1019. *Adducts from Quinones and Diazoalkanes. Part III.*[1] 1,4-*Naphthaquinone and Diazomethane.*

By F. M. Dean and Peter G. Jones.

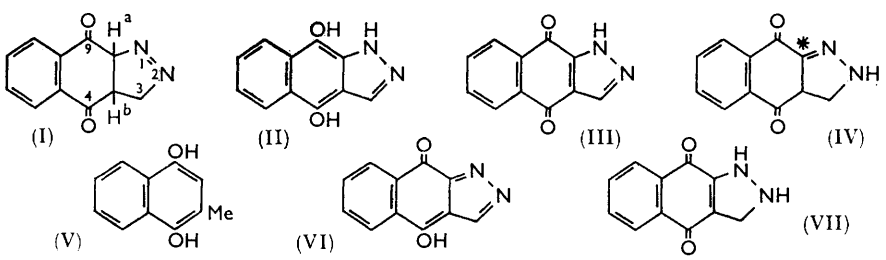
The addition of diazomethane to 1,4-naphthaquinone has been re-examined and what is believed to be the true primary adduct (I) has been isolated. This readily isomerises to the known yellow compound. The yellow compound is not a quinol, and a revised structure (IV) is suggested.

The addition of diazomethane to 1,4-naphthaquinone would be expected to give adduct (I) although previous investigators [2,3] seem not to have encountered it. We believe that we have now obtained this adduct. It isomerises to the yellow compound described by Fieser and Peters [2] and thought to be a quinol (II) because of the solubility in alkali and ease of oxidation to quinone (III). However, reasons will be advanced for regarding the yellow compound, not as a quinol, but as a tautomer (IV).

In ether, diazomethane adds rapidly to 1,4-naphthaquinone, giving a compound $C_{11}H_8N_2O_2$ which is colourless but different from that studied by previous workers.[2,3] The new compound tends to explode if dry, and soon changes into a yellow isomer if damp. Hence no extensive examination was undertaken, and structure (I) is supported mainly by the infrared spectrum determined for mulls in paraffin oil, in which the compound is relatively stable. Strong bands at 1684 and 1669 cm.$^{-1}$ indicate that two conjugated carbonyl groups are present, while a fairly strong band at 1548 cm.$^{-1}$ corresponds to the azo-link.[1] The lack of absorption close to 1620 cm.$^{-1}$ shows that the 2,3-double bond of the naphthaquinone nucleus [4] has been removed, and the transparency in the 3 μ region confirms the absence of hydroxyl or imino-groups.

The spontaneous, mildly explosive decomposition of adduct (I) leaves a dark mass composed largely of 2-methylnaphthalene-1,4-diol (V) (isolated as the diacetate) and a dihydrobenzindazole derivative, the quinone (III). Thus the decomposition consists mainly in the loss of nitrogen from some of the adduct to give 2-methylnaphthaquinone, together with oxidation–reduction between this and the rest of the adduct or its tautomers. "Blocked" adducts, *e.g.*, (I; Me for H^a), are not prone to spontaneous decomposition,[1] which means that it is not the azo-group but the possibility of oxidation–reduction that is chiefly responsible for the instability.

In part, the arguments to be advanced in support of structure (IV) for the yellow isomer rely on the structure (III) allocated by Fieser and Peters [2] to the oxidation product.



Unlike all other quinones, this product is colourless, its ready solubility in alkali suggests that it is an enol such as (VI) rather than an imine such as (III), and its acetate absorbs

[1] Part II, preceding paper.
[2] Fieser and Peters, *J. Amer. Chem. Soc.*, 1931, **53**, 4080.
[3] Pechmann and Seel, *Ber.*, 1899, **32**, 2292.
[4] Yates, Ardas, and Fieser, *J. Amer. Chem. Soc.*, 1956, **78**, 650.

at 1761 cm.$^{-1}$, a frequency too high for most amides. On the other hand, the ultraviolet spectrum bears the expected resemblance [5] to that of anthraquinone; the weak acidity of pyrazole would be much enhanced by conjugation with two carbonyl groups; and, finally, analogy with *N*-acetyl-imidazoles and -triazoles [6] strongly suggests that the absorption of *N*-acetylpyrazoles would not be far from 1760 cm.$^{-1}$. That the acetyl derivative rapidly reverts to the original compound when warmed with alcohols is consistent with formulation as a kind of acid anhydride or of diacylimine and permits no clear decision. However, the methylation product [2,3] must be an *N*-methyl derivative (negative Zeisel and Kuhn–Roth determinations; absence of enol-ether absorption near 1250 cm.$^{-1}$), and its ultraviolet spectrum is nearly identical with that of the original compound, which therefore contains an imino- and not an enolic hydroxyl group. In confirmation, the single carbonyl band shown by both compounds near 6 μ must represent two carbonyl groups, for both compounds form mono-oximes still possessing strong absorption at this point. But there is no evidence as to which of the nitrogen atoms carries the mobile hydrogen, and expression (III) is used merely because of precedent.

The yellow isomer of adduct (I) is soluble in aqueous sodium carbonate and in solution is rapidly oxidised by air to quinone (III). Conversely, reductive acetylation of the quinone affords a triacetate obtainable directly from the yellow compound. This acetate has no carbonyl absorption other than that due to the acetyl groups, and therefore corresponds to structure (II). Nevertheless, the yellow compound itself cannot be formulated as quinol (II), for it absorbs strongly at 1692 and 1669 and rather less strongly at 1631 cm.$^{-1}$. The first two bands correspond to carbonyl groups but the last is difficult to account for as there is no band of similar position and intensity in the spectra of any of the other compounds studied in this series.

Of the two hydrogen atoms (a) and (b) in adduct (I), (a) would be the more mobile (tautomerism has not been noted in any adduct having some other group in its place [1]) and it would settle at position 2, giving structure (IV). Atom (b) might now be mobile and, if so, would move, giving the quinonoid cyclic hydrazine (VII). If the carbonyl groups are to be retained there are no other possibilities, but acids or bases could induce further tautomerisation to derivatives of quinol (II). The yellow isomer was too insoluble for the ^{1}H resonance spectrum to be determined, although the visible spectrum could be determined approximately in dimethyl sulphoxide. Maximal absorption was noted at 243, 316, and 398 mμ, but this long-wavelength band (ε ~ 520) seems to fit the cyclic hydrazine structure (VII) badly, for a close resemblance to 2-aminonaphthaquinone (λ 450 mμ) would have been expected. However, the argument is not conclusive as we do not know how the chromophores in the alternative structure (IV) would behave. Fortunately, intensity measurements in the infrared region also tended to exclude structure (VII). These measurements could not be made in solution by the accepted methods, so mulls had to be employed and quinone (III) used for reference purposes. This compound contains one NH group and two carbonyl groups. The areas under the appropriate bands in the 3 and the 6 μ region were therefore estimated and found to be 285 and 252 (arbitrary) units, respectively, the ratio being 1·13 : 1 and, of course, more or less independent of the state of the sample and similar factors. The corresponding areas for the yellow compound [determined for a mull made as nearly as possible like that of quinone (III)] were 292 and 226 units: the ratio here is therefore 1·29 : 1 and it is reasonable to conclude that the yellow compound also possesses one NH group and two carbonyl groups, *i.e.*, that it has structure (IV). The unusual absorption at 1631 cm.$^{-1}$ might now be attributed to the double bond marked in (IV): this bond is electronically analogous to the olefinic bond in the grouping O=C·C=C·O· which absorbs near 1630 cm.$^{-1}$ with unusual intensity.[7]

[5] Jaffe and Orchin, " Theory and Applications of Ultraviolet Spectroscopy," Wiley and Sons, New York, 1962, p. 355.
[6] Otting, *Chem. Ber.*, 1956, **89**, 1940.
[7] Bader, *Helv. Chim. Acta*, 1953, **36**, 215.

Experimental

3a,4,9,9a-*Tetrahydro*-4,9-*dioxo*-3*H*-*benz*[*f*]*indazole* (I).—When diazomethane from methylnitrosourea (2 g.) in ether (20 ml.) was added to 1,4-naphthaquinone (1·0 g.) in ice-cooled ether (80 ml.), the yellow colour faded in about 5 sec. and nearly colourless plates separated. Air was excluded as much as possible by a stream of nitrogen while the ether was decanted and the crystals were washed with more ether (3 × 10 ml.). The moist solid was at once transferred to a blackened desiccator filled with nitrogen, and were dried by suction. Sooner or later the product (*ca.* 1·2 g.) decomposed vigorously and spontaneously and so it could not be purified further; nor a melting point determined; but it is considered to be the *tetrahydrodioxobenzindazole* in a satisfactorily pure state although it was difficult to obtain reproducible analyses because of explosions (Found: C, 66·2; H, 3·7; N, 14·3. $C_{11}H_8N_2O_2$ requires C, 66·0; H, 4·0; N, 14·3%). This compound was relatively stable as a mull in mineral oil but slowly decomposed in a beam of infrared light, so the absorption from 2 to 14 μ was determined in small segments, by using five different samples. The method gave reproducible results, the chief of which were mentioned above. The ultraviolet spectrum was not examined because the compound could not be obtained in solution without much decomposition.

4,9-*Dihydro*-4,9-*dioxo*-1*H*-*benz*[*f*]*indazole* (III).—The brown-black residue left after spontaneous decomposition of the foregoing tetrahydroindazole (1·2 g.) was triturated with ether (3 × 15 ml.) to remove the dark colour. When purified from acetic acid, the residue gave the dihydrobenzindazole as tiny crystals (0·6 g.), m. p. *ca.* 345° (decomp.) $\varepsilon_{max.}$ 3215 (NH) and 1669 cm.$^{-1}$ (C=O), $\lambda_{max.}$ (in EtOH) 243 and 317 mμ (log ε 4·61 and 3·60), identified with an authentic specimen [2] by means of the infrared spectrum (Found: C, 66·7; H, 3·2; N, 14·2. Calc. for $C_{11}H_6N_2O_2$: C, 66·65; H, 3·05; N, 14·1%). The *acetyl derivative* was obtained by heating the dihydroindazole with acetic anhydride for 20 min. and crystallised from acetic anhydride as faintly yellow needles, m. p. 218—220° (decomp.), $\nu_{max.}$ 1761 and 1684 cm.$^{-1}$ (Found on sample dried at 150°/1 mm. for 3 hr.: C, 65·1; H, 3·5; N, 11·5. $C_{13}H_8N_2O_3$ requires C, 65·0; H, 3·4; N, 11·7%). When warmed with ethanol, this derivative reverted to the original dihydroindazole. The *oxime* was produced by keeping the dihydroindazole (0·20 g.) in 0·1N-aqueous sodium hydroxide (10 ml.) containing hydroxylamine hydrochloride (0·08 g.) at 95° for 6 hr., and it separated from pyridine as needles, m. p. 312° (decomp.), $\nu_{max.}$ 3291 (OH), 3090 (NH), and 1653 cm.$^{-1}$ (C=O) (Found: C, 62·0; H, 3·25; N, 19·7. $C_{11}H_7N_3O_2$ requires C, 62·0; H, 3·3; N, 19·7%). Evaporation of the ether used for the triturations left a blue-black solid which seemed to behave as a quinhydrone but could not be recrystallised and was therefore acetylated (acetic anhydride–pyridine). The nearly colourless product crystallised from ethanol, giving 1,4-diacetoxy-2-methylnaphthalene in prisms (0·09 g.), m. p. and mixed m. p. 113° (Found: C, 69·6; H, 5·45. Calc. for $C_{15}H_{14}O_4$: C, 69·75; H, 5·5%).

4,9-*Dihydro*-1-*methyl*-4,9-*dioxobenz*[*f*]*indazole*.—Methyl sulphate (0·1 ml.) was added to the dihydroindazole (0·1 g.) in N-aqueous sodium hydroxide (2 ml.). A solid separated immediately and was crystallised from ethanol, giving the 1-methylindazole [2,3] as needles (0·08 g.), m. p. *ca.* 310° (decomp.; sublimes above 250°), $\lambda_{max.}$ (in EtOH) 246, 271, and 318 mμ (log ε 4·57, 4·17, and 3·70) [cf. anthraquinone, $\lambda_{max.}$ 251, 272, and 325 mμ (log ε 4·71, 4·32, and 3·76)], $\nu_{max.}$ 1669 cm.$^{-1}$ (C=O) (Found: C, 67·8; H, 3·9; N, 12·9; *C*-Me, 0; OMe, 0. Calc. for $C_{12}H_8N_2O_2$: C, 67·9; H, 3·8; N, 13·2%). Reaction with hydroxylamine hydrochloride in pyridine furnished the *oxime*, crystallising from aqueous pyridine in needles, m. p. 253°, $\nu_{max.}$ 3270 (OH) and 1656 (C=O) (Found: C, 63·2; H, 4·2; N, 18·4. $C_{12}H_9N_3O_2$ requires C, 63·4; H, 4·0; N, 18·5%).

3,3a,4,9-*Tetrahydro*-4,9-*dioxo*-2*H*-*benz*[*f*]*indazole* (IV).—Naphthaquinone (1·0 g.) and diazomethane were allowed to react as before, but the mixture was kept for 5 hr. during which the ether assumed a deep yellow colour and the precipitate did likewise though it remained crystalline. These changes were greatly accelerated by adding a drop of water to the ether. The solid could not be recrystallised without decomposition and became brown and then white in air; however, it is considered to be satisfactorily pure 3,3a,4,9-*tetrahydro*-4,9-*dioxo*-2*H*-*benz*[*f*]*indazole* and it was consistently obtained as fine yellow needles (1·1 g.), m. p. *ca.* 280° (decomp.) (Found: C, 65·8; H, 4·2; N, 13·9. $C_{11}H_8N_2O_2$ requires C, 66·0; H, 4·0; N, 14·0%). It slowly dissolved in hot methanol, ethyl acetate, or acetic acid, but the colour was discharged simultaneously and the product was the dihydrobenzindazole, m. p. *ca.* 345°, identified by its infrared spectrum. The same product resulted when the tetrahydrobenzindazole was warmed with sodium hydrogen carbonate solution: the emerald-green solution which was formed

slowly lost its colour on cooling, giving (quantitatively) the oxidation product as white crystals (identified spectroscopically). The tetrahydrobenzindazole (0·20 g.) dissolved in boiling acetic anhydride (5 ml.) and the colour soon faded: the product was the acetyl derivative of the dihydrobenzindazole. Repeated under nitrogen, this experiment again induced loss of colour but the product was 4,9-*diacetoxy*-1-*acetylbenz*[*f*]*indazole* (II; OAc for OH and NAc for NH), which crystallised from ethanol in needles (0·12 g.), m. p. 182—183°, $\nu_{max.}$ 1754 and 1730 cm.$^{-1}$ (Found: C, 62·2; H, 4·35; N, 8·55. $C_{17}H_{14}N_2O_5$ requires C, 62·6; H, 4·3; N, 8·6%). This compound (0·19 g.) was also obtained by reductive acetylation of the dihydrobenzindazole (0·20 g.) with acetic anhydride (10 ml.), one drop of pyridine, and zinc powder (0·30 g.) on the steam-bath for 1 hr.

THE ROBERT ROBINSON LABORATORIES,
UNIVERSITY OF LIVERPOOL.

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