ring to 40° where an exothermic reaction began. The temperature of the solution was maintained at 40–50° for one hour by intermittent cooling with an ice-bath. The mixture was then quenched in 150 ml. of ice-water and the aqueous solution extracted with three 50-ml. portions of methylene chloride. The combined extracts were washed with 10% sodium bicarbonate solution and dried over magnesium sulfate. Evaporation of the solvent under reduced pressure yielded 6.5 g. (72%) of colorless crystalline dimethylnitramine, m.p. 55–56° (lit. m.p. 57°[4]).

N-Nitromorpholine (Procedure B).—To a solution of 11.6 g. (0.1 mole) of N-nitrosomorpholine in 37 ml. of trifluoroacetic acid was added at 20° with stirring 4.1 ml. (0.15 mole) of 90% hydrogen peroxide. Slight heating with a water-bath was required to initiate the exothermic reaction. The temperature was maintained at 40–50° by intermittent cooling for one hour. The solution was then worked up in the manner described above. There was obtained 10.0 g. (76%) of colorless crystalline N-nitromorpholine, m.p. 52–53° (lit. m.p. 53–54°[8]).

HUNTSVILLE, ALABAMA

[CONTRIBUTION FROM THE ROHM AND HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION]

Peroxytrifluoroacetic Acid. II. The Oxidation of Anilines to Nitrobenzenes[1]

BY WILLIAM D. EMMONS

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It has been established that peroxytrifluoroacetic acid is a general reagent for the oxidation of anilines to nitrobenzenes in essentially quantitative yields. The reagent is particularly effective for negatively substituted anilines.

The oxidation of a wide variety of anilines to the corresponding nitrobenzenes has been carried out smoothly in almost quantitative yields with peroxytrifluoroacetic acid. This reaction has in the

$$\mathrm{ArNH_2} \xrightarrow{\mathrm{CF_3CO_3H}} \mathrm{ArNO_2}$$

past been accomplished with both peroxyacetic acid[2,3] and with Caro's acid,[4,5] but yields of nitrobenzenes obtained generally have been extremely poor. Thus the oxidation of aniline with peroxyacetic acid has been shown by Greenspan to give 11% nitrobenzene and 71% azoxybenzene.[3] The formation of substantial quantities of azoxybenzenes is, in fact, the major disadvantage of oxidation of anilines with peroxyacetic acid. In contrast, the products obtained from peroxytrifluoroacetic acid oxidation were of an excellent state of purity, and no indication of azoxybenzene formation has been observed. The high acidity of the reaction medium is of course responsible for the fact that secondary condensation reactions such as azoxybenzene formation do not occur.

The oxidation of aromatic amines was carried out with peroxytrifluoroacetic acid prepared from trifluoroacetic anhydride and 90% hydrogen peroxide in methylene chloride and also with solutions of 90% hydrogen peroxide in trifluoroacetic acid. The anhydrous reagent in methylene chloride was somewhat more reactive, and oxidation reactions with it usually could be run at a lower temperature. Peroxytrifluoroacetic acid in methylene chloride was also to be preferred since it gave slightly higher yields and a somewhat better grade of product. Furthermore, the reactions were run at the reflux temperature of this solvent and under these conditions were much easier to control. A summary of the experimental investigations may be found in Table I. The yields are in most cases based on the products initially isolated from the reaction but generally these products were fairly pure. The oxidation of *m*- and *p*-phenylenediamine to the corresponding dinitrobenzenes in high yield is particularly noteworthy, and indeed represents the only such examples reported in the literature. N-Methylaniline also was oxidized and was converted to nitrobenzene in excellent yield. As a synthetic method the oxidation of anilines to nitrobenzenes is obviously of value in cases where the nitrobenzene cannot be made by direct nitration of an available starting material. Thus this oxidation is very probably the method of choice for preparation of such compounds as 2,4,6-tribromonitrobenzene, 2,4,6-trichloronitrobenzene and 1,2,4-trinitrobenzene. In general the oxidation of anilines with peroxytrifluoroacetic acid proceeds quite rapidly at the reflux temperature of methylene chloride. In most of the experiments a 30% excess of the peroxyacid over the three equivalents required was used in the reaction.

TABLE I

OXIDATION OF ANILINES TO NITROBENZENES

Aniline	Nitrobenzene	Yield,[a] %
Aniline	Nitrobenzene	89 (79)
N-Methylaniline	Nitrobenzene	84
p-Bromoaniline	*p*-Bromonitrobenzene	90 (85)
p-Chloroaniline	*p*-Chloronitrobenzene	87
o-Nitroaniline	*o*-Dinitrobenzene	92 (81)
m-Nitroaniline	*m*-Dinitrobenzene	86 (92)
p-Nitroaniline	*p*-Dinitrobenzene	94 (86)
m-Phenylenediamine	*m*-Dinitrobenzene	76 (76)
p-Phenylenediamine	*p*-Dinitrobenzene	86 (89)
p-Aminobenzonitrile	*p*-Nitrobenzonitrile	96 (98)
p-Toluidine	*p*-Nitrotoluene	78
o-Toluidine	*o*-Nitrotoluene	71
p-Aminobenzoic acid	*p*-Nitrobenzoic acid	92
Ethyl *p*-aminobenzoate	Ethyl *p*-nitrobenzoate	99
2,4,6-Tribromoaniline	2,4,6-Tribromonitrobenzene	100
2,4,6-Trichloroaniline	2,4,6-Trichloronitrobenzene	98
2-Amino-*p*-cymene	2-Nitro-*p*-cymene	54
2,4-Dinitroaniline	1,2,4-Trinitrobenzene	87

[a] The figures in parentheses represent yields obtained with 90% hydrogen peroxide in trifluoroacetic acid.

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(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) J. D'Ans and A. Kneip, *Ber.*, **48**, 1144 (1915).

(3) F. P. Greenspan, *Ind. Eng. Chem.*, **39**, 847 (1947).

(4) E. Bamberger and F. Tschirmer, *Ber.*, **32**, 1675 (1899).

(5) W. D. Langley, *Org. Syntheses*, **22**, 44 (1942).

Unfortunately, the oxidation of anilines with peroxytrifluoroacetic acid is not a completely general reaction. Thus picramide did not react with the reagent. This may be due to steric factors or possibly to the low order of nucleophilicity exhibited by this amine. A more serious limitation to the use of peroxytrifluoroacetic acid in synthesis of nitrobenzenes is that it has a very high order of reactivity toward aromatic nuclei. Indeed it has been observed that this reagent in contrast to other organic peracids attacks benzene itself to yield a complex mixture containing phenols. Consequently, a nitrobenzene having electron donating groups cannot be readily prepared by amine oxidation since the reagent will attack the aromatic nucleus. Thus *p*-anisidine reacted with peroxytrifluoroacetic acid to yield a complex mixture from which no *p*-nitroanisole could be isolated. The oxidation of β-naphthylamine also yielded an intractable mixture of products presumably derived from attack of peroxytrifluoroacetic acid on the naphthalene nucleus. 2-Amino-*p*-cymene with its two alkyl substituents could be oxidized to the corresponding nitrobenzene, but the yield was only 54% and the quality of the product was relatively poor. On the other hand, the fact that *o*- and *p*-toluidine were smoothly converted to the corresponding nitrobenzenes in excellent yield indicates that the reaction is useful for preparation of monoalkyl nitrobenzenes.

The oxidation of aromatic amines to nitro compounds with 30% hydrogen peroxide in trifluoroacetic acid also has been examined. Unfortunately, however, 30% hydrogen peroxide is not a suitable reagent for this oxidation reaction, at least under the conditions we have employed. The yields were considerably lower than with 90% hydrogen peroxide and the quality of the product obtained was relatively poor except in a few cases. Thus, *p*-bromoaniline, *p*-chloroaniline and *p*-aminobenzonitrile were oxidized cleanly to *p*-bromonitrobenzene, *p*-chloronitrobenzene and *p*-nitrobenzonitrile in yields of 86, 71 and 85%, respectively. In these three cases the crude products obtained were relatively pure. The oxidation of *o*-, *m*- and *p*-nitroaniline was an unsatisfactory reaction with 30% hydrogen peroxide in trifluoroacetic acid since the yields were only fair and the crude products obtained were impure. Aniline itself gave nitrobenzene in only 16% yield with 30% hydrogen peroxide.

It is quite probable that the oxidation of an aromatic amine involves attack of peroxytrifluoroacetic acid on the free amine rather than its salt. There is, in fact, considerable qualitative evidence to support this hypothesis. Thus negatively substituted anilines which are less basic in character normally may be oxidized at lower temperatures and under milder conditions than aniline itself. This difference in reactivity is particularly noticeable when 90% hydrogen peroxide in trifluoroacetic acid is employed as the oxidizing agent. Further more, all of the older procedures[2,3] employing peroxyacetic acid for aniline oxidation were carried out in the presence of a base such as sodium bicarbonate; this was presumably necessary in order to maintain a sufficiently high concentration of free amine for the reaction to take place at a practical rate. Peroxytrifluoroacetic acid is, however, so reactive that even the relatively small concentration of free aromatic amine present in the acidic reaction medium is sufficient for the oxidation reaction to occur rapidly. Indeed, it is rather surprising that the oxidation of anilines to nitrobenzenes with peroxytrifluoroacetic acid goes so rapidly under rather mild conditions in such an acidic medium.

Experimental

Oxidation of Aniline to Nitrobenzene.—A solution of peroxytrifluoroacetic acid was prepared by addition of 34.0 ml. (0.24 mole) of trifluoroacetic anhydride to a suspension of 5.4 ml. (0.2 mole) of 90% hydrogen peroxide in 100 ml. of methylene chloride cooled in an ice-bath. The resulting solution was stirred five minutes and the cooling bath was removed. To this solution was added dropwise over a 30-minute period 4.7 g. (0.05 mole) of aniline in 20 ml. of methylene chloride. The exothermic reaction which occurred caused the solution to boil during this period. After addition was complete, the solution was heated under reflux one hour. It was then washed with two 100-ml. portions of water and two 100-ml. volumes of 10% sodium carbonate solution. The methylene chloride extract was dried over magnesium sulfate and the volatile solvent was evaporated. The residual oil was steam distilled to yield 5.5 g. (89%) of nitrobenzene, n^{20}_{D} 1.5522.

Oxidation of *p*-Toluidine to *p*-Nitrotoluene.—To 50 ml. of methylene chloride and 3.3 ml. (0.12 mole) of 90% hydrogen peroxide cooled in an ice-bath was added 20.3 ml. (0.144 mole) of trifluoroacetic anhydride. The solution was stirred five minutes in the ice-bath and then allowed to warm up to room temperature. To this solution was added 3.2 g. (0.03 mole) of freshly distilled *p*-toluidine in 10 ml. of methylene chloride over a 15-minute period. The solution was allowed to boil during this addition. The resulting red solution was then heated under reflux for one hour. It was cooled and washed with two 100-ml. portions of water. The extract was dried over magnesium sulfate and the solvent evaporated under reduced pressure. There was obtained 3.2 g. (78%) of yellow *p*-nitrotoluene, m.p. 48–50°. After recrystallization from ethanol the product melted at 51–52°. A mixture melting point with an authentic sample of *p*-nitrotoluene showed no depression.

Oxidation of *m*-Phenylenediamine to *m*-Dinitrobenzene.—A solution of peroxytrifluoroacetic acid in 100 ml. of methylene chloride was prepared in the usual fashion from 34.0 ml. (0.24 mole) of trifluoroacetic anhydride and 5.4 ml. (0.2 mole) of 90% hydrogen peroxide. To this solution was added over a 20-minute period 2.6 g. (0.025 mole) of *m*-phenylenediamine in 20 ml. of methylene chloride. The solution spontaneously boiled throughout this addition and was then heated under reflux for one hour. It was washed with two 100-ml. portions of water and two 100-ml. volumes of 10% sodium carbonate solution. The extract was dried over magnesium sulfate and the volatile solvent removed under reduced pressure. There was obtained 3.2 g. (76%) of crude yellow *m*-dinitrobenzene, m.p. 83–85°. After recrystallization from ethanol the product melted at 87–89°. A mixture melting point with an authentic sample of *m*-dinitrobenzene showed no depression.

Oxidation of 2,4-Dinitroaniline to 1,2,4-Trinitrobenzene.—A solution of peroxytrifluoroacetic acid was prepared from 5.4 ml. (0.2 mole) of 90% hydrogen peroxide, 34.0 ml. (0.24 mole) of trifluoroacetic anhydride and 50 ml. of chloroform. This solution was rapidly heated to reflux and 9.2 g. (0.05 mole) of 2,4-dinitroaniline was added in small portions. After the vigorous exothermic reaction was over, the volatile solvent was removed at reduced pressure. To the residual oil was added 50 ml. of ice-water and the oil crystallized after being scratched with a glass rod. This product was recrystallized from 25 ml. of ethanol to yield 9.3 g. (88%) of yellow crystalline 1,2,4-trinitrobenzene, m.p. 57–59° (lit. m.p. 60°[6]).

Oxidation of 2,4,6-Tribromoaniline to 2,4,6-Tribromonitrobenzene.—To 3.3 ml. (0.12 mole) of 90% hydrogen

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[6] W. Borsche, *Ber.*, **56**, 1498 (1923).

peroxide in 100 ml. of methylene chloride was added at room temperature 20.2 ml. (0.144 mole) of trifluoroacetic anhydride in one portion. After an induction period of one or two minutes an exothermic reaction took place causing the solution to reflux. The homogeneous mixture was then stirred a few minutes and a slurry of 9.3 g. (0.03 mole) of 2,4,6-tribromoaniline in 20 ml. of methylene chloride was added over a ten-minute period. The solution was then heated under reflux 30 minutes. It was cooled and washed with 100 ml. of water. The turbid brown methylene chloride extract was separated and the volatile solvent was removed under reduced pressure. There was obtained as a residue 10.2 g. (100%) of yellow 2,4,6-tribromonitrobenzene, m.p. 113–115°. This was recrystallized once from ethanol and melted at 124–125° (lit. m.p. 125°[7]).

Oxidation of *p*-Bromoaniline to *p*-Bromonitrobenzene.—A solution of peroxytrifluoroacetic acid was prepared by addition of 5.4 ml. (0.2 mole) of 90% hydrogen peroxide to 50 ml. of trifluoroacetic acid. To this solution was added 6.9 g. (0.04 mole) of *p*-bromoaniline in one portion. The solution was then warmed to 55° where an exothermic reaction was observed. The temperature of the solution was allowed to increase to 85° and was maintained at 75–85° by intermittent cooling with an ice-bath. After 15 minutes, evolution of heat had ceased, and the mixture was allowed to cool to room temperature. The solution was then poured into 200 ml. of a crushed ice–water mixture and the light tan solid which separated was collected on a filter. There was obtained 6.9 g. (85%) of *p*-bromonitrobenzene, m.p. 122–124°. After recrystallization from ethanol the sample melted at 125–126°.

Oxidation of *p*-Phenylenediamine to *p*-Dinitrobenzene.—To 40 ml. of trifluoroacetic acid was added at room temperature 2.2 g. (0.02 mole) of *p*-phenylenediamine in one portion. To this solution was added with stirring 5.4 ml. (0.2 mole) of 90% hydrogen peroxide. No evolution of heat was observed until the mixture was heated to 50°. At this point an exothermic reaction was noted, and the temperature was kept between 60–70° for 45 minutes by intermittent cooling with an ice-bath. After the reaction was over the solution was heated at 60° for 15 minutes. The mixture was then quenched in 200 ml. of a crushed ice–water mixture. The solid *p*-dinitrobenzene so obtained was collected on a filter and dried; yield 3.0 g. (89%), m.p. 160–164°. The sample was recrystallized from ethanol once and melted at 169–171°.

Oxidation of *p*-Chloroaniline to *p*-Chloronitrobenzene with 30% Hydrogen Peroxide.—A solution of 6.4 g. of *p*-chloroaniline (0.05 mole) in 50 ml. of trifluoroacetic acid was heated to reflux. To this refluxing solution was added 28.3 g. (0.25 mole) of 30% hydrogen peroxide over a 30-minute period. The solution was then heated under reflux for 30 minutes and cooled. It was poured into 150 ml. of crushed ice-water mixture, and the light brown precipitate of *p*-chloronitrobenzene was collected on a filter and dried; yield 6.0 g. (71%), m.p. 73–75°. A sample of this material was purified by vacuum sublimation, m.p. 76–78°. Attempts to raise the melting point to the literature value of 83°[8] by further purification were unsuccessful.

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(7) K. J. P. Orton, *J. Chem. Soc.*, **83**, 797 (1903).

(8) I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1946, p. 503.

HUNTSVILLE, ALABAMA

[CONTRIBUTION FROM THE ROHM AND HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION]

Peroxytrifluoroacetic Acid. III. The Hydroxylation of Olefins[1]

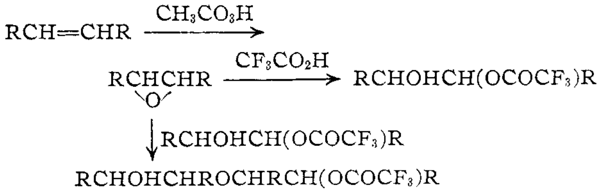
BY WILLIAM D. EMMONS, ANGELO S. PAGANO AND JEREMIAH P. FREEMAN

RECEIVED MARCH 8, 1954

Peroxytrifluoroacetic acid has been found to be a superior reagent for olefin hydroxylation. The reagent is particularly useful for preparation of water-soluble α-glycols and for hydroxylation of negatively substituted olefins.

Peroxytrifluoroacetic acid has been found to be extremely reactive in the hydroxylation of olefins and excellent yields of the corresponding α-glycols have been obtained. Most organic peroxyacids have at one time or another been employed for olefin hydroxylation,[2] and performic acid is particularly effective in this reaction. Peroxytrifluoroacetic acid is, however, far more reactive than this reagent and in addition offers some practical advantages in synthesis of water-soluble α-glycols.

Peroxytrifluoroacetic acid, prepared from trifluoroacetic anhydride and 90% hydrogen peroxide in methylene chloride, reacted almost instantaneously even at ice-bath temperatures with all the simple olefins investigated. The products obtained were hydroxytrifluoroacetates derived from the ring opening of the intermediate epoxide with trifluoroacetic acid. These esters could, however, readily be converted to the α-glycols by methanolysis.[3] Initially it was found that the glycols were contaminated by high-boiling products of the cellosolve type. These were undoubtedly derived from condensation of the epoxide, initially formed in the reaction, with the hydroxytrifluoroacetate which accumulates as the reaction proceeds. Formation of these high boiling ethers was prevented, however, by increasing the effective concentration of trifluoroacetate ions present in the reaction medium; this was conveniently accomplished by addition of triethylammonium trifluoroacetate to the solvent in which the oxidation was carried out, and under these conditions pure α-glycols were obtained. In this connection it was observed that the salts of tertiary aliphatic amines and trifluoroacetic acid are extremely soluble in those chlorinated solvents which are capable of hydrogen bonding. A summary of the experimental investigations may be found in Table I.



$$\begin{array}{l} \mathrm{RCH{=}CHR} \xrightarrow{\mathrm{CH_3CO_3H}} \\ \qquad \underset{\diagdown\mathrm{O}\diagup}{\mathrm{RCHCHR}} \xrightarrow{\mathrm{CF_3CO_2H}} \mathrm{RCHOHCH(OCOCF_3)R} \\ \qquad \big\downarrow \mathrm{RCHOHCH(OCOCF_3)R} \\ \quad \mathrm{RCHOHCHROCHRCH(OCOCF_3)R} \end{array}$$

In general the oxidations were carried out by addition of a methylene chloride solution of peroxytrifluoroacetic acid to the olefin and triethylammo-

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(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) D. Swern, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 378.

(3) E. J. Bourne, C. E. M. Tatlow and J. C. Tedder, *J. Chem. Soc.*, 1367 (1950).