TABLE IV

PYRIDOTETRAZOLECARBOXYLIC ACIDS FROM OXIDATION OF A CORRESPONDING METHYLPYRIDOTETRAZOLE WITH LITHIUM CHROMATE[a]

Substituent	Yield, %	Dec., °C.	Molecular formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Oxygen, % Calcd.	Oxygen, % Found
5-Carboxy[b]	14	208–209	$C_6H_4N_4O_2$	43.91	43.77	2.46	2.44	34.14	34.09	19.49	19.69
6-Carboxy[b]	33	223–225	$C_6H_4N_4O_2$	43.91	42.99[c]	2.46	2.60	34.14	33.87	19.49	20.61[c]
7-Carboxy	33	228–230	$C_6H_4N_4O_2$	43.91	44.01	2.46	2.59	34.14	33.93	19.49	19.37
8-Carboxy[b]	33	245–247	$C_6H_4N_4O_2$	43.91	43.90	2.46	2.59	34.14	34.04	19.49	19.23
5(or 7)-Methyl-7(or 5)-carboxy[b,d]	16	238–240	$C_7H_6N_4O_2$	47.18	46.91	3.39	3.54	31.44	31.24	17.96	17.72

[a] Experiments with pyridotetrazole and 5-carboxypyridotetrazole established oxidative degradation of the pyridine ring at 85–90°. [b] Blue fluorescence to ultraviolet light. [c] Assumed to be in error. [d] Apparently a mixture of the two possible compounds. Attempts to obtain a dicarboxylic acid by oxidation at 60° were unsuccessful; at higher temperatures oxidation destroyed the molecule.

TABLE V

ACIDS FROM CARBONATION OF LITHIUM SALTS OF PYRIDOTETRAZOLE AND ITS METHYL DERIVATIVES

Lithium salt of	Acid	Yield, %	M.p., dec., °C.	Molecular formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Oxygen, % Calcd.	Oxygen, % Found
I	III	28	243–244	$C_7H_4N_4O_4$	40.40	40.47	1.94	2.12	26.91	26.91	30.76	31.31
IIa	IVa	41	179–180	$C_7H_6N_4O_2$	47.18	47.47	3.39	3.50	31.44	31.43	17.96	17.67
IIb	IVb	11	207–208	$C_8H_6N_4O_4$	43.28	43.20	2.72	2.94	25.21	25.47	[a]	
IIc	IVc	5	214–215	$C_7H_6N_4O_2$	47.18	47.24	3.39	3.29	31.44	30.90	17.96	19.19[b]
IId	IVd	18	245–248	$C_7H_6N_4O_2$	47.18	46.85	3.39	3.13	31.44	32.03	17.96	18.04

[a] Not analyzed for oxygen. [b] Assumed to be in error.

rated as a tan powder which recrystallized from hot water as colorless needles, m.p. 179–180° dec.

Anal. Calcd. for $C_7H_6N_4O_2$: C, 47.18; H, 3.39; N, 31.44; O, 17.96. Found: C, 47.47; H, 3.50; N, 31.43; O, 17.67.

A similar procedure was followed in transforming pyridotetrazole[7] and its 6-, 7- and 8-methyl derivatives into carboxylic acid derivatives. The results are contained in Table V. In KBr disks, samples of 5,8-dicarboxypyridotetrazole (III) from both I and IVd gave absorption in the infrared at 3200–2400, 2000, 1695, 1621, 1575, 1515, 1422, 1342, 1307, 1266, 1202, 1135, 1120, 1088, 1033, 1003, 990, 901, 823, 800, 761, 730 and 681 cm.$^{-1}$.

Ethyl 5-pyridotetrazoyl acetate was obtained in 4% yield by treating the appropriate mixture of lithium salts with ethanol saturated with hydrogen chloride. It recrystallized from aqueous ethanol as colorless needles, m.p. 110–111.5°.

Anal. Calcd. for $C_9H_{10}N_4O_2$: C, 52.47; H, 4.89; N, 27.19; O, 15.53. Found: C, 52.35; H, 5.14; N, 27.12; O, 15.60.

NEW ORLEANS, LA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, TULANE UNIVERSITY]

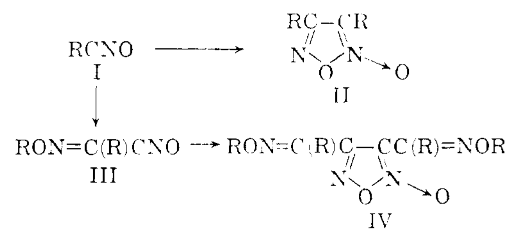
The Identification of $C_{32}H_{20}N_4O_8$, a Product from Acetophenone and Nitric Acid[1]

BY J. H. BOYER AND M. S. CHANG

RECEIVED SEPTEMBER 8, 1959

A minor product from acetophenone and nitric acid has been identified as the dibenzoate ester of bis-(benzoylformaldoximino)-furoxan (IV, R = C_6H_5CO).

The proposed formation of dibenzoylfuroxan (II, R = C_6H_5CO) by dimerization of benzoylnitrile oxide[2] (I, R = C_6H_5CO) in the reaction of acetophenone and nitric acid[3] opened a new approach to the identification of a minor product[3] which has been described as isomeric[2–5] and dimeric[6,7] with II (R = C_6H_5CO) and also is obtained from 1,6-diphenyl-1,3,4,6-hexanetetraone and nitric acid[8] and from chloroisonitrosoacetophenone in acetic acid containing sodium acetate.[4] An identification of the minor product as the dibenzoate ester of bis-(benzoylformaldoximino)-furoxan[9] (IV, R = C_6H_5CO) has developed from the observations reported here.



The molecular formula $C_{32}H_{20}N_4O_8$,[6] confirmed by new elemental analyses and molecular weight determinations, establishes the product as a tetramer of benzoylnitrile oxide. In contrast with

(1) Financial assistance under Contract No. DA-01-009-ORD-428 with the Office of Ordnance Research, U. S. Army is gratefully acknowledged.

(2) N. E. Boyer, G. M. Czerniak, H. S. Gutowsky and H. R. Snyder, THIS JOURNAL, **77**, 4238 (1955).

(3) A. F. Holleman, *Ber.*, **20**, 3359 (1887); **21**, 2835 (1888).

(4) G. Ponzio, *Gazz. chim. ital.*, **62**, 415, 633 (1932).

(5) R. Scarpati and M. Rippa *ibid.*, **88**, 804 (1958).

(6) M. J. Boeseken, *Rec. trav. chim.*, **29**, 275 (1909).

(7) G. Ruggeri, *Gazz. chim. ital.*, **54**, 72 (1924).

(8) O. Widman and E. Virgin, *Ber.*, **42**, 2798 (1909).

(9) J. H. Boyer and M. S. Chang, *Chemistry and Industry*, 730 (1959).

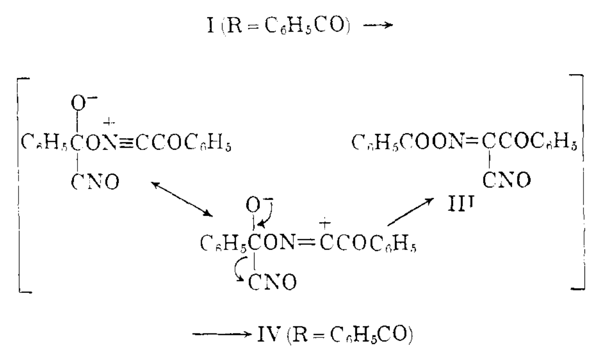
TABLE I

INFRARED ABSORPTION DATA (CM.$^{-1}$) FROM KBr DISKS

Benzoate ester of the α-monoxime of benzil[a,b]	3448m, 3058m, *1745s*, *1689s*, 1597s, 1495m, 1449m, 1312m, 1274m, 1238s, 1209s, 1174s, 1104m, 1080m, 950m, 869m, 855s, 795m, 784m, 734m, 705–701s, 683s, 652s, 614m, 525–523m, 497–496m, 420m
Benzoate ester of the β-monoxime of benzil[a,b]	3067m, *1761s*, *1686s*, 1597s, 1495m, 1453s, 1332m, 1316m, 1242–1236s, 1178s, 1080s, 1066s, 1047s, 1025s, 1001s, 950s, 930m, 883s, 857s, 796m, 775m, 730s, 704–702s, 682s, 675s
Benzoate ester of benzophenone oxime[c,b]	3448m, 3058m, *1739s*, 1600m, 1592m, 1565m, 1490m, 1445s, 1328s, 1304m, 1239s, 1172m, 1086s, 1064s, 1022s, 982s, 873s, 797m, 778s, 768s, 730m, 702–701s, 688s, 671s, 650m
3(or 4)-Benzoylformaldoximinofuroxan (V)[d]	3067m, 3021m, 2976m, 2933m, *1661s*, 1570–1563s, 1477s, 1447s, *1414m*, 1376s, *1328s*, 1285s, *1156s*, 1100m, 1071m, *1026m*, *1000m*, 962m, *923s*, *893s*, *826m*, 797s, 735s, 702s, 679s
Dibenzoate ester of bis-(benzoylformaldoximino)-furoxan IV (R = C_6H_5CO)[d]	3106m, *1770m*, *1665m*, *1610s*, 1408m, *1450m*, *1415m*, *1325m*, *1310w*, 1290m, 1220s, *1185m*, 1082m, *1040m*, *1000s*, 966m, *940w*, *900s*, *840w*, 802–808w, 790w, 743m, 730m, 712w, 695s, 672–679w, 653w
$C_{20}H_{15}N_7O_7$	3460m, 3344m, 3125m, 2924m, 2841m, 1678m, 1658m, 1570m, 1493m, 1449m, 1292m, 1188m, 1171m, 1091m, 1070m, 1040m, 1025m, 1015m, 1000m, 963m, 943m, 905m, 889m, 811m, 754m, 692m, 684m

[a] Ref. 18. Carbonyl bands italicized. [c] O. Exner, *C. A.*, **49**, 14674 (1955). [d] Carbonyl and furoxan bands underlined.

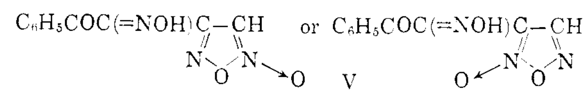
dimers and trimers, few examples of tetramers of nitrile oxides have been reported. Isocyanilic acid (IV, R = H), a tetramer of fulminic acid (I, R = H), apparently is formed by the dimerization of oximinoacetonitrile oxide (III, R = H), a dimer of fulminic acid.[10] The transformation I → III → IV has not been extended to nitrile oxides in which R is alkyl, aryl or acyl. The present demonstration that acylnitrile oxides (I, R = R′CO) may undergo the change I → IV with III as a suggested intermediate calls for a probable explanation of the change I → III (R = R′CO). It is proposed that a dimerization of I (R = C_6H_5CO) results from an initial attack at a carbonyl group followed by or accompanied with a migration of a nitrile oxide anion which cannot, with the present data, be described as either inter- or intramolecular; however, it is unlikely that a nitrile oxide group is at any time completely dissociated.

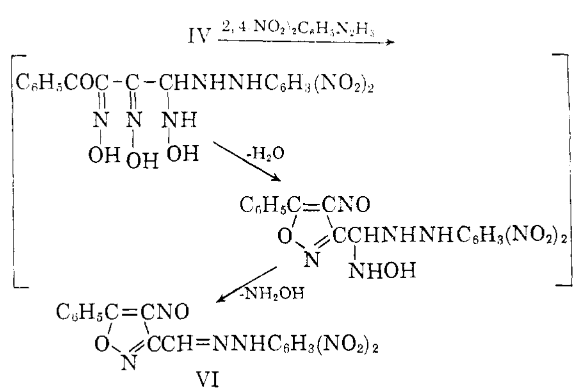


An assignment[2] of IV (R = C_6H_5CO), hereinafter referred to as DBFF, as an unidentified furoxan based upon infrared absorption from a Nujol mull at 1610, 1425, 1335, 1315, 1185, 1040, 1005, 970, 905 and 840 cm.$^{-1}$ is supported by ultraviolet absorption in chloroform at 263 mμ, (log ε 4.45).[11] Infrared absorption (Table I) for DBFF at 1770 cm.$^{-1}$ is characteristic of the carbonyl group in O-acyl derivatives of oximes[12] and at 1665 cm.$^{-1}$ is characteristic of the keto-carbonyl group in an ester of a monoxime of an α-diketone (1689 and 1686 cm.$^{-1}$, respectively, are observed (Table I) for the keto-carbonyl in the benzoate ester of α- and of β-monoxime of benzil).

Compound IV (R = C_6H_5CO) is easily hydrolyzed; in refluxing moist benzene it gives benzoic acid. In both dilute sodium hydroxide and sulfuric acid, benzoyl and benzoyloxy groups in DBFF undergo nearly quantitative transformation to benzoic acid. Under similar conditions benzoic acid has been obtained from dibenzoylfuroxan (II, R = C_6H_5CO).[2] The presence of two benzoyloxy groups in DBFF is required for catalytic reduction to two moles of benzoic acid.[13]

The removal of one side chain and hydrolysis of the oxime ester in the other are realized upon treatment of DBFF with hydroxylamine in alcoholic potassium hydroxide. Benzoic acid and 3(or 4)-benzoylformaldoximinofuroxan (V) are formed.





The latter is identified by its elemental analysis, infrared and ultraviolet absorption, a dinitrophenylhydrazone derivative and quantitative alkaline hydrolysis to one mole of benzoic acid. Treatment of DBFF with 2,4-dinitrophenylhydrazine does not give the dinitrophenylhydrazone of V.

(10) H. Wieland, A. Bauman, C. Reisenegger, W. Scherer, J. Thiele, J. Will, H. Haussmann and W. Frank, *Ann.*, **444**, 7 (1925).

(11) Absorption in the range 255–285 mμ has been found characteristic of the furoxan ring (J. H. Boyer, U. Toggweiler and G. A. Stoner, THIS JOURNAL, **79**, 1748 (1957). It is now observed that dibenzoylfuroxan in chloroform absorbs at 267 mμ (log ε 4.41).

(12) W. P. Jencks, THIS JOURNAL, **80**, 4581 (1958); W. Z. Heldt, THIS JOURNAL, **80**, 5880 (1958).

(13) Reduction of the material now described as DBFF over Raney nickel to isonitrosoacetophenone, m.p. 118–120° (Claisen, *Ber.*, **20**, 656 (1887)), gave m.p. 125–126°), in 50% yield has been reported.[5] This product has not been detected in our work.

Instead ring transformation to an isoxazole derivative VI apparently occurs.[14]

Pyrolysis of DBFF at 200° (0.4 mm.) gives a product tentatively identified as benzoic anhydride together with unidentified materials.

Acknowledgment.—We are indebted to Mr. R. T. O'Connor, Southern Regional Research Laboratory, for ultraviolet and infrared absorption data.

Experimental[15]

To 60.0 g. (0.5 mole) of acetophenone in 50 ml. of glacial acetic acid at 90–100°, 75 ml. of 69% nitric acid (d. 1.42) in 50 ml. of glacial acetic acid was added in one portion with stirring. Immediately 0.2 g. of sodum nitrite was added. Stirring was continued for several minutes until the exothermic reaction subsided. Dilution with 500 ml. of water caused separation of a pale green oil which solidified. The solid was washed with aqueous sodium carbonate and with ether. The residue recrystallized from glacial acetic acid as colorless needles, 3.9 g. (5.3%), m.p. 186–187°,[16] of bis-(benzoylformaldoximino)-furoxan (IV, R = C_6H_5CO) (DBFF). Infrared absorption for DBFF is described in Table I.

Anal. Calcd. for $(C_8H_6NO_2)_4$: C, 65.31; H, 3.42; N, 9.52; mol. wt., 588. Found: C, 65.29; H, 3.51; N, 9.51; mol. wt., 580.[17]

Dibenzoylfuroxan may be obtained from the ether extracts of the reaction product.

Hydrolysis and Related Reactions of DBFF.—A suspension of 0.30 g. (0.51 mmole) of DBFF in 5 ml. of 5% aqueous potassium hydroxide was shaken at room temperature for three days as a strong ammoniacal odor became noticeable and the mixture became a solution. On acidification with hydrochloric acid and extraction with ether, 0.20 g. (81% based on the conversion of DBFF to four moles of acid) of benzoic acid, m.p. and mixture m.p. 121–122°, was obtained.

Under similar conditions dibenzoylfuroxan (II, R = C_6H_5CO) gives benzoic acid in 42% yield (based on the conversion of II, R = C_6H_5CO, to two moles of acid), and the benzoate ester of the α-monoxime[18] of benzil gave benzoic acid in 69% yield.

The substitution of 50% aqueous sodium hydroxide for 5% aqueous potassium hydroxide in the hydrolysis of DBFF gave benzoic acid in 65% yield; DBFF in aqueous pyridine at room temperature gave benzoic acid in 30% yield, based on conversion to two moles of acid.

A suspension of 0.30 g. (0.51 mmole) of DBFF in 5 ml. of concentrated sulfuric acid was stirred at or near room temperature for one hour as a clear solution developed. Dilution with 15 ml. of cold water gave benzoic acid, m.p. and mixture m.p. 121–122°, 0.24 g. (96% based on conversion to four moles of acid); DBFF is insoluble in refluxing concentrated hydrochloric acid and is quantitatively recovered after 48 hours.

A suspension of 5.0 g. (8.5 mmoles) of DBFF in 600 ml. of refluxing ethanol was treated with 100 ml. of concentrated hydrochloric acid and heated at reflux for 2 hours as a clear solution developed. Benzene extractions of the residue obtained after removal of ethanol were washed with aqueous sodium carbonate and on distillation gave ethyl benzoate, b.p. 210–212°, $n^{25}D$ 1.5050, 2.0 g. (39% based on conversion to four moles of ester). A trace of benzoic acid was obtained on acidification of combined sodium carbonate washes.

A suspension of 1.0 g. (1.7 mmoles) of DBFF in 40 ml. of a 10% ethanol solution of sodium ethoxide was heated at reflux for 48 hours. The isolated solid material on treatment with aqueous mineral acid gave 0.44 g. (53% based on conversion to 4 moles of acid) of benzoic acid, m.p. and mixture m.p. 121–122°. Distillation of the ethanol filtrate gave a trace of ethyl benzoate, b.p. 208–210°, $n^{25}D$ 1.5050. The same yield of benzoic acid was obtained when alcoholic potassium hydroxide was substituted for alcoholic sodium ethoxide.

A mixture of 40 g. (196 mmoles) of aluminum isopropoxide in 200 ml. of anhydrous isopropyl alcohol and 5.88 g. (10 mmoles) of DBFF was heated at reflux under a condenser set for distillation for 3 hours or until acetone was no longer detected in the distillate. After removal of isopropyl alcohol, the residue was acidified with dilute hydrochloric acid and extracted with ether. Distillation of the combined dried ether extracts gave isopropyl benzoate, 2.3 g. (70% based on conversion to two moles of ester), b.p. 218–220°, $n^{25}D$ 1.5172.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.22; H, 7.37; O, 19.51. Found: C, 73.94; H, 7.37; O, 18.63.

A reduction product from DBFF corresponding to the oxidation of isopropyl alcohol to acetone was not found.

A mixture of 0.5 g. (0.8 mmole) of DBFF in 200 ml. of refluxing ethanol was treated with 0.05 g. (1.6 mmoles) of hydrazine as a clear solution developed. The volume was concentrated to 20 ml. and a few drops of glacial acetic acid were added. Dilution with water gave 0.35 g. of dibenzoylhydrazine (91% based on hydrazine) which recrystallized from dilute ethanol as colorless prisms, m.p. and mixture m.p. 240–241°.[19]

Anal. Calcd. for $C_{14}H_{12}N_2O_2$: C, 69.98; H, 5.03; N, 11.66; O, 13.31. Found: C, 70.25; H, 5.16; N, 11.80; O, 13.47.

The reaction was repeated with the substitution of 0.5 g. (15.6 mmoles) of hydrazine for 0.05 g. (1.5 mmoles). The hydrazide of benzoic acid, m.p. and mixture m.p. 117–118°,[20] was isolated, 0.2 g. (46% based on conversion of DBFF to 4 moles of hydrazide).

In a similar reaction with 3.0 g. (17 mmoles) of *p*-bromoaniline, 2.5 g. (4.2 mmoles) of DBFF gave 0.7 g. of N-benzoyl-*p*-bromoanilide (30% based on conversion to two moles of anilide), m.p. 200–202°[21] after recrystallization from acetic acid.

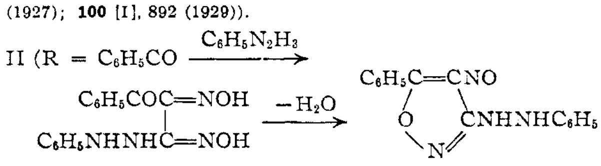
Excess phenylhydrazine converts DBFF in ethanol to a phenylhydrazide of benzoic acid, m.p. 168–170°[22] in 59% yield.

A mixture of 1.0 g. (1.7 mmoles) of DBFF, 0.67 g. (3.4 mmoles) of 2,4-dinitrophenylhydrazine and a few drops of concentrated hydrochloric acid in 300 ml. of ethanol was heated at reflux for 20 hours as a clear solution developed (after about 3 hours) and became cloudy. A precipitate isolated from the hot solution recrystallized from nitromethane as an orange crystalline solid, m.p. 230–231° dec., 0.2 g. (32%), identified as the 2,4-dinitrophenylhydrazone (VI) of 3-formyl-4-nitroso-5-phenylisoxazole.

Anal. Calcd. for $C_{16}H_{10}N_6O_6$: C, 50.26; H, 2.62; N, 22.00; O, 25.13. Found: C, 49.93; H, 2.99; N, 22.05; O, 25.48.

3(or 4)-Benzoylformaldoximinofuroxan (V).—A mixture of 1.0 g. (1.7 mmoles) of DBFF and 3.0 g. (43 mmoles) of hydroxylamine hydrochloride in 400 ml. of ethanol was treated with 3.0 g. (53 mmoles) of potassium hydroxide in 50 ml. of methanol added dropwise over one hour while main-

(14) The formation of 3-β-phenylhydrazino-4-nitroso-5-phenylisoxazole from dibenzoylfuroxan and phenylhydrazine has been suggested to occur with the formation of an intermediate glyoxime (G. Ruggieri, *Gazz. chim. ital.*, **55**, 72 (1925); W. Quist, *Chem. Zentr.*, **98**, [II], 1700 (1927); **100** [I], 892 (1929)).



Benzoylphenylhydrazide also was produced.

(15) Semi-micro analyses by Alfred Bernhardt, Max Planck Institut Microanalytisches Laboratorium, Mülheim (Ruhr), Germany, and Midwest Microlab., Inc., Indianapolis, Ind. Melting points are uncorrected.

(16) Lit. m.p. 179°,[4] 181°,[8] 187° (G. Ruggeri, *Gazz. chim. ital.*, **54**, 72 (1924)).

(17) Ebullioscopic determination in benzene by Huffman Microanalytical Laboratories, Wheatridge, Colo. It previously was reported[9] in error as a cryoscopic determination. Other runs gave the less satisfactory results of 222, 281 and 396. Values of 584 and 563 were obtained by the ebullioscopic method in benzene.[6]

(18) J. Meisenheimer, *Ber.*, **54**, 3206 (1921).

(19) R. S. Curtiss, A. R. Koch and E. J. Bartelis, This Journal, **31**, 416 (1909), reported m.p. 241–242°.

(20) M. Busch and M. Starke, *J. prakt. Chem.*, [2] **93**, 49 (1916), footnote 2, reports m.p. 116.5°.

(21) W. Autenrieth, *Ber.*, **38**, 2545 (1905), reports m.p. 202°.

(22) E. Fischer, *Ann.*, **190**, 125 (1877), reported m.p. 168°.

taining the temperature at 25°. The mixture was stirred an additional hour at room temperature and filtered. A yellow crude precipitate, 0.85 g., contained the potassium salt of 3(or 4)-benzoylformaldoximinofuroxan, m.p. 235–240° dec. after purification in methanol and in water.

Anal. Calcd. for $C_{10}H_6N_3O_4K$: C, 44.28; H, 2.23; N, 15.49; O, 23.59; K, 14.38. Found: C, 44.41; H, 2.58; N, 15.66; O, 22.59; K, 14.00.

Evaporation of the acidified alcoholic filtrate from the reaction mixture gave benzoic acid, 0.05 g. (12% based on conversion of DBFF to 2 moles of acid), m.p. and mixture m.p. 121–122° after recrystallization.

Acidification of the crude yellow solid product gave 0.2 g. (50% based on DBFF) of 3(or 4)-benzoylformaldoximinofuroxan (V) as colorless needles, m.p. 55–56° after recrystallization from aqueous ethanol.

Anal. Calcd. for $C_{10}H_7N_3O_4$: C, 51.50; H, 3.02; N, 18.01; O, 27.44. Found: C, 51.67; H, 3.31; N, 17.97; O, 27.00.

An ethanol solution of V absorbs in the ultraviolet at 270 mμ (log ϵ 3.16). Infrared absorption is described in Table I.

An alcohol solution of 0.12 g. (0.5 mmole) of 3(or 4)-benzoylformaldoximinofuroxan (V), 0.1 g. (0.5 mmole) of 2,4-dinitrophenylhydrazine and one drop of concentrated hydrochloric acid was heated at reflux for 12 hours. After cooling, a precipitate, 0.13 g. (63%), m.p. 180–182°, of a 2,4-dinitrophenylhydrazone of 3(or 4)-benzoylformaldoximinofuroxan was separated and recrystallized from alcohol as bright yellow plates, m.p. 182–183.°

Anal. Calcd. for $C_{16}H_{11}N_7O_7$: C, 46.48; H, 2.66; N, 23.72; O, 27.11. Found: C, 46.70; H, 2.62; N, 23.51; O, 27.01.

A solution of 0.1 g. (0.4 mmole) of 3(or 4)-benzoylformaldoximinofuroxan (V) in 4 ml. of 5% aqueous sodium hydroxide was stored at room temperature for 4 days. On acidification with concentrated hydrochloric acid crude benzoic acid, 45 mg. (92%), m.p. 119–121°, separated and after recrystallization from water had a m.p. and mixture m.p. 120–121°.

In a similar reaction benzoic acid in 37% yield was obtained from 3(or 4)-benzoylformaldoximinofuroxan and potassium permanganate in refluxing aqueous acetone.

Reduction of DBFF.—To a suspension of 0.5 g. of platinum oxide in 100 ml. of ethanol treated with hydrogen for a few minutes, 5.0 g. (8.5 mmoles) of DBFF in 200 ml. of ethanol was added and the mixture was shaken for 24 hours under 50 pounds of hydrogen at 35–40°. After separation of catalyst, a solid mixture, 5.0 g., was separated from a dark red filtrate after concentration. Benzoic acid, 1.2 g., was extracted from the solid mixture with *n*-hexane and purified by sublimation which gave 1.0 g. (48%) of benzoic acid, m.p. and mixture m.p. 121–122°. The hexane-insoluble portion was soluble in benzene from which it was reprecipitated by the addition of *n*-hexane as a dark brown to black unidentified solid, m.p. 140–160°.

A suspension of 1.0 g. (1.7 mmoles) of DBFF in 50 ml. of dioxane was shaken at room temperature and normal pressure with hydrogen over Raney nickel until 3.4 mmoles of hydrogen had reacted. Catalyst was separated and the solution was poured into 1.5 liters of cold dilute hydrochloric acid. Combined ether extracts of the acid solution were dried and evaporated. The solid residue was taken up in 15% sodium hydroxide (a trace of insoluble material was removed) and acidified with hydrochloric acid to precipitate benzoic acid, 0.4 g. (97% based on conversion to two moles of acid), m.p. and mixture m.p. 121–122° after recrystallization from water.

To 1.5 g. (2.5 mmoles) of DBFF in 10 ml. of glacial acetic acid 5.0 g. of zinc dust was added slowly with stirring while the temperature was held under 50° by external cooling. The mixture was treated with 75 ml. of cold water and filtered. Evaporation of combined ether extracts of the filtrate left 0.35 g. of a yellow solid which on sublimation gave 0.2 g. of benzoic acid (33% based on conversion to two moles of acid), m.p. and mixture m.p. 121–122°.

The same yield of benzoic acid was obtained when amalgamated zinc in hydrochloric acid was substituted for zinc in acetic acid.

Pyrolysis of DBFF.—In a distillation unit, 4.0 g. (6.8 mmoles) of DBFF was heated at 195–200° (0.4 mm.). During one hour a yellow liquid, 1.36 g., distilled at 157–165°.[23] The distillate dissolved in ether except for 0.1 g., m.p. 210–213°, of a colorless solid which recrystallized from ethanol as unidentified colorless prisms, m.p. 220–221°. The ether solution was evaporated and the residue was treated with 20 ml. of 10% sodium hydroxide at reflux temperature for 45 minutes. Unreacted oil, 0.25 g., was separated by extraction with ether. The cold aqueous solution acidified with hydrochloric acid gave 0.68 g. of benzoic acid, m.p. and mixture m.p. 121–122° (20%[24] based on conversion of DBFF to four moles of acid). Pyrolysis at normal pressure and in the presence of air occurs explosively with a luminous flame at about 200°.

DBFF and Potassium Cyanide.—A stirred suspension of 2.0 g. (3.4 mmoles) of DBFF in 16 ml. of ethanol was treated with 1.2 g. (1.8 mmoles) of potassium cyanide in 4 ml. of water at room temperature for 3 hours. After concentration, a yellow solid, 0.4 g., separated. Acidification of its aqueous solution gave a colorless unidentified solid which recrystallized from chloroform and from benzene as needles, m.p. 164–165°.

Anal. Calcd. for $C_{20}H_{15}N_7O_7$: C, 51.60; H, 3.25; N, 21.07; O, 24.07. Found: C, 51.45; H, 3.31; N, 21.63; O, 23.42. Repeat: C, 51.45; H, 3.28; N, 21.22; O, 23.92.

In ethanol the compound $C_{20}H_{15}N_7O_7$ absorbs in the ultraviolet at 257 mμ (log ϵ 4.23). Infrared absorption is described in Table I.

Acidification of combined ether extracts of the filtrate from which the yellow solid separated gave 0.25 g. of benzoic acid, m.p. and mixture m.p. 121–122° after recrystallization.

Miscellaneous Unsuccessful Reactions.—Unidentified oils were obtained from treatment of DBFF with sodium borohydride, with *o*-phenylenediamine, with ammonium chloride in alcoholic potassium hydroxide or with aqueous ammonium hydroxide in dioxane.

DBFF was not changed by stannous chloride in hydrochloric acid at 80° for 10 minutes (DBFF is insoluble in aqueous hydrochloric acid), by polyphosphoric acid at 100° for 30 minutes, by chlorine in alcohol at room temperature, by hydrogen peroxide in acetone at 45°, by 6 *N* ammonium hydroxide at room temperature for 72 hours, by phosphorus pentachloride at 110° for 30 minutes or in refluxing ether for 3 hours, by hydrazine dihydrochloride in refluxing alcohol for several hours, or by semicarbazide hydrochloride in aqueous alcohol containing sodium acetate at reflux for 2 hours.

3(or 4)-Benzoylformaldoximinofuroxan (V) gave unidentified oils with hydroxylamine hydrochloride, phenylhydrazine, semicarbazide, nitrous acid and pyruvic acid.

NEW ORLEANS, LA.

(23) W. Autenrieth and G. Thomae, *Ber.*, **57**, 430 (1924), record b.p. 205–210° (13 mm.) for benzoic anhydride.

(24) Reported[9] in error as 62%.