REACTIONS WITH DIAZOALKANES

III. 1,4-NAPHTHAQUINONE AND DIAZOALKANES*

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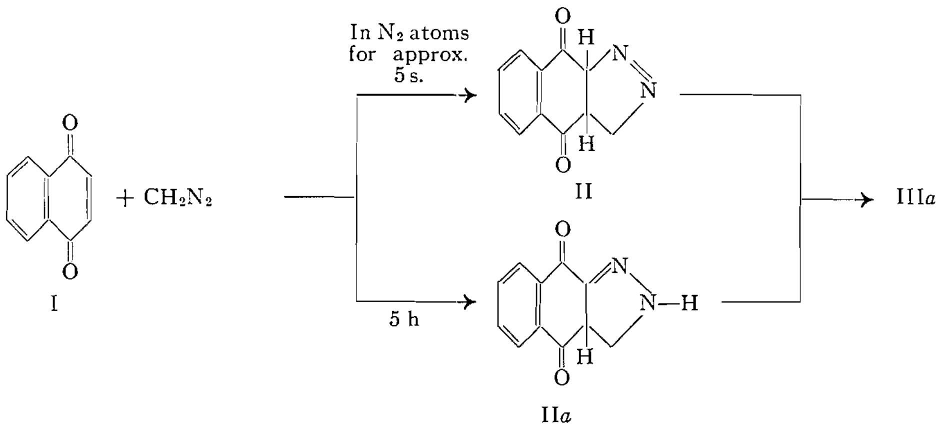
ABSTRACT

The addition of diazomethane to 1,4-naphthaquinone has been reexamined. Two products are isolated from this reaction, one of them (III*a*) has been previously reported. Similarly, diazoethane gives two products. The constitution of these products is discussed, particularly in the light of their ultraviolet and infrared spectra. The thermal stability of diazoalkane adducts to I is discussed.

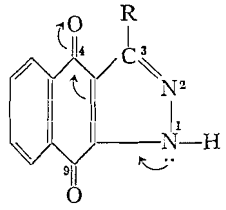
A recent publication by Dean and Jones (1), which describes *inter alia* compounds derived from diazomethane and 1,4-naphthaquinone, prompts us to publish our related work on this topic. Dean *et al.* (1) suggested the following mechanism:



The elucidation of the structure of the immediately formed compound as 3*a*,4,9,9*a*-tetrahydro-3*H*-benz[*f*]indazole (II) may be uncertain. The band described for the azo linkage at 1548 cm^{-1} is unreliable, as similar bands appear in the case of III*a* at 1538 cm^{-1}. The lack of absorption close to 1620 cm^{-1}, from which it was concluded that the 2,3-double bond of the naphthaquinone nucleus has been removed, is actually a negative proof. In reality, this band is also absent in other compounds where it is expected, e.g. III*a*, III*b*, and VII.

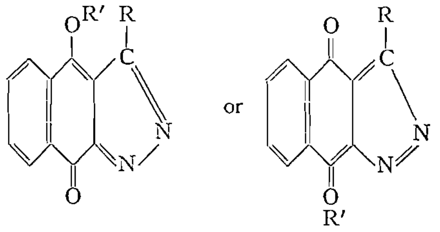
It was found, however, in the present investigation that the reaction of diazomethane with I yields two products, one having a high melting point (345°) (III*a*) and the other a low melting point (172°) (IV*a*). These products are at a higher oxidation level than those described by Dean *et al.* (1). The latter compound has not been described either by early investigators (2, 3) or by recent ones (1). The fact that a mixture of compounds results from such a reaction may throw some doubt on the purity of the uncrystallized product used by Dean (1) for the analysis of the supposed II*a* (which, however, was at a lower level of oxidation than the compounds isolated in our work).

**Part II. W.I. Awad, S.M.A.R. Omran, and M. Sobhy, J. Chem. U.A.R. In press.*



III

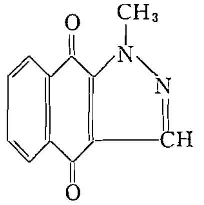
III*a*; R = H
III*b*; R = CH_3



IV

IV*a*; R = H, R′ = CH_3
IV*b*; R = CH_3, R′ = C_2H_5

The structure of IV*a* is based upon (i) absence of N—H stretching frequency near 3333 cm^{-1}, (ii) analytical data, (iii) presence of C=O stretching frequency of 1666 cm^{-1}, (iv) presence of a strong band at 1250 cm^{-1} (absent in IIIa and V) which is characteristic of enol–ether linkage (4), and (v) the fact that methylation of III*a* with dimethyl sulphate in alkaline medium gives two products—(*a*) a high melting compound (310°), which was previously isolated (1, 2, 3) and assigned the N–CH_3 structure (1) (V), and (*b*) a low melting compound (172°). The latter compound was identical with IV*a* isolated from the diazomethane experiment, as shown by mixed melting point determinations and infrared spectra.



V

The ultraviolet spectra of III*a*, IV*a*, and V (Fig. 1) indicate that III*a* and V are of similar structure and that IV*a* is quite different. The action of diazomethane on III*a* gave mainly IV*a* together with a small quantity of V. Comparison of the ultraviolet spectra of III*a* in alcohol and in alkaline solution (Fig. 2) indicates that, in alkaline solution, there is only a slight bathochromic shift and a hyperchromic effect, and that the hybrid anion is fundamentally similar to III*a* (cf. curved arrows in III*a*).

Diazoethane has also been allowed to react with I. Two products have been isolated—a high melting compound to which structure III*b* is assigned and a low melting compound to which structure IV*b* is assigned. The structure III*b* is confirmed by (i) analytical data, (ii) infrared spectrum that shows N—H stretching frequency at 3333 cm^{-1} and a carbonyl stretching frequency at 1666 cm^{-1}, (iii) solubility in alkali, and (iv) its ultraviolet spectrum (Fig. 3), which shows its clear resemblance to that of III*a*. The structure of IV*b* is based upon (i) analytical data, (ii) the absence of a N—H stretching frequency near 3333 cm^{-1}, the presence of a carbonyl stretching frequency at 1665 cm^{-1} and the presence of a enol–ether stretching frequency at 1250 cm^{-1}, (iii) insolubility in alkali, and (iv) its ultraviolet spectrum (Fig. 3), which shows its resemblance to that of IV*a*.

The pyrolysis of diazoalkane derivatives from naphthaquinone is of interest. It is known (2, 5) that VI decomposes on pyrolysis with loss of nitrogen, that VII is stable

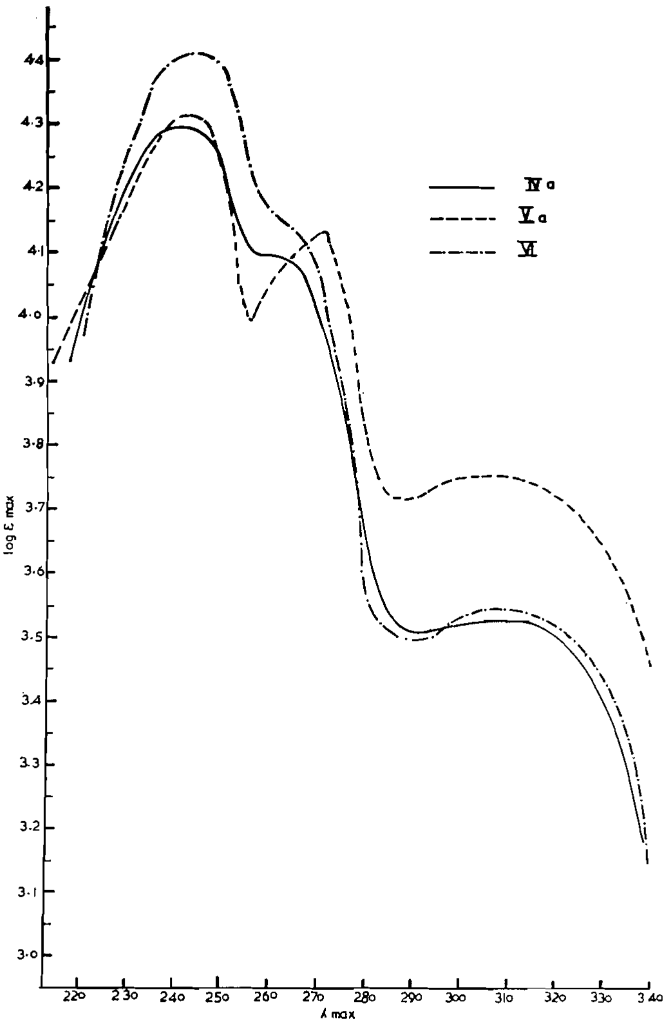
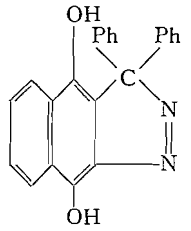
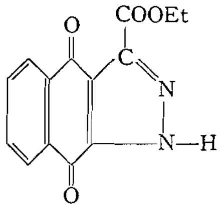


Fig. 1.

(2), that the corresponding acid can be decarboxylated (2), and that the oxidation product of VI, namely VIII, sublimes unchanged upon heating. We can conclude that



VI



VII

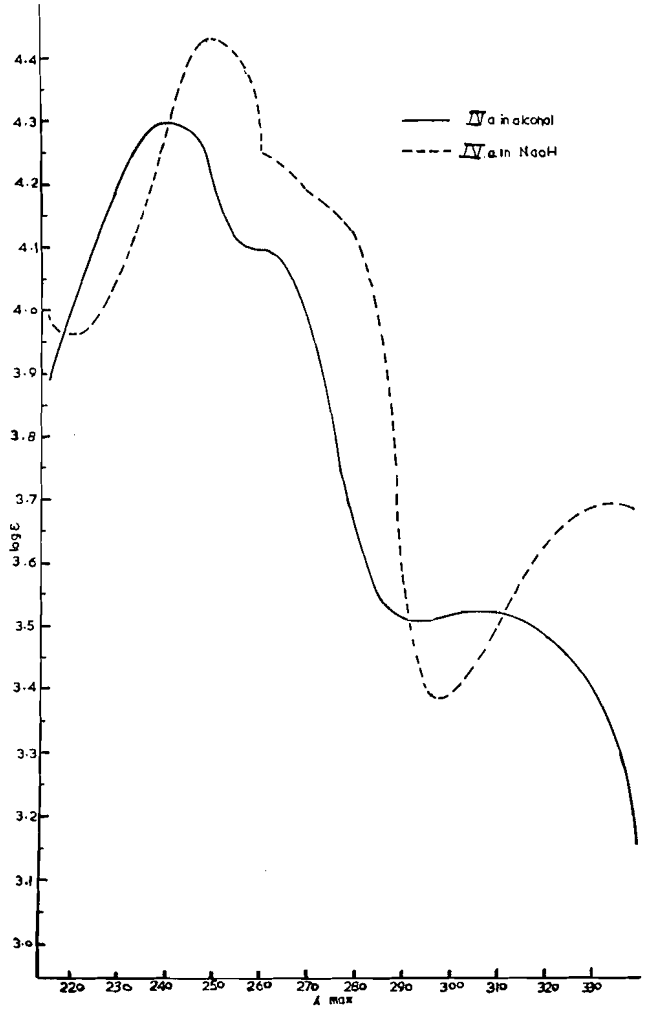
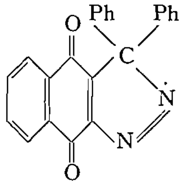


FIG. 2.

the heterocyclic ring is more stable when fused with quininoid rings rather than with benzenoid rings. Compounds III*a*, III*b*, VII, and VIII are thus thermally stable, and VI is thermally unstable.



VIII

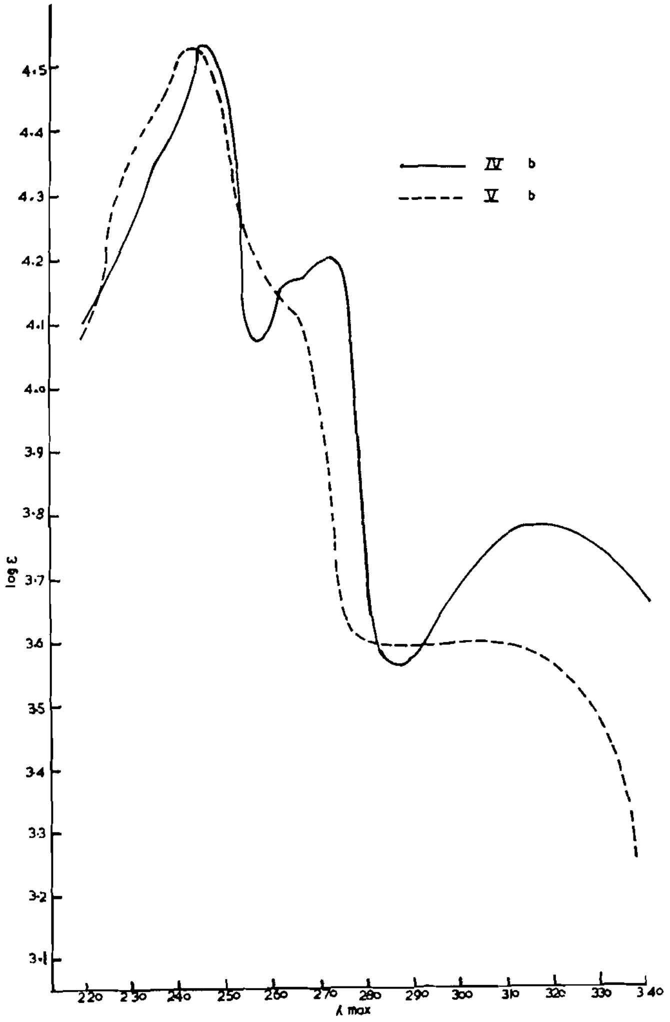


FIG. 3.

EXPERIMENTAL

Melting points are uncorrected. Analyses were carried out by Alfred Bernhardt, Max-Plank Institute, Mulheim, Germany. Infrared spectra were measured on a Perkin–Elmer Infracord Model 137 spectrophotometer, using the KBr Wafer technique. Ultraviolet spectra were measured on a Perkin–Elmer Spectracord Model 4000A spectrophotometer with ethyl alcohol solutions, except in case of III*a* (Fig. 2—the dotted curve) where it is carried out in 5% sodium hydroxide solution.

4,9-Dihydro-4,9-dioxo-1H-benz[f]indazol (IIIa) and its O-Methyl Derivative (IVa)

Naphthaquinone (1.0 g) and diazomethane (from nitrosomethyl urea, 4.0 g) were left for a couple of hours in ice-cooled ether (ca. 100 ml). The reaction began at once with the separation of a brownish precipitate. This precipitate was filtered off (0.65 g) and III*a* was crystallized from acetic acid as colorless crystals, m.p. ≈ 345°.

Calcd. for $C_{11}H_6O_2N_2$: C, 66.65; H, 3.05; N, 14.1. Found: C, 66.4; H, 3.3; N, 13.9.

III*a* sublimed unchanged *in vacuo*. The ethereal mother liquor was concentrated and cooled, at which time IV*a* separated out (0.2 g). It was crystallized from light petroleum (80–100°) as colorless crystals, m.p. 172°. IV*a* was insoluble in alkali.

Calcd. for $C_{12}H_8O_2N_2$: C, 67.9; H, 3.8; N, 13.2. Found: C, 67.9; H, 3.7; N, 13.1.

Action of Dimethyl Sulphate on IIIa

Methyl sulphate (0.1 ml) was added to a filtered solution of III*a* (0.2 g) in 2 ml 5% NaOH. The mixture was shaken well and the precipitate formed was filtered off. The precipitate was boiled with light petroleum (80–100°). The fraction, which was soluble in light petroleum, crystallized out as colorless crystals (0.05 g), m.p. 172° (undepressed on admixture with IV*a* obtained previously). The insoluble fraction, 4,9-dihydro-1-methyl-4,9-dioxobenz[*f*]indazole, was crystallized from alcohol (0.05 g), m.p. 310° (2, 3, 4).

Action of Diazomethane on IIIa

An ice-cooled ethereal diazomethane solution (from methyl nitroso urea, 4 g) was added to III*a* (0.5 g) and left overnight. The insoluble part (0.1 g), which crystallized from EtOH, was proved to be V by means of mixed melting point determinations. The ethereal solution was concentrated to give IV*a* (0.40 g), crystallized from light petroleum (80–100°), and identified by melting points and mixed melting points.

4,9-Dihydro-4,9-dioxo-1H,3-methyl-benz[f]indazol (IIIb) and its O-Ethyl Derivative (IVb)

Naphthaquinone (7.00 g) and diazoethane (from ethyl nitroso urea, 20 g) were left in ice-cooled ether (ca. 350 ml) for a couple of hours. The reaction was similar to that described for diazomethane. The ether-insoluble product (4.0 g) was filtered off. III*b* was crystallized from ethyl alcohol as colorless crystals, m.p. 292°. Calcd. for $C_{12}H_8O_2N_2$: C, 67.9; H, 3.8; N, 13.8. Found: C, 68.1; H, 4.1; N, 13.6.

This product was soluble in 5% NaOH solution and sublimed unchanged *in vacuo*. The ethereal mother liquor was concentrated to give IV*b* (0.70 g), which was crystallized from light petroleum (80–100°) as colorless crystals, m.p. 119°. It was insoluble in alkali (cf. Fig. 3 for ultraviolet spectra).

Calcd. for $C_{14}H_{12}O_2N_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 70.5; H, 5.1; N, 11.5.

Action of Heat on VII and VIII

Both compounds (3) were heated under vacuum (2 mm/Hg), where they sublimed unchanged, as shown by melting points and mixed melting points.

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