reacted with a 2-molar quantity of NBS in presence of benzoyl peroxide as catalyst. When the bromine-red color appeared, the solvent and bromine were distilled from the reaction vessel, with simultaneous addition to the reaction mixture of requisite pure solvent. Upon exhaustion of solid NBS, the product was collected and purified in the usual manner. Application of this procedure to hesperetin triacetate gave diosmetin triacetate (4'-methoxy-3', 5,7-triacetoxyflavone) in 86% yield.[10] Naringenin triacetate gave apigenin triacetate (4',5,7-triacet-oxyflavone) in 95% yield. A bromine containing flavone[11] of undetermined structure was obtained from 5-methoxyflavanone.

EXPERIMENTAL

Dehydrogenation of hesperetin triacetate. In a two-necked flask equipped with dropping funnel, and side arm connected to a cooled receiving vessel, were placed 1 g. of hesperetin triacetate, m.p. 143-144°,[12] 0.83 g. of NBS, a few grains (*ca.* 1 mg.) of benzoyl peroxide, and 50 ml. of carbon tetrachloride. After 15 min. of heating, bromine evolution began. The heat was increased so that solvent and bromine distilled from the side arm and collected in the receiver. Fresh solvent was added through the dropping funnel, and benzoyl peroxide was added as needed to maintain bromine evolution. The reaction was complete in 2 hr. A 2.15 mmol. (92% of theory) quantity of sodium bisulfite was required to decolorize the distillate.

The volume of liquid in the reaction vessel was reduced to 25 ml. and the mixture cooled to 0°. The precipitated solid was removed by filtration and washed with 100 ml. of hot water. After drying, the residue weighed 0.86 g. (86%), m.p. 195-197°. Repeated crystallization from ethanol gave diosmetin triacetate, m.p. 198.5-199° (lit.[13] m.p. 195-196°). The infrared spectrum was identical with that of diosmetin triacetate prepared by an independent procedure (elimination of hydrogen bromide from 3-bromohesperetin triacetate).[12]

Dehydrogenation of naringenin triacetate. A 1.0 g. quantity of naringenin triacetate, m.p. 116-117°,[14] was reacted with 0.89 g. of NBS in the same manner as described immediately above. The reaction was complete in 30 min. A 0.94 g. quantity (95%) of apigenin triacetate, m.p. 186-187° (lit.[15] m.p. 186°) resulted. Deacetylation of this product gave apigenin, m.p. 350-352° (lit.[15] m.p. 352°).

Reaction of 5-methoxyflavanone with NBS. A 0.45 g. quantity of 5-methoxyflavanone, m.p. 144-146°,[16] was reacted

(10) An alternate procedure involving the use of pyridine to remove HBr and prevent bromine formation [see ref. (9)] gave *ca.* a 45% yield of diosmetin triacetate, m.p. 180-188° after one crystallization from ethanol.

(11) Other workers also have observed nuclear bromination during reaction of methoxyflavanones with NBS. See ref. (5) (b) and (6).

(12) Arthur *et. al.* (ref. (5) (f)) report m.p. 139-141° for (±)-Hesperetin triacetate.

(13) A. Lovecy, R. Robinson, and S. Sugasawa, *J. Chem. Soc.*, **1930**, 817.

(14) M. K. Seikel and T. A. Geissman [*J. Am. Chem. Soc.*, **72**, 5725 (1950)] report a m.p. of 125.5-126.5° for pure naringenin triacetate.

(15) M. Nakano, *J. Pharm. Soc. Japan*, **52**, 341 (1932); Chem. Abstr., **26**, 4334 (1932).

(16) Prepared in this laboratory by W. W. Hanneman by the procedure of T. R. Seshadri and V. Venkateswarlu [*Proc. Indian Acad. Sci.*, **26A**, 189 (1948)], who report a m.p. of 148-150°.

with 0.66 g. of NBS according to the procedure previously outlined. Chilling of the carbon tetrachloride solution gave a precipitate (0.26 g. after removal of succinimide). Two recrystallizations from ethanol gave a compound, m.p. 186-189°. A magnesium-hydrochloric acid test was positive (orange color). Analysis indicated the presence of bromine.

Anal. Calcd. for $C_{18}H_{11}O_5Br$: Br, 24.1. Found: Br, 21.4.

The infrared spectrum (KBr disk) of the NBS bromination product of 5-methoxyflavanone showed strong or medium bands at 1643, 1590, 1480, 1454, 1444, 1373, 1285, 1107, 1094, 1037, 1023, 837, 798, 775, 767, 745, 688, 666, and 643 cm.$^{-1}$. The carbonyl band at 1643 cm.$^{-1}$ is considered to be indicative of a flavone rather than a flavanone derivative.[17] The strong bands at 837 and 745 cm.$^{-1}$ have no corresponding bands in the spectrum of 5-methoxyflavone, and are interpreted as indicating a difference in arrangement of substituents (including the substituent bromine) on a benzene ring.[18] 5-Methoxyflavone,[19] m.p. 131°, in KBr disk gave an infrared spectrum showing absorption maxima at 1645, 1600, 1476, 1456, 1442, 1380, 1305, 1288, 1268, 1097, 1035, 1021, 851, 799, 775, 760, 764, 715, 677, and 648 cm.$^{-1}$. The virtually identical location of 12 bands (5 cm.$^{-1}$ difference or less) indicates a marked similarity in the structure of the two compounds.

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(17) H. L. Hergert and E. F. Kurth [*J. Am. Chem. Soc.*, **75**, 1622 (1953)] report that, in solid state spectra, flavanone itself shows a carbonyl band at 1680 cm.$^{-1}$ and three acetoxy-flavanones show bands in the range 1680 to 1703 cm.$^{-1}$. However, a pentamethoxyflavanone showed a band at 1649 cm.$^{-1}$ In solid state spectra, flavones showed carbonyl bands in the region 1638 to 1655 cm.$^{-1}$ In solution, flavones without a 3-hydroxyl or methoxyl group displayed carbonyl bands between 1638 and 1655 cm.$^{-1}$ (B. L. Shaw and T. H. Simpson, *J. Chem. Soc.*, **1955**, 655). In view of the manner of synthesis and marked similarity of the spectrum of the NBS bromination product with that of authentic 5-methoxyflavone, a flavone structure seems indicated.

(18) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 64-8.

(19) Prepared in this laboratory by W. W. Hanneman and J. I. Dappen by the procedure of S. Rajagopalan, K. V. Rao, and T. R. Seshadri, *Proc. Indian Acad. of Sci.*, **25A**, 432 (1946). The Indian workers report m.p. 130-131°.

Infrared Spectra of Some p-Benzoquinone Monoximes

G. E. PHILBROOK AND T. C. GETTEN[1]

The infrared spectra of *p*-benzoquinone-4-oximes in the solid state are similar to those of the *p*-benzoquinones. The spectrum of the addition complex formed by the nitrosation of 3-chlorophenol confirms the structure proposed by Kraaijeveld and Havinga. In no case does a nitrosophenol structure appear to be present.

Hodgson[2] assigned quinone monoxime or nitroso

(1) Taken in part from the Masters thesis of T. C. Getten.

(2) H. H. Hodgson and F. H. Moore, *J. Chem. Soc.*, **127**, 2260 (1925).

TABLE I

MAJOR ABSORPTION BANDS[a] OF p-BENZOQUINONE-4-OXIMES
(in cm.[-1])

Unsub-stituted	2-Methyl	2-i-Propyl 5-methyl	2,6-Di-methyl	2-Chloro	2-Bromo	3-Chloro	Addition Compound[b]
3289sh	3125sh	3125	3175	3390	3165	3145	3115b
3155	2994sh	3021	3077	3175	1629bs	3030	2188s
1656sh	1637s	1637s	1647sh	1653	1553	1626s	2165
1645s	1600s	1603s	1634s	1637s	1312s	1553s	1634s
1563s	1550s	1567	1608s	1563	1206	1445s	1600
1366sh	1350	1441	1558	1439sh	1117	1348	1511s
1155	1316	1370sh	1427	1316s	1063sh	1305	1481s
1057	1266	1239	1342	1307s	1050s	1127s	1399
1035s	1235	1056s	1305s	1073s	985s	1053s	1294
870	1109s	1015s	1049s	1064s	906s	1006	1247
809s	1032	1002s	1004	1006	866	895	1131s
797	989	907s	919s	906	856s	862	1073s
	899s	853s	717	885s	823s	798s	1050
	820b	777		826s	807	781	1008
	784			773w			925
	730						881s
							808
							769

[a] b-broad; s-strong; sh-shoulder; w-weak. [b] 3-chloro-p-benzoquinone-4-oxime: 3-chlorobenzene-6-diazo oxide.

phenol structures to a number of compounds in 1925. Anderson[3] and his co-workers confirmed Hodgson's assignment for 3-chloro-p-benzoquinone-4-oxime but rejected his structure for 3-chloro-4-nitrosophenol without suggesting an alternative. Hodgson[4] defended his conclusions and reviewed the field in 1937. Kraaijeveld and Havinga[5] demonstrated in 1954 that Hodgson's 3-halo-4-nitrosophenols are 1:1 addition compounds of 3-halo-p-benzoquinone-4-oxime and 3-halobenzene-6-diazooxide.

We have examined the infrared spectra of a number of substituted p-benzoquinone-4-oximes and the addition complex formed by the nitrosation of 3-chlorophenol. The major absorption bands of the compounds are given in Table I.

EXPERIMENTAL

The quinone oximes were prepared from the corresponding phenols by standard nitrosation methods. In addition samples of p-benzoquinone-4-oxime and the 2-chloro- and 2-bromo- derivatives were prepared by the oximation of the corresponding quinone. Except in the case of the 2-chloro-derivative the spectra were not distinguishable from those made on samples prepared by nitrosation.

Spectra of the oximes were determined on mineral oil mulls using the cell-in cell-out technique on a Perkin-Elmer Model 112 spectrometer with sodium chloride optics. A rock salt plate was used as the reference. The instrument was calibrated with carbon dioxide, water vapor, and ammonia. Mineral oil mulls of the addition compound were stable for only five to ten minutes. The point by point spectrum of this compound was determined on a potassium bromide pellet. Comparison of automatically recorded energy

traces of the mull and pellet form showed no significant differences.

The insolubility of these compounds in suitable solvents prevented a study of the solution spectra.

DISCUSSION

Region 3350–2860 cm.[-1]. With the exceptions of 2-bromo-p-benzoquinone-4-oxime, which shows only a weak side hill at 3049 cm.[-1], and the addition compound of 3-chloro-p-benzoquinone-4-oxime, all of the compounds examined show two distinct bands in this region. One band, present in all compounds, is almost constant in position and falls in the region 3175–3115 cm.[-1] A band occurs in this region in cyclopentanone oxime[6] (3175 cm.[-1]), cyclohexanone oxime[6] (3175 cm.[-1]), and 1,4-naphthoquinone-4-oxime[6] (3125 cm.[-1]). The frequency of this band is high for C-H stretching in trans olefins and we therefore assign it to the OH stretching vibration. The band is sharp.

Region 2860–1667 cm.[-1]. In the addition compound of 3-chloro-p-benzoquinone-4-oxime with 3-chlorobenzene-6-diazo oxide a strong band is present at 2188 cm.[-1] and a second medium strength band is present at 2165 cm.[-1]. These bands are near the upper limit of 2165 cm.[-1] given by Shenker and Syrkin[7] for the azido group. There appears to be no other reasonable source for these bands. This confirms the assignment of structure made for this compound by Kraaijeveld and Havinga.[5]

A very weak band was found at 2165 cm.[-1] in the spectrum of the 2-chloro- derivative prepared by nitrosation. This band was absent in the sample

(3) L. C. Anderson and M. B. Geiger, J. Am. Chem. Soc., 54, 3064 (1932); L. C. Anderson and R. L. Yanke, J. Am. Chem. Soc., 56, 732 (1934).

(4) H. H. Hodgson, J. Chem. Soc., 140, 520 (1937).

(5) A. Kraaijeveld and E. Havinga, Rec. Trav. Chim. 73, 537 (1954).

(6) Unpublished data from this laboratory.

(7) Yu. N. Shenker and Ya. N. Syrkin, Izvest. Akad. Nauk. S. S. S. R., Ser. Fiz., 14, 478 (1950); Chem. Abstr., 45, 3246 (1951).

prepared by oximation of the quinone and probably arises from contamination by a small quantity of diazo oxide. It could not be removed by recrystallization. No band appears in this region for any other compound examined.

Region 1667-1538 cm.⁻¹. Yates, Ardao, and Fieser[3] have discussed the spectra of p-benzoquinones between five and fifteen microns (2000-667 cm.⁻¹). They assign absorptions in the 5.97-6.14μ (1675-1629 cm.⁻¹) region to the carbonyl stretching vibration and observe that this band is split into two bands in some instances. All of our compounds show a strong band in the range 1645-1626 cm.⁻¹ which is probably the carbonyl absorption. In three cases a second weaker band at 1656-1647 cm.⁻¹ appears. This band is probably the C=N stretching vibration. The C=N band varies in intensity and position[9] and failure to identify this band in all compounds is not surprising.

Yates *et al.*[8] assign bands in the 6.17-6.49μ (1621-1543 cm.⁻¹) region to C=C stretching. All of our compounds show a medium to strong band between 1567 cm.⁻¹ and 1550 cm.⁻¹ which we assign to the C=C stretching. In the alkyl substituted compounds and in the addition complex an additional band is present at 1608-1600 cm.⁻¹.

Region 1538-667 cm.⁻¹. Numerous bands occur in this region. The majority cannot be assigned to any definite structural feature. Yates *et al.*[8] observe that quinones with an isolated hydrogen atom on the ring show a medium to strong band in the 10.8-11.4μ (926-877 cm.⁻¹) region in the solid state. The same feature is present in our spectra. p-Benzoquinone-4-oxime has no band in this region. The same authors report that carbon disulfide solutions of compounds having adjacent hydrogen atoms on the ring show a band at 11.9-12.4μ (840-807 cm.⁻¹). They do not report a band in this region in most of their solid state spectra. In the quinone oximes studied all compounds with adjacent hydrogen atoms on the ring show a medium to strong band in the 826-794 cm.⁻¹ region. This band is absent in compounds without adjacent hydrogens.

In the region from 769 cm.⁻¹ to 667 cm.⁻¹ only very shallow, very broad absorptions are present. The spectra are immediately recognizable as non-aromatic in character.

Conclusion. The bands which are characteristic of aromatic structures at 2000 cm.⁻¹ to 1660 cm.⁻¹, at 1600 cm.⁻¹ to 1500 cm.⁻¹, and from 1200 cm.⁻¹ to 667 cm.⁻¹ could not be identified in these compounds. This fact coupled with the presence of the carbonyl absorption and the olefinic absorption together with the close over-all similarity to the

spectra of p-benzoquinones makes it almost certain that the structure of these compounds in the solid state is quinoid. There appears to be no justification for the assignment of a nitroso phenol structure.

Structures of 4-Nitro- and 5-Nitro-2-propionylpyrroles

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In a previous paper,[1] the structure 5-nitro-2-propionylpyrrole was suggested for the product, m.p. 100-101°, prepared by nitrating 2-propionylpyrrole. The assignment of structure was based on a negative Ehrlich test which usually indicates complete substitution in the α-positions in pyrrole compounds.

It has been pointed out to us by Professor H. J. Anderson[2] that the work of Rinkes[3] and Anderson[4] would indicate that nitration would more likely occur preferentially in the 4- than in the 5-position. Further examination of our product confirms this prediction. Extraction of a sodium carbonate solution of the nitration product with ether[3] yields a larger proportion of a less acidic 4-nitro-2-propionylpyrrole, m.p. 136-137° and on acidification a lesser amount of more acidic 5-nitro-2-propionylpyrrole, m.p. 134-135°. Mixed m.p. of roughly equal proportions, 102-104°.

Both the mono nitro-2-propionylpyrroles fail to give the Ehrlich test given by the parent substance, 2-propionylpyrrole. Similarly, 4-nitro and 5-nitro-2-acetylpyrrole failed to give the Ehrlich test, while the parent substance, 2-acetylpyrrole, gave a positive test.

The assignment of structure above follows Rinkes[3] and is further supported by an absolute proof of structure. Rinkes[3] states that acidity of the nitration products of 2-acetyl- or 2-carboxyethylpyrrole is determined by the proximity of the nitro group to the acidic NH, the closer the group the more acidic the product. However, there does not appear to be any absolute proof to support this reasonable assertion.

(8) P. Yates, M. A. Ardao, and L. Fieser, *J. Am. Chem. Soc.*, **78**, 650 (1956).

(9) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, 1st. Ed., John Wiley and Sons, Inc., New York, 1954, p. 226.

(1) T. S. Gardner, E. Wenis, and J. Lee, *J. Org. Chem.*, **23**, 823 (1958).

(2) H. J. Anderson, private communication, July 12, 1958.

(3) I. J. Rinkes, *Rec. trav. chim.*, **53**, 1167 (1934).

(4) H. J. Anderson, *Can. J. Chem.*, **35**, 21 (1957).