infrared spectra. Standards for compounds I, II and III were synthesized or obtained as follows:

2-*p*-Xylyl-2-methylbutane (I).—To the Grignard prepared from 2 moles of 2-bromo-*p*-xylene (Eastman Kodak Co.) and 48.6 g. of magnesium turnings in 620 ml. ether was added 2 moles of acetone (Reagent grade, M., C. and B.) in 155 ml. of ether. Additional ether (280 ml.) was added to ease the stirring; the addition took 4 hours. The mixture was allowed to stand overnight and then hydrolyzed with aqueous ammonium chloride. Fractionation *in vacuo* yielded 2-*p*-xylylpropanol-2 (b.p. 93° (2.5 mm.), $n^{20}D$ 1.5248–1.5254).

Treatment of the carbinol in *n*-pentane solution with hydrogen chloride gas at 0° for 1.75 hours produced the corresponding chloride derivative which was isolated by separation of the organic layer and then evaporation *in vacuo* at room temperature by means of a water aspirator to remove the solvent and excess hydrogen chloride. The chloride was added in ether solution with stirring to an ether solution of the Grignard reagent prepared from ethyl bromide. The addition required 4 hours. Stirring under reflux was continued for 3.5 days. Hydrolysis and fractionation produced I (over-all yield, 8%), b.p. 230°, $n^{20}D$ 1.5083).

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44; mol. wt., 176. Found: C, 87.8; H, 11.75; mol. wt., 176 (by m.s.).

2-*p*-Xylyl-3-methylbutane (II).—2-*p*-xylyl-3-methylbutanol-2 (b.p. 92° (1 mm.), $n^{20}D$ 1.5187) was prepared by the addition of the Grignard of 2-bromo-*p*-xylene to 3-methylbutanone-2.

The carbinol was dehydrated by treatment with a crystal or two of iodine at 140–150° to form what was probably 2-*p*-xylyl-3-methylbutene-1 (b.p. 218°, $n^{20}D$ 1.5099–1.5113; strong band at 11.14 μ indicative of a $R_2C{=}CH_2$ olefin). This olefin was hydrogenated in pentane at 10 p.s.i.g. in the presence of Adams platinum catalyst to yield II, b.p. 221°, $n^{20}D$ 1.4985.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44; mol. wt., 176. Found: C, 88.33; H, 11.59; mol. wt., 176 (by m.s.).

Di-*p*-xylylmethane (III).—The compound boiling at 318° was found identical by melting point (62–62.5°), mixed melting point (62°), as well as by infrared and mass spectrometry, with a sample synthesized by Welch and Smith[18] from *p*-xylene with formaldehyde.[19]

C_{16}-Diphenylmethane Derivatives.—The material boiling 302–308° (n^{20} 1.5491–1.5620) showed a strong mass spectrograph parent mass peak at 210 and secondary peaks at 196 characteristic of 2,5,4′-trimethyldiphenylmethane.[20] However, the identity of the components in this mixture was not established.

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[18] C. M. Welch and H. A. Smith, THIS JOURNAL, **73**, 4391 (1951).

[19] We are grateful to Dr. H. A. Smith for making this sample available to us.

[20] Sample supplied to us through the courtesy of Professor G. W. Wheland and Dr. George Kurhajec of the University of Chicago.

HARVEY, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The $BF_3·N_2O_5$ Complex. Its Use as a Nitrating Agent[1]

BY G. BRYANT BACHMAN AND JAMES L. DEVER

RECEIVED JUNE 2, 1958

Boron trifluoride reacts with dinitrogen pentoxide to form a stable, colorless complex, $BF_3·N_2O_5$. Physical and chemical properties suggest that the structure is best represented as $(F_3B \leftarrow ONO_2)^-(NO_2)^+$. The complex is an excellent nitrating agent in the aromatic series and is of some utility in the nitration of aliphatics.

It has been reported that boron trifluoride forms a 1:1 addition complex with dinitrogen tetroxide,[2] which is an excellent nitrating agent. More recently it has been found that boron trifluoride also forms a 1:1 addition complex with dinitrogen trioxide,[3] which is a weak nitrating agent and a powerful diazotizing agent for aromatic amines. It has now been found that dinitrogen pentoxide also forms a 1:1 complex with boron trifluoride. The complex is a colorless, stable liquid in the presense of polychlorinated alkanes and a white solid in nitroalkanes. It is insoluble in all substances tested except those with which it reacts. The complex decomposes at about 75° in inert solvents as evidenced by the evolution of brown NO_2 fumes. These properties together with the chemical properties described below suggest that the complex is ionic and is formed as illustrated in equation 1.

$$BF_3 + O_2N{-}O{-}NO_2 \longrightarrow (F_3B{\leftarrow}ONO_2)^-(NO_2)^+ \quad (1)$$

The $BF_3·N_2O_5$ complex reacts rapidly with substances with which BF_3 and N_2O_5 react separately, including water, alcohols, ethers, amines and pyridine. Also, the complex affords a ready means for introducing the NO_2 group into aromatic nuclei; thus, nitrobenzene reacts with a two-mole ratio of the complex in carbon tetrachloride to give an 86% yield of *m*-dinitrobenzene after 18 hours at 75°. Yields of 80–90% have been reported[4] using excess fuming HNO_3 and concentrated H_2SO_4 mixtures at about 100°. Benzoic acid reacts with a three-mole ratio of the complex in carbon tetrachloride in 36 hours at 70° to form 3,5-dinitrobenzoic acid (70% yield) and *m*-nitrobenzoic acid (9.3% yield). The results compare favorably with results obtained using other nitrating agents. Yields of 54–60% of 3,5-dinitrobenzoic acid have been reported[5,6] using an excess of mixtures of fuming nitric acid and concentrated sulfuric acid at above 100°. Other nitration results are shown in Table I.

An attempt was made to nitrate 2,6-di-*t*-butylphenol using a 1:1 mole ratio of the reactants in carbon tetrachloride at room temperature for five hours. The only product isolated was 2,2′,6,6′-tetra-*t*-butyl-4,4′-biphenylquinone, in 50% yield. In addition to this there was considerable tar formation. The fact that the only pure product obtained was the above-mentioned biphenylquinone indicates that the complex is also a strong oxidizing agent.

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[1] From the M. S. Thesis of James L. Dever, Purdue University, January, 1958.

[2] G. B. Bachman, H. Feuer, B. R. Bluestein and C. M. Vogt, THIS JOURNAL, **77**, 6188 (1955).

[3] G. B. Bachman and T. Hokama, *ibid.*, **79**, 4370 (1957).

[4] E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1954, p. 456.

[5] R. Q. Brewster and B. Wiliams, *Org. Syntheses*, **22**, 48 (1942).

[6] R. Phillips, *ibid.*, **22**, 49 (1942).

TABLE I

AROMATIC NITRATIONS WITH $BF_3 \cdot N_2O_5$

Reactant	Mole ratio complex/ reactant	Products	Yield,[a] %	Time, hr.	Temp., °C.	Solvent
Nitrobenzene	2	*m*-Dinitrobenzene	86	18	75	CCl_4
Benzoic acid	3	3,5-Dinitrobenzoic acid	70	36	70	CCl_4
		m-Nitrobenzoic acid	9			
Benzotrifluoride	2	*m*-Nitrobenzotrifluoride	84	36	60	CCl_4
		3,5-Dinitrobenzotrifluoride	3			
Chlorobenzene	0.5	Mixture of nitrochlorobenzenes	178[b]	12	60	CCl_4
Benzonitrile	3	*m*-Nitrobenzoic acid	81	48	65	CCl_4

[a] Yield based on reactant. [b] Yield based on complex.

A reaction of considerable interest was that of the complex with *m*-dinitrobenzene in an attempt to obtain *sym*-trinitrobenzene. This reaction was carried out several times and each time the crude product obtained melted a little higher than the starting material, *m*-dinitrobenzene (m.p. 89.5°). This could indicate the presence of considerable amounts of the trinitrobenzene, but an attempt to effect separation by means of chromatography using activated magnesium oxide[7] as the adsorbent proved unsatisfactory. Furthermore, spectroscopic evidence indicated that little if any trinitrobenzene had been formed in the reaction.

The above results show that the boron trifluoride–dinitrogen pentoxide complex is at least equivalent to "mixed acid" as far as nitrating ability at moderate temperature is concerned and in some cases, *e. g.*, benzoic acid, it appears to be somewhat stronger. For nitrations requiring temperatures above about 75°, *e. g.*, of dinitrobenzene, it is unsuitable because of its instability.

Several attempts were made to prepare aliphatic dinitro compounds. Heating the complex in 2-nitropropane at 100° for five hours resulted in decomposition of the complex but no nitration. Fractionation of the remaining liquid yielded only unreacted 2-nitropropane.

The oxidation of oximes to nitroparaffins has recently been reported.[8] It was felt that since the complex is both an oxidizing agent and a nitrating agent there was a possibility that reaction of the complex with an oxime could result in the formation of a *gem*-dinitro compound. Therefore ethyl methyl ketoxime was treated in carbon tetrachloride with a 1.5-to-1 mole ratio of complex to oxime. At 0° there was no reaction apparent; however, when the ice-bath was removed, a very vigorous reaction occurred, which eventually led to a fume-off. No products were isolated.

The reaction of diethyl malonate with a 2-mole ratio of complex at room temperature for six hours gave diethyl nitromalonate in 61.1% yield.

Experimental

Preparation of N_2O_5.—Two moles of nitric acid (fuming, 90% by weight) were placed in a three-necked, 500-ml. flask equipped with a gas inlet tube extending below the surface of the nitric acid and an exit tube to which was attached a receiving flask for the N_2O_5. The flask was immersed in a Dry Ice–Triclene-bath. Oxygen was bubbled through the nitric acid for one hour to remove volatile impurities and to ensure an oxidizing atmosphere for the reaction. The nitric acid was frozen by immersing the reaction flask in a Dry Ice–Triclene-bath. The Dry Ice-bath was replaced with a water-bath and about 100 g. of P_2O_5 was added to the reaction flask in 5-g. portions. The temperature of the water-bath was raised gradually to 45–50°, and the reaction mixture was maintained at this temperature for 3 to 6 hours. The receiver containing the distilled N_2O_5 was removed and the desired solvent was added. Conversions of 60 to 70% were obtained.

Preparation of $BF_3 \cdot N_2O_5$ Complex.—The three-necked, 500-ml. flask containing the N_2O_5 and solvent was fitted with a stirrer, reflux condenser with a drying tube, and a gas inlet tube which extended just below the surface of the solvent. The flask was cooled to 0° and gaseous boron trifluoride was introduced to precipitate the complex. Completion of the reaction was indicated when white fumes escaped from the mouth of the condenser.

In a series of five experiments, the combining mole ratios of reactants were determined as summarized in Table II. These data indicate that the dinitrogen pentoxide–boron trifluoride complex is a 1:1 compound.

TABLE II

COMPOSITION OF THE COMPLEX BY COMBINING WEIGHTS

N_2O_5, g.	N_2O_5, mole	BF_3, g.	BF_3, mole	Mole ratio N_2O_5/BF_3
27.1	0.26	16.9	0.24	1.04
72.9	.675	46.2	.69	0.98
30.4	.356	24.2	.362	0.985
64.8	.60	40.1	.59	1.02
35.6	.33	20.9	.311	1.06

Aromatic Nitration Procedure.—The complex usually was prepared in carbon tetrachloride, and the material to be nitrated was added in various mole ratios as indicated in Table I. The temperature of mixing was adjusted to the expected reactivity of the aromatic compound, being about 0° for a substance like chlorobenzene and room temperature for a substance like benzoic acid. The reaction mixture was then heated as indicated in Table I. Eventually the mixture was cooled, poured into ice-water, the organic layer separated, dried, and distilled. In cases where a solid separated (*e.g.*, dinitrobenzene), it was filtered off, washed with water, and recrystallized.

Attempted Nitration of 2,6-Di-*t*-butylphenol.—The complex, 0.34 mole, in carbon tetrachloride was placed in a 500-ml. flask equipped with a stirrer and a reflux condenser, and the flask was immersed in an ice-bath. A solution of 61.9 g. (0.30 mole) of 2,6-di-*t*-butylphenol in carbon tetrachloride was added dropwise with stirring. The temperature was allowed to increase to room temperature and stirring was continued for several hours. The reaction mixture was hydrolyzed and the water and solvent were allowed to evaporate leaving a violet-black solid. This material was dissolved in boiling acetone and deep purple crystals of 2,2′,6,6′-tetra-*t*-butylbiphenylquinone, m.p. 244–245°, were obtained on cooling (weight 31.0 g., 50.5% yield). The mother liquor was evaporated to a tar which failed to yield additional crystalline material.

Nitration of Diethyl Malonate.—The complex, 0.494 mole, in carbon tetrachloride, was placed in a 500-ml., round-bottom flask equipped with a stirrer, reflux condenser and dropping funnel. The reaction flask was immersed in an

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(7) K. Cruse and R. Mittag, *Z. Elektrochem.*, **54**, 418 (1950).

(8) W. D. Emmons and A. S. Pagano, THIS JOURNAL, **77**, 4557 (1955).

ice-bath and 78.1 g. (0.494 mole) of diethyl malonate was added dropwise. The addition required one hour. After the addition was completed, the ice-bath was removed and the mixture was stirred at 25–35° until no more heat was evolved. The reaction mixture was hydrolyzed by pouring it onto crushed ice, and the lower layer was dried and distilled; yield of diethyl nitromalonate,[9] 45.5 g. (61.1%), b.p. 97–103° (1 mm.), $n^{21}D$ 1.4273.

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[9] David I. Weisblat and Douglas A. Lyttle (to Upjohn Co.), U. S. Patent 2,644,838, July 7, 1953.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE R. B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

Maleic Hydrazide. I. Reactions with Selected Electrophilic Reagents[1]

BY HENRY FEUER AND HARRY RUBINSTEIN[2]

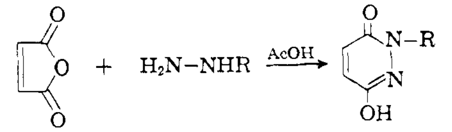
RECEIVED APRIL 14, 1958

It has been established that the reaction of maleic hydrazide with benzenesulfonyl chloride or with acetic anhydride leads to O-substituted maleic hydrazides, 3-(1H-6-pyridazinonyl) benzenesulfonate (I) and 3-(1H-6-pyridazinonyl) acetate (II). Treatment of 1-benzenesulfonyl-2-(3-carboxyacryloyl)-hydrazine (III) and 1-acetyl-2-(3-carboxyacryloyl)-hydrazine (IV), respectively, with glacial acetic acid gives the N-substituted compounds, 2-benzenesulfonyl-6-hydroxy-3(2H)-pyridazinone (V) and 2-acetyl-6-hydroxy-3(2H)-pyridazinone (VI) which are distinctly different from I and II with regard to infrared spectra and acidity characteristics. The five-membered ring isomer of V, N-benzenesulfonylaminomaleimide (VIIa) is obtained by refluxing III with thionyl chloride; VIIa is converted in basic or acidic medium as well as in dry xylene to the six-membered compound V, and the latter, on further treatment with base, undergoes ring opening and is reconverted to III.

The alkylation reactions of maleic hydrazide have received much attention, and the structures of the alkylated products are well established for the N- and O-methylated compounds.[3,4] This, however, is not so for the acylated derivatives of maleic hydrazide.

A patent for the acylation of maleic hydrazide[5] states that it is not known whether these acylated derivatives are N- or O-substituted. Stefanye and Howard[6] have reported the benzoylation of maleic hydrazide with benzoyl chloride and claimed that this reaction gave the O-derivative. Their proof that O-substitution had occurred was based on the ease of formation and hydrolysis of the product. O-Derivatives of phthalyl hydrazide have been reported to hydrolyze very readily.[7]

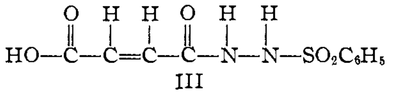
Maleic hydrazide was found to react with benzenesulfonyl chloride[8] and with acetic anhydride[5,8] to give products which could be either the N- or O-substituted derivatives. In order to establish the course of substitution that had taken place in these and in similar reactions, an unambiguous synthesis of N- or O-substituted derivatives was undertaken. Two possible reaction schemes were considered. The first was the reaction of 6-chloro-3-pyridazinone with silver or sodium acetate to form the O-derivative; the second was the preparation of the N-substituted hydrazides, benzenesulfonyl hydrazide (VIIIa) and acetyl hydrazide (VIIIb) followed by their reactions with maleic anhydride to give the N-substituted maleic hydrazides, 2-benzenesulfonyl-6-hydroxy-3(2H)-pyridazinone (V) and 2-acetyl-6-hydroxy-3(2H)-pyridazinone (VI).



VIIIa, R = $SO_2C_6H_5$ V, R = $SO_2C_6H_5$
b, R = $COCH_3$ VI, R = $COCH_3$

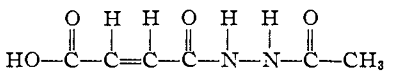
When the first scheme was attempted, no reaction took place; the failure can be ascribed to the inertness of the halogen in 6-chloro-3-pyridazinone. A somewhat similar observation has been made by Druey[4] in the case of 3,6-dichloropyridazine.

The second reaction scheme then was attempted by treating VIIIa and VIIIb with maleic anhydride in glacial acetic acid. This reaction when carried out at room temperature gave materials which were identified by their elemental analyses, acidity characteristics and infrared data, as 1-benzenesulfonyl-2-(3-carboxyacryloyl)-hydrazine (III) and 1-acetyl-2-(3-carboxyacryloyl)-hydrazine (IV), respectively. On titration with base, these compounds behaved like dibasic acids, III exhibiting pK_a values of 3.5 and 8.1 and IV of about 3.15 and 10.8.[9] Examination of the infrared spectra disclosed absorption maxima for the carbonyl group at 5.92μ for III and at 5.94μ for IV. These maxima indicate the presence of a conjugated carboxylic acid.[10]



$$\mathrm{HO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle H}{\overset{|}{C}}{=}\overset{\displaystyle H}{\overset{|}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle H}{\overset{|}{N}}{-}\overset{\displaystyle H}{\overset{|}{N}}{-}SO_2C_6H_5}$$

III



$$\mathrm{HO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle H}{\overset{|}{C}}{=}\overset{\displaystyle H}{\overset{|}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle H}{\overset{|}{N}}{-}\overset{\displaystyle H}{\overset{|}{N}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3}$$

IV

By refluxing compounds III and IV in glacial acetic acid, products were obtained the elemental analyses of which were compatible with V and VI. Compound V also formed when III was heated in

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[1] (a) From the Ph.D. thesis of Harry Rubinstein, Purdue University, 1958; (b) presented before the Division of Organic Chemistry at the San Francisco Meeting of the American Chemical Society, April, 1958.

[2] Purdue Research Foundation Fellow 1956–1957.

[3] K. Eichenberger, A. Staehelin and J. Druey, *Helv. Chim. Acta*, **37**, 837 (1954).

[4] J. Druey, Kd. Meier and K. Eichenberger, *ibid.*, **37**, 121 (1954).

[5] J. W. Zukel and W. D. Harris, U. S. Patent 2,614,917 (Oct. 21, 1952); *C. A.*, **47**, 1889h (1953).

[6] D. Stefanye and W. L. Howard, *J. Org. Chem.*, **19**, 115 (1954).

[7] F. M. Rowe and A. T. Peters, *J. Chem. Soc.*, 1331 (1933).

[8] H. Rubinstein, Master's Thesis, Purdue University, February, 1956.

[9] We are very grateful to Dr. H. Boaz of Eli Lilly and Co. for carrying out this titration.

[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 140.