main products were recovered. By evaporation of the fractions intensely violet coloured there was obtained 2-amino-3-(2'-methylallylamino)-1,4-naphthoquinone (V) m.p. 84-86° (from ethanol); nmr (deuteriochloroform): δ 1.82 (3H, s, CH_3); δ 3.74 (2H, s, CH_2); δ 4.60 (3H, broad signal, vanishes with deuterium oxide, NH); δ 5.00 and δ 5.16 (2H, 2s —C=C$\begin{matrix}H\\H\end{matrix}$); δ 7.55-8.15 (4H, m, aromatics).

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.83; N, 11.56. Found: C, 69.11; H, 5.72; N, 11.63.

By continuing the elution of the column, there was obtained fractions containing a blue coloured compound; from them by evaporation was obtained 2,2-dimethyl-1,2,3,4,5,10-hexahydrobenzo[*g*]quinoxaline (IV) m.p. 164-165° (from ethanol); nmr (deuteriochloroform): δ 1.25 (6H, s, CH_3); δ 3.08 (2H, s, CH_2); δ 4.68 and δ 4.92 (2H, broad signals, vanishes by addition of deuterium oxide; NH); δ 7.45-7.98 (4H, m, aromatics).

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.83; N, 11.56. Found: C, 69.34; H, 5.97; N, 11.49.

By further elution of the column, intensely violet coloured fractions were obtained; by evaporation of these fraction there was obtained 2,3-diamino-1,4-naphthoquinone (VI) which was characterized by comparison with an authentic sample (11).

Finally were obtained yellow coloured fractions, from which, by evaporation, was obtained 2-isopropyl-1*H*-naphthoimidazole-4,9-dione (VII), characterized by comparison with an authentic sample.

Thermal Decomposition of III in Xylene.

Solutions of 0.003 mole of III dissolved in 100 ml. of anhydrous xylene were termally decomposed at three different temperatures; in refluxing xylene for one hour, in xylene at 120° for eight hours and in xylene at 100° for three days. In all cases the decomposition reaction gave the same products. The relative yields of the compounds obtained are summarized in Table I. The work up of the resulting reaction mixtures was carried out as descried in the isomerization with sodium iodide.

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(1) This research was supported by Consiglio Nazionale delle Richerche.

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