1101. *The Interaction of Sydnones and* 1,4-*Quinones*

By D. Ll. Hammick and Denys J. Voaden

Sydnones react in tetrahydrofuran solution with 1,4-quinones possessing two adjacent unsubstituted hydrogen atoms, to give derivatives of 2*H*-indazole-4,7-quinone. Carbon dioxide is lost from the sydnone molecule and the reaction is parallel to that in which sydnones and olefins form pyrazole derivatives.

These multi-ring carbonyl compounds are unstable to acids, alkalis, and certain other reagents, but the proposed structures are supported by infrared-spectral features and the similarity of the ultraviolet spectra to those of naphthaquinone, anthraquinone, and previously-described indazolequinones.

Whilst numerous hydroaromatic compounds may be dehydrogenated with quinones or other hydrogen acceptors, 3′,4′-dihydroquinolino[1′,2′-*c*]sydnone[1] reacts with *p*-benzoquinone in tetrahydrofuran solution to give a yellow crystalline solid with the composition $C_{15}H_{10}N_2O_2$, for which the structure 5,6,7,10-tetrahydro-7,10-dioxoquino[1,2-*b*]indazole (I) is proposed. During the reaction, carbon dioxide was evolved and quinhydrone was a by-product. In some of the experiments there appeared a much less soluble substance (II) with the composition $C_{24}H_{16}N_4O_2$, which must have been formed from two molecules of the sydnone and one of the quinone. The reaction[2] is general for at least two other sydnones and two more *p*-quinones with free 2,3-positions; it failed with tetrachloro-1,4-benzoquinone and with 1,2-naphthaquinone.

Soviet workers[3] later demonstrated that interaction of sydnones and acrylic acid derivatives produces pyrazoles and pyrazolines. The general reaction, which involves a type of 1,3-addition,[4] was extended by Huisgen,[5] who has shown that numerous olefins and acetylenes react with sydnones to form new five-membered ring compounds and carbon dioxide. Huisgen postulates[6] the formation of an initial adduct which has not been isolated in the sydnone–quinone case. The two angular hydrogen atoms which would be present are removed by excess of quinone and this is followed by release of carbon dioxide and aromatisation of the five-membered ring.

The suggested structure for compound (I) is supported by chemical evidence and by the preparation of analogues which for the most part have the expected spectroscopic properties. The yellow colour and the liberation of iodine from acidified potassium iodide solution suggest a quinonoid arrangement of the oxygen atoms in (I). There are indications that sparingly soluble phenylhydrazones may be formed,[7] but these have not been purified, and most methods of chemical examination decompose compound (I) and its analogues. However, a stable bromine adduct was prepared, and the loss of colour in this derivative indicates loss of conjugation in the bond joining the carbonyl groups. In this connection it should be noted that compounds (II), (III), (VII), (VIII), and (IX) are much less intensely coloured than (I), (IV), or (VI).

The symmetrical formulæ[2] for (II) and (III) are used because of a general tendency for *p*-benzoquinone to form 2,5-disubstituted derivatives with reagents such as aniline or methanol, but there is not yet any definite proof for this assumption.

The wavelengths of the carbonyl absorption bands in the infrared spectra of these complex quinones or ketones lie close to those of the parent quinones (see Table). Other structural features can be inferred from the spectra, such as the bands in (I) at 3·39—3·43

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[1] D. Ll. Hammick and D. J. Voaden, *J.*, 1961, 3305.

[2] D. Ll. Hammick and D. J. Voaden, *Chem. and Ind.*, 1956, 739.

[3] V. G. Yashunskiĭ, V. F. Vasil'eva, and M. N. Shchukina, *Zhur. obshchei Khim.*, 1960, **30**, 698; 1961, **31**, 1501; 1962, **32**, 3107.

[4] L. I. Smith, *Chem. Rev.* 1938, **23**, 193.

[5] R. Huisgen, *Angew. Chem.*, 1962, **74**, 29, 30; 1963, **75**, 604, 742.

[6] R. Huisgen, *Angew. Chem.*, 1963, **75**, 624.

[7] J. M. Clark, Part II, Thesis, Oxford, 1958.

and 3·53, 11·85, and 13·10 μ, derived from the $(CH_2{\cdot}CH_2)$, (CH:CH), and (CH:CH–CH:CH) groupings, respectively.

Compounds (II), (IV), and (V) lacked a band at 11·85 μ, as expected, but the last two possessed bands at 11·26 and 11·33 μ, respectively, from the unsubstituted hydrogen in $[C(CH_3){:}CH–]$. In general, such correlations were found in the other compounds prepared.

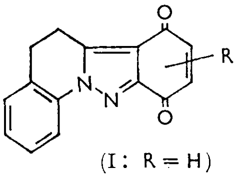
Finally, the colourless compound (III) possesses two phenyl rings which account for ten of the twelve hydrogens and which absorb strongly at 13·22 and 13·32 μ. Useful confirmation of the remaining two hydrogen atoms is given by the band at 3·23 μ which is found in a number of five-membered ring compounds and in sydnones unsubstituted at C-4, notably in the precursor of (III), 3-phenylsydnone itself.

Spectral data

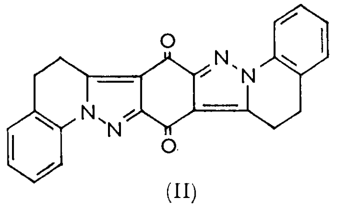
Compound	$\lambda_{C:O}$ (μ)	$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$	$\lambda_{min.}$ (Å)	$\varepsilon_{min.}$
(I)	5·98, 6·02	2700, 3250	4·32, 3·42	2300, 3150	4·07, 3·4
(II)	5·98, 6·03	2950	3·78	2400	3·24
(III)	5·97				
(IV)	6·04	2725, 3300	4·51, 3·47	2300, 3100	4·1, 3·39
(V)	6·03	2600, 3200*	4·15, 3·36	2300	3·87
(VI)	6·02	2400, 3275	4·28, 3·42	2775	2·82
(VII)	6·03				
(VIII)	5·98	2475, 3175	4·54, 3·75	2250, 2850	4·12, 3·48
(IX)	5·95, 6·02	2375, 2775 3300	4·44, 4·85 3·93	2500, 3250	4·36, 3·89

All infrared spectra were measured in mineral oil mulls; ultraviolet spectra of (I), (IV), and (V) in methanol, and the remainder in ethanol. The ε values for (II) are uncertain because of sparing solubility.

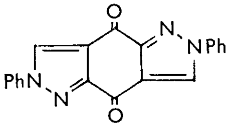
* Inflexion.



(I: R = H)
(IV and V: R = Me)



(II)



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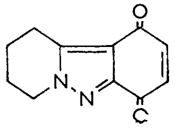
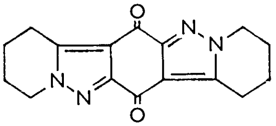
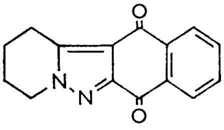


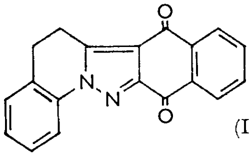
(VI)



(VII)



(VIII)



(IX)

The ultraviolet spectra of these complex ketones support the assigned structures. A prominent band found in the 3000—4000-Å range in several benzoquinone derivatives [8] is seen in the spectra of (I), (IV), (V), and (VI) between 3200 and 3300 Å. It is absent in (II) and is less prominent in the spectra of (VIII) and (IX). These last three compounds are colourless, or almost so, and do not possess a –CO–CH:CH–CO– system.

It is possible to relate the ultraviolet spectra of the hexahydrodioxopyridoindazole (VI) and hexahydrodioxopyridobenzoindazole (VIII) to those of 1,4-naphthaquinone

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[8] E. A. Braude, *J.*, 1945, 490.

and 9,10-anthraquinone, respectively,[9] which Spruit[10] has compared with the spectra of benzo[*f*]indazole-4,9-quinone, and its 1-methyl derivative. All six spectra are very similar in general form, but in Spruit's quinones a " plateau " with more fine structure takes the place of the noticeable minimum in the other spectra. For the purpose of comparison, (VI) and (VIII) may be considered roughly equivalent to dialkyl-substituted naphthaquinone and anthraquinone, as replacement of –CH= by –N= in an aromatic ring, or of –CH:CH–CH= by two hetero-atoms often causes little change in the ultraviolet spectrum.[11]

EXPERIMENTAL

All (capillary) m.p.s are corrected unless otherwise stated.

5,6,7,10-*Tetrahydro*-7,10-*dioxoquino*[1,2-b]*indazole* (I).—(*a*) 3′,4′-Dihydroquinolino[1′,2′-*c*]sydnone (1 g.) and 1,4-benzoquinone (1·2 g.) were heated under reflux for 48 hr. in purified tetrahydrofuran. The mixture was filtered and evaporated and the residue triturated with aqueous sulphur dioxide and ammonia, and washed to give the crude *quinoindazole* (0·85 g., 64%) which formed yellow needles, m. p. 204° (decomp., previous blackening), when crystallised twice from ethanol–acetone [Found: C, 72·2, 72·2; H, 4·4, 4·2; N, 11·2, 11·6%; *M* (Rast), 290, but decomposed in camphor. $C_{15}H_{10}N_2O_2$ requires C, 72·0; H, 4·0; N, 11·2%; *M*, 250].

(*b*) Dihydroquinolinosydnone (1·88 g.) and 1,4-benzoquinone (1·08 g.), refluxed for 24 hr. in ethanol (50 ml.), gave 1·54 g. (62%) of (I). The substance was not affected by sulphur dioxide, sodium dithionite, or methyl iodide, but it oxidised acidified potassium iodide solution. Treatment with hot dilute acids or alkalis, and attempted acetylation, reductive acetylation, and addition of aniline, led to extensive decomposition.

8,9-*Dibromo*-5,6,7,8,9,10-*hexahydro*-7,10-*dioxoquino*[1,2-b]*indazole*.—The quinoindazole (I) (45 mg.) in warm acetic acid (2·5 ml.), treated with 40% bromine in acetic acid (0·4 ml.), quickly deposited the *dibromide* (55 mg., 72%) which formed stout white needles, m. p. >280°, from ethanol or 2-methoxyethanol (Found: C, 44·1; H, 2·5; Br, 39·4; $C_{15}H_{10}Br_2N_2O_2$ requires C, 43·9; H, 2·5; Br, 39·0%).

Methyltetrahydrodioxoquinoindazoles (IV), (V).—(*a*) Dihydroquinolinosydnone (0·85 g.) and methyl-1,4-quinone (1·2 g.) reacted as in the preparation of (I) gave small yellow crystals of *tetrahydro*-8(or 9)-*methyl*-7,10-*dioxoquino*[1,2-b]*indazole quarter-ethanolate* (IV), m. p. 171·5—173·5° (decomp.) after three recrystallisations from ethanol (Found: C, 71·9; 71·7; H, 4·6, 4·5; N, 10·1. $C_{16}H_{12}N_2O_2,\frac{1}{4}C_2H_6O$ requires C, 71·9; H, 4·9; N, 10·2%).

(*b*) Dihydroquinolinosydnone (0·62 g.) and methylbenzoquinone (0·4 g.), heated under reflux for 3 days in tetrahydrofuran (10 ml.) and left for 3 days at room temperature, deposited small yellow crystals (50 mg., 6%) of tetrahydro-9(or 8)-methyl-7,10-dioxoquino[1,2-*b*]indazole (V), m. p. 229° (decomp.) from ethanol. Consistent analyses were not obtained; again there were indications of ethanol of crystallisation.

Concentration of the mother-liquors gave 0·48 g. (55%) of the lower-melting isomer (IV).

Preparation of Other Indazoles.—The appropriate sydnones and quinones were heated under reflux for 48—96 hr. in tetrahydrofuran, and the following were obtained after cooling or concentration, and recrystallisation from tetrahydrofuran: 6,7,15,16-*tetrahydro*-7,16-*dioxo*-5H,14H-*diquino*[1,2-e:1′,2′-e′]*benzo*[1,2-c:4,5-c′]*dipyrazole* (II) (49%), a pale yellow, very insoluble and unreactive powder, m. p. >335°, was the major product when the sydnone was in excess;[2] 2,4,6,8-tetrahydro-4,8-dioxo-2,6-diphenylpyrazolo[3,4-*f*]indazole (III) (3%), colourless felted needles,[2] m. p. >335°; 1,4,7,8,9,10-*hexahydro*-1,4-*dioxopyrido*[1,2-b]*indazole* (VI) (25%), bronze crystals, m. p. 208·5° (decomp.) (Found: C, 65·1; H, 5·3; N, 13·8. $C_{11}H_{10}N_2O_2$ requires C, 65·3; H, 5·0; N, 13·9%). From ethanol, compound (VI) deposited a brighter-hued *quarter-ethanolate*, m. p. 206·5° (decomp.) [Found: C, 64·6; H, 5·4%; *M* (Rast), 212; $C_{11}H_{10}N_2O_2,\frac{1}{4}C_2H_6O$ requires C, 64·6; H, 5·4%; *M*, 214]; 1,2,4,5,8,9,11,12-octahydro-5,12-dioxo-3*H*,10*H*-dipyrido[1,2-*e*:1′, 2′-*e*′]benzo[1,2-*c*:4,5-*c*′]dipyrazole (VII) (1%), m. p. >290°, separated from the mother-liquors of (VI); 1,2,3,4,7,12-*hexahydro*-7,12-*dioxopyrido*[1,2-b]*benzo*[f]*indazole* (VIII) (6%), pale cream crystals,[2] m. p. 278—279°; the *quarter-ethanolate*

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[9] R. A. Friedel and M. Orchin, " Ultra-violet Spectra of Aromatic Compounds," Wiley, New York, 1951, Figures 254, 395.

[10] C. J. P. Spruit, *Rec. Trav. chim.*, 1949, **68**, 312, 327.

[11] A. E. Gillam and E. S. Stern, " An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Arnold, London, 1954, p. 134.

formed very slender colourless needles (Found: C, 70·3; H, 4·9. $C_{15}H_{12}N_2O_2,\frac{1}{4}C_2H_6O$ requires C, 70·6; H, 5·2%); 5,6,7,12-*tetrahydro*-7,12-*dioxoquino*[1,2-b]*benzo*[f]*indazole* (IX) (8%), small cream needles, m. p. 274—275° (Kofler) (Found: C, 75·9; H, 4·0; N, 9·4. $C_{19}H_{12}N_2O_2$ requires C, 76·0; H, 4·0; N, 9·3%).

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY.
[Present address (D. J. V.): PESTICIDE CHEMICALS RESEARCH BRANCH,
U.S. DEPARTMENT OF AGRICULTURE, BELTSVILLE,
MARYLAND, U.S.A.]

[*Received, October* 21*st*, 1964.]