yields but in incomplete conversions. Fourteen g. of PTT were recovered despite the long heating period. The only other product was a 4-g. fraction of the $CF_3N{=}CF_2$ dimer. There was no material boiling above 80.5°.

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A New Procedure for the Dehydrogenation of Flavanones with *N*-Bromosuccinimide[1]

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The application of *N*-bromosuccinimide (NBS) to dehydrogenation of flavanone derivatives has been reported by Lorette, Gage, and Wender,[4] who converted flavanone glycosides to flavone glycosides, and subsequently by a number of workers[5] to dehydrogenation of other flavanone derivatives. In each case, the essential steps were bromination with *N*-bromosuccinimide and dehydrohalogenation of the bromination product with an organic or inorganic base. It is noteworthy that two groups[5b,6] described the bromination mixture as assuming a reddish-brown color, which later disappeared. In the present note, we report that the usual NBS dehydrogenation procedure can be modified by removing by-product bromine, with marked improvement in the yield of flavone.

In applying the NBS reaction to hesperetin triacetate (4′-methoxy-3′,5,7-triacetoxyflavanone) we observed rapid development of a reddish-brown product. Since this substance was volatile with the carbon tetrachloride vapors and blackened moist starch-iodide paper, it was considered to be bromine. Concomitant formation of hydrogen bromide could not be detected. Later, the bromine-red color increased in intensity, but after the solid NBS had disappeared, diminished rapidly and finally faded completely. Hydrogen bromide was evolved during this late reaction stage. In another experiment, the solvent, carrying with it bromine, was distilled from the reaction vessel and collected. Titration of the distillate with standard sodium bisulfite solution showed that it contained most of the bromine originally present in the NBS. The residue afforded a good yield of diosmetin triacetate (sequel).

These observations are interpreted as indicating that the NBS first brominated the flavanone, possibly in the 2-position.[7] Then the bromoflavanone yielded the flavone by elimination of hydrogen bromide, which attacked unreacted NBS to produce bromine and succinimide.[8] A possible final step would be bromination of the flavone by free bromine. This sequence, which is somewhat similar to that proposed by Stuckwisch and coworkers[9] in their study of the oxidation of alcohols by NBS, is shown in Chart 1.

(1) Flavanone + NBS ⟶ 2- or 3-Bromoflavanone + Succinimide

(2) Bromoflavanone ⟶ Flavone + HBr

(3) HBr + NBS ⟶ Br_2 + Succinimide

(4) Flavone + Br_2 ⟶ Brominated flavone + HBr

CHART I

A practical result of these observations has been development of a new procedure for the dehydrogenation of flavanones. From Chart 1, it is apparent that step (4) would be undesirable, and the key step in our procedure is removal of bromine by distillation. This method affords an alternative to the recently described neutralization of hydrogen bromide in NBS reaction mixtures[9] which also prevents deleterious side reactions due to bromine. The flavanone in carbon tetrachloride solution was

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(3) Abstracted from a portion of the Ph.D. thesis of Myron J. Holm, University of Nebraska, 1958.

(4) N. B. Lorette, T. B. Gage, and S. H. Wender, *J. Org. Chem.*, **16**, 930 (1951).

(5) (a) R. C. Chen and C. H. Yang, *J. Taiwan Pharm. Assoc.*, **3**, 39 (1951); *Chem. Abstr.*, **49**, 10277 (1955); (b) N. R. Bannerjee and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **36A**, 134 (1952); (c) S. Hishida, S. Sasaki, M. Suzuki, and M. Takatori, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **74**, 697 (1953); *Chem. Abstr.*, **48**, 12094 (1954); (d) K. Nakagawa and H. Tsukashima, *J. Chem. Soc. Japan*, **75**, 485 (1954); Chem. Abstr. **51**, 11339 (1957); (e) R. Bognar and M. Rakosi, *Chem. & Ind. (London)*, **1955**, 773; (f) H. R. Arthur, W. H. Hui, and C. N. Ma, *J. Chem. Soc.*, **1956**, 632.

(6) G. W. K. Cavill, F. M. Dean, A. McGookin, B. M. Marshall, and A. Robertson, *J. Chem. Soc.*, **1954**, 4573.

(7) This possibility is based partly on the observation of Stuckwisch and co-workers [ref. (9)] that bromination of the position *alpha* to a carbonyl group in certain ketones is effected by by-product bromine rather than by the primary reactant, NBS. In addition, we have noted (unpublished observations) that the 3-bromohesperetin triacetate of G. Zemplen and R. Bognar [*Ber.*, **76B**, 454 (1943)] does not undergo elimination of hydrogen bromide under the conditions of the NBS reaction.

(8) An observation that a very unstable bromo compound can undergo dehydrohalogenation before bromination is complete, liberate free bromine by reaction of evolved hydrogen bromide with NBS, and cause side reactions due to bromine has been recorded by P. Wieland and K. Miescher, *Helv. Chim. Acta*, **30**, 1876 (1947). Also see R. A. Barnes *J. Am. Chem. Soc.*, **70**, 145 (1948), who attributed an orange-red color in NBS reaction mixtures to the equilibrium, HBr + NBS → succinimide + Br_2, and stated that it is diagnostic for HBr in the mixture.

(9) C. G. Stuckwisch, G. G. Hammer, and N. F. Blau, *J. Org. Chem.*, **22**, 1678 (1957).

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-triacetoxyflavone) 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 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 $C_{16}H_{11}O_3Br$: 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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(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°.

(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 acetoxyflavanones 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

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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).