charged form of the three-electron bond[2] which might be stabilized by solvation in polar solvents. The rates of dissociation also would increase in the same direction, as demonstrated by the increased rate in acetone as compared to toluene for the unsubstituted compound. It is possible that a process of desolvation partially contributes to the recombination activation energies, but the question of the effect of solvation for any of the steps could be answered only by a complete study in a series of solvents.

**Acknowledgments.**—This work was greatly facilitated by a grant from the Research Corporation and a grant from the National Science Foundation.

LOS ANGELES 7, CALIFORNIA

---

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

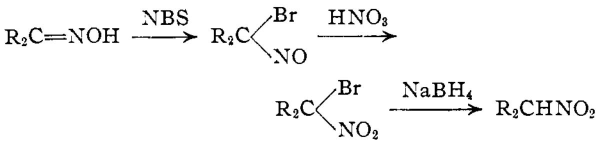
# Peroxytrifluoroacetic Acid. VI. The Oxidation of Oximes to Nitroparaffins[1,2]

BY WILLIAM D. EMMONS AND ANGELO S. PAGANO

RECEIVED MARCH 14, 1955

Under suitable conditions peroxytrifluoroacetic acid has been found to be a general reagent for oxidation of oximes to nitroparaffins. The reagent is particularly valuable for preparation of secondary nitroparaffins.

It has been found that under the proper conditions peroxytrifluoroacetic acid is a remarkably efficient and general reagent for oxidation of oximes to nitroparaffins. Previous methods of effecting this reaction have been rather unsatisfactory. Bamberger has, for example, reported the oxidation of benzaldehyde oxime to phenylnitromethane, but the yield was very low and a complex mixture of products was obtained.[3] In a recent series of papers Iffland has described a three-step procedure for conversion of oximes to nitroparaffins.[4] This procedure is based on the bromination of the oxime to the bromonitroso compound with N-bromosuccinimide, oxidation of this to the bromonitroparaffin with nitric acid and finally reduction of the bromonitroparaffin with sodium borohydride. However, this procedure is rather tedious and the yields, particularly in the aliphatic series, are frequently poor. In contrast, the procedures employing peroxytrifluoroacetic acid are one-step reactions which generally may be carried out in fairly good yields.



$$R_2C{=}NOH \xrightarrow{NBS} R_2C\begin{matrix}Br\\NO\end{matrix} \xrightarrow{HNO_3} R_2C\begin{matrix}Br\\NO_2\end{matrix} \xrightarrow{NaBH_4} R_2CHNO_2$$

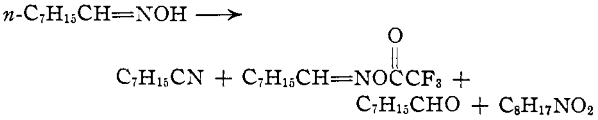
It was found initially in this work that the oxidation of those oximes which yielded resonance stabilized *aci*-nitroparaffins could be carried out using peroxytrifluoroacetic acid in typical procedures which had been developed previously for oxidation of anilines and nitrosamines.[5] Thus the oxidation of diethyl oximinomalonate gave diethyl nitromalonate in 66% yield when carried out in trifluoroacetic acid as solvent. In similar fashion oximinomalonamide was converted to nitromalonamide in 49% yield and phenylglyoxal aldoxime to $\omega$-nitroacetophenone in 76% yield. The oxidation of $\alpha$-oximinoacetoacetic ester yielded ethyl nitroacetate in 40% yield and also some oxalic acid.[6] In all of the cases described here, the *aci*-nitroparaffin which presumably is formed as the first product of the oxidation is relatively stable and is not destroyed before a prototropic shift to form the nitroparaffin takes place.

$$HON{=}C(COOC_2H_5)_2 \xrightarrow{CF_3CO_3H} NO_2CH(COOC_2H_5)_2$$

$$C_6H_5COCH{=}NOH \xrightarrow{CF_3CO_3H} C_6H_5COCH_2NO_2$$

$$CH_3COC{=}NOH(COOC_2H_5) \xrightarrow{CF_3CO_3H} NO_2CH_2COOC_2H_5$$

The oxidation of monofunctional oximes such as *n*-octyl aldehyde oxime with peroxytrifluoroacetic acid in chlorinated solvents was a completely unsatisfactory reaction. This oxime yielded on treatment with anhydrous peroxytrifluoroacetic acid in ethylene chloride at reflux a complex mixture of products consisting of caprylonitrile, the trifluoroacetate ester of the oxime, *n*-octyl aldehyde and some 1-nitroöctane. All of the components of the mixture were not characterized completely; however, infrared spectra of the crude mixture and its partially fractionated components indicated that substantial amounts of each of the four products mentioned above were present. The nitrile presumably originated from elimination of trifluoroacetic acid from the oxime trifluoroacetate. The aldehyde may have come from hydrolysis of the oxime or, as is more likely the case, from a Nef reaction of the *aci*-nitroparaffin. In order to avoid formation of the oxime trifluoroacetate and the nitrile derived from it, the oxidation of *n*-octyl aldehyde oxime was repeated in ethylene chloride using a disodium hydrogen phosphate buffer to scavenge trifluoroacetic



$$n\text{-}C_7H_{15}CH{=}NOH \longrightarrow C_7H_{15}CN + C_7H_{15}CH{=}NO\overset{\overset{O}{\|}}{C}CF_3 + C_7H_{15}CHO + C_8H_{17}NO_2$$

---

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

[2] For the preceding paper in this series, see W. D. Emmons and G. B. Lucas, THIS JOURNAL, **77**, 2287 (1955).

[3] E. Bamberger, *Ber.*, **33**, 1781 (1900).

[4] D. C. Iffland, *et al.*, THIS JOURNAL, **75**, 4044 (1953); D. C. Iffland and G. X. Criner, *ibid.*, **75**, 4047 (1953); D. C. Iffland and Teh-Fu Yen, *ibid.*, **76**, 4083 (1954).

[5] W. D. Emmons, *ibid.*, **76**, 3468, 3470 (1954).

[6] An oxidation of ethyl oximinoacetoacetate to ethyl nitroacetate in 61% yield has been reported previously; V. M. Rodionov, I. V. Machinskaya and V. M. Belikov, *Zhur. Obshchei Khim.* **18**, 917 (1948).

acid from the system and hence prevent formation of the oxime trifluoroacetate. The use of such buffers previously had been very successful in the epoxidation of olefins with peroxytrifluoroacetic acid.[7] Indeed, under these conditions, no nitrile or oxime trifluoroacetate was formed; however, there was very little nitroparaffin either.

Extensive investigation of the reaction conditions for oxime oxidation has shown that in acetonitrile at reflux and in the presence of a buffer such as disodium hydrogen phosphate or sodium bicarbonate, good yields of nitroparaffins may be obtained. Sodium bicarbonate was more satisfactory in oxidation of aliphatic oximes while dibasic sodium phosphate gave higher yields with aromatic and alicyclic oximes. It also was found that addition of small amounts of urea for scavenging any nitrogen oxides increased the yields significantly. The oxidation normally was carried out by the slow addition of an anhydrous solution of peroxytrifluoroacetic acid in acetonitrile to an acetonitrile solution of the oxime in which the buffer was slurried. The mixture was kept at gentle reflux throughout the addition and it should be emphasized that too rapid addition of the peracid or overheating of the reaction mixture lowered the yield of nitroparaffin markedly.

The experimental results are summarized in Table I along with the physical properties of the nitroparaffins obtained. All the compounds prepared here have been reported previously in the literature, and the physical properties of our products were in excellent agreement with the literature values. The crude products obtained from the reaction were generally contaminated by small amounts of ketones formed either by a Nef reaction or by hydrolysis of the oxime. Consequently, in most cases the nitroparaffins were fractionated in order to obtain pure products. The yields obtained generally ranged from 50 to 80%, and the reaction appears to be quite general for preparation of primary, secondary and alicyclic nitroparaffins. Indeed this procedure is probably the method of choice for preparation of most secondary nitroparaffins since the Victor Meyer reaction cannot be used to obtain these compounds in good yields.[8] The only oximes which could not be oxidized successfully were those of pinacolone and trimethylacetaldehyde. In the former case a trace of nitroparaffin was obtained and in the latter a 15% yield of crude nitroparaffin was isolated. In both cases most of the oxime was recovered. The failure of these two compounds to undergo oxidation is undoubtedly dependent on steric strain in the transition state.

TABLE I

THE OXIDATION OF OXIMES TO NITROPARAFFINS[a]

| Nitroalkane | Yield from oxime, % | Base employed | B.p. or m.p. °C. | Mm. | $n^{20}D$ |
|---|---|---|---|---|---|
| Diethyl nitromalonate[b] | 66 | None | 80–83 | 0.3 | 1.4276 |
| ω-Nitroacetophenone | 76 | None | 106–107 | | |
| Ethyl nitroacetate[c,d] | 40 | None | 65–66 | 0.6 | 1.4250 |
| Nitromalonamide[b] | 49 | None | 171–173 | | |
| 1-Nitroheptane | 72 | $NaHCO_3$ | 74–76 | 4 | 1.4288[e] |
| 1-Nitroöctane | 63 | $NaHCO_3$ | 86–87 | 1 | 1.4312[f] |
| Phenylnitromethane | 77 | $Na_2HPO_4$ | 97–99 | 4 | 1.5344 |
| Nitrocyclopentane | 60 | $Na_2HPO_4$ | 90–92 | 40 | 1.4514[g] |
| Nitrocyclohexane | 62 | $Na_2HPO_4$ | 106–108 | 40 | 1.4619 |
| Nitrocycloheptane | 51 | $Na_2HPO_4$ | 99–102 | 15 | 1.4720 |
| 4-Nitroheptane | 64 | $NaHCO_3$ | 58–60 | 3 | 1.4217 |
| 2-Nitrobutane | 47 | $NaHCO_3$ | 64–66 | 70 | 1.4039 |
| 2-Nitroheptane | 59 | $NaHCO_3$ | 76–79 | 6 | 1.4248[g] |
| 2-Nitropentane | 43 | $NaHCO_3$ | 88–90 | 100 | 1.4088[f] |
| 2-Nitro-3-methylbutane | 49 | $NaHCO_3$ | 87–88 | 100 | 1.4122[f] |
| α-Phenylnitroethane | 69 | $Na_2HPO_4$ | 75–76 | 0.7 | 1.5212[f] |

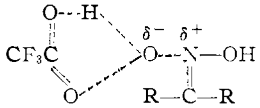
[a] Unless otherwise indicated the oxidations were run in acetonitrile at reflux. [b] In trifluoroacetic acid as solvent. [c] In chloroform as solvent. [d] Prepared by oxidation of ethyl α-oximinoacetoacetate. [e] At 19°. [f] At 25°. [g] At 23°.

The role of acetonitrile as solvent for the oxidation of oximes to nitroparaffins is certainly a crucial one. It seems reasonable to assume that it functions as a base which catalyzes the prototropic conversion of the *aci*-nitroparaffin (II) to its stable tautomer III. In the absence of a basic solvent

$$\underset{\text{I}}{R_2C{=}NOH} \xrightarrow{CF_3CO_3H} \underset{\text{II}}{R_2C{=}NO_2H} \longrightarrow \underset{\text{III}}{R_2CHNO_2}$$

such as acetonitrile this conversion undoubtedly will take place, but its rate will be many times slower; consequently the unstable *aci*-nitroparaffin will accumulate and much of it will be lost *via* a Nef reaction as well as by other degradative reactions. Indeed the superiority of acetonitrile in this reaction suggests that it might be a useful solvent for acidification of the sodium salts of nitroparaffins in cases where a non-aqueous system is desired and decomposition of the *aci*-nitroparaffin is a problem.

The excellence of peroxytrifluoroacetic acid in this reaction undoubtedly is due to the demonstrated proclivity of the oxygen–oxygen bond toward heterolytic cleavage. A reasonable model of the transition state for the oxidation of oximes is indicated below. This model is based on the assumption that the peracid reacts through a cyclic hydrogen-bonded form. This type of structure for peracids has been demonstrated spectroscopically with performic acid,[9] and Overberger also has presented evidence that the perbenzoic acid oxidation of sulfides probably proceeds through a similar intermediate.[10] That peroxytrifluoroacetic acid may exist in an intramolecular cyclic hydrogen-bonded form is suggested by the very great volatility of the peroxyacid as compared to trifluoroacetic acid itself.



## Experimental

**Oxidation of Benzaldehyde Oxime to Phenylnitromethane.**—A solution of peroxytrifluoroacetic acid was prepared from 5.5 ml. (0.2 mole) of 90% hydrogen peroxide, 34.0 ml. (0.24 mole) of trifluoroacetic anhydride and 50 ml. of acetonitrile. This was added over a 75-minute period to a well-stirred mixture of 2.0 g. of urea, 78 g. (0.55 mole) of dibasic sodium phosphate and 12.1 g. (0.1 mole) of benzaldehyde oxime in 200 ml. of acetonitrile. The mixture was heated under gentle reflux throughout addition and for one hour

---

[7] W. D. Emmons and A. S. Pagano, THIS JOURNAL, **77**, 89 (1955).

[8] N. Kornblum, B. Taub and H. E. Ungnade, *ibid.*, **76**, 3209 (1954).

[9] P. A. Giguère and A. W. Olmos, *Can. J. Chem.*, **30**, 821 (1952).

[10] C. G. Overberger and R. W. Cummins, THIS JOURNAL, **75**, 4250 (1953).

after the addition had been completed. It was then cooled and added to 400 ml. of water. The resulting solution was extracted with four 100-ml. portions of methylene chloride. The combined extracts were washed with three 100-ml. portions of 10% sodium bicarbonate solution and dried over magnesium sulfate. The solvent was evaporated under reduced pressure and the residual liquid was fractionated through a Holzman column.[11] After a small forerun had distilled, there was obtained 10.6 g. (77%) of colorless phenylnitromethane, b.p. 97–99° (4.0 mm.). The infrared spectrum of this sample was identical to that of an authentic specimen of phenylnitromethane.

**Oxidation of Cyclopentanone Oxime to Nitrocyclopentane.**—A solution of peroxytrifluoroacetic acid was prepared as described above. This solution was added over a one-hour period to a mixture of 2.0 g. of urea, 78 g. (0.55 mole) of disodium hydrogen phosphate, 9.9 g. (0.1 mole) of cyclopentanone oxime and 200 ml. of acetonitrile maintained at gentle reflux. After the addition was over, the mixture was heated under reflux one hour. The insoluble inorganic salts then were removed by centrifugation and the acetonitrile solvent was evaporated under reduced pressure. During this process a considerable quantity of inorganic salt precipitated. Accordingly, 150 ml. of water was added to dissolve these salts. The aqueous solution so obtained was extracted with one 300-ml. and two 50-ml. portions of methylene chloride. The combined organic extracts were washed with 100 ml. of 10% sodium bicarbonate solution and dried over magnesium sulfate. Evaporation of the solvent under reduced pressure yielded a residual oil which gave after fractionation through the Holzman column 6.9 g. (60%) of nitrocyclopentane,[4] b.p. 90–92° (40 mm.).

**Oxidation of Dipropyl Ketone Oxime to 4-Nitroheptane.**—A solution of peroxytrifluoroacetic acid in acetonitrile prepared as described above was added over an 80-minute period to a well-stirred suspension of 47 g. (0.55 mole) of sodium bicarbonate in a solution of 2 g. of urea, 12.9 g. (0.1 mole) of dipropyl ketoxime and 200 ml. of acetonitrile. Throughout the addition and for one hour after, the solution was heated under gentle reflux. The solution then was poured into 600 ml. of cold water and worked up in the usual manner. Fractionation of the product through the Holzman column yielded 9.3 g. (64%) of 4-nitroheptane,[4] b.p. 58–60° (3 mm.).

**Oxidation of Diethyl Oximinomalonate to Diethyl Nitromalonate.**—To a solution of 5.3 ml. (0.195 mole) of 90% hydrogen peroxide in 50 ml. of trifluoroacetic acid at 60° was added slowly 15.0 g. (0.0795 mole) of diethyl oximinomalonate. Addition was accompanied by a vigorous reaction which raised the temperature to 87°. The reaction mixture was then cooled with an ice-bath and at this point some evolution of nitrogen oxides was observed. The mixture was immediately quenched in 200 ml. of ice-water and the aqueous solution was extracted with three 100-ml. portions of methylene chloride. The combined extracts were washed with 100 ml. of 10% sodium bisulfite solution and then with 100 ml. of water. The methylene chloride solution was dried over magnesium sulfate and the solvent evaporated under reduced pressure to yield 12.0 g. (74%) of crude diethyl nitromalonate. Distillation of this product yielded 10.8 g. (66%) of diethyl nitromalonate, b.p. 80–83° (0.3 mm.), whose infrared spectrum was identical with that of an authentic sample.[12]

**Oxidation of Phenylglyoxal Aldoxime to $\omega$-Nitroacetophenone.**—To a solution of 3.7 ml. (0.136 mole) of 90% hydrogen peroxide in 50 ml. of chloroform containing 0.3 g. of urea and 7.2 ml. (0.094 mole) of trifluoroacetic acid was added at 60° in small portions 7.45 g. (0.05 mole) of phenylglyoxal aldoxime. The resulting solution was heated under reflux for 90 minutes and 50 ml. of methylene chloride then was added. The methylene chloride–chloroform solution was washed with 15 ml. of water and the extract was dried over magnesium sulfate. Evaporation of the solvent yielded 7.0 g. (85%) of crude $\omega$-nitroacetophenone, m.p. 90–100°. After recrystallization from an ether–petroleum ether mixture, there was obtained 6.3 g. (76%) of product, m.p. 106–107° (lit. m.p. 106–107°[13]). The infrared spectrum showed a nitro band at 1552 cm.$^{-1}$ and a carbonyl band at 1689 cm.$^{-1}$.

**Oxidation of Ethyl $\alpha$-Oximinoacetoacetate to Ethyl Nitroacetate.**—To 50 ml. of chloroform was added 8 ml. (0.104 mole) of trifluoroacetic acid, 3 ml. (0.11 mole) of hydrogen peroxide and a pinch of urea. A solution of 9.0 g. (0.0565 mole) of ethyl oximinoacetoacetate in 20 ml. of chloroform was added at 55–60°. When addition of the oxime had been completed, an additional 1.5 ml. of 90% hydrogen peroxide was added. After the exothermic reaction had subsided, 200 ml. of methylene chloride was added, and the resulting solution was washed with 50 ml. of water and dried. Evaporation of the solvent yielded 5.5 g. of oil which on distillation yielded 3.0 g. (40%) of ethyl nitroacetate, b.p. 65–66° (0.6 mm.). The infrared spectrum of this product was identical with that of an authentic sample of ethyl nitroacetate.[14] Crystallization of the distillation pot residue yielded 0.3 g. of oxalic acid.

---

[11] C. W. Gould, G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

[12] D. I. Weisblat and D. A. Lyttle, THIS JOURNAL, **71**, 3079 (1949).

[13] H. Wieland, *Ber.*, **36**, 2561 (1903).

[14] W. Steinkopf, *ibid.*, **37**, 4625 (1904).

HUNTSVILLE, ALABAMA

---

[JOINT CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF MONTANA STATE UNIVERSITY AND THE UNIVERSITY OF WISCONSIN]

# Secondary Products from the Catalytic Hydrogenation of Nitriles[1,2]

BY RICHARD JUDAY AND HOMER ADKINS[3]

RECEIVED SEPTEMBER 1, 1954

Secondary products formed during the Raney nickel hydrogenation of aliphatic and aromatic nitriles alone, or in the presence of various amines, have been studied. Aliphatic nitriles have been found to form secondary amines consistent with the mechanism first suggested by von Braun. Aromatic nitriles, however, formed Schiff bases, possibly through the intermediate formation of the dimer of an imine followed by hydrogenolysis.

The formation of secondary products, in addition to primary amines, during the hydrogenation of nitriles over nickel catalysts was noted by the first workers in the field.[4,5] Secondary and tertiary amines as well as Schiff bases have been reported as being formed. Two principal mechanisms have been proposed to explain the formation of the secondary products isolated. That of von Braun[6] presumes an interaction between an aldimine and a primary amine according to equations I, II or Ia and IIa, where R is either alkyl or aryl. Mignonac,[5] working only with aromatic nitriles, identified the

---

[1] This paper is based on a Ph.D. thesis submitted at the University of Wisconsin in 1943. The data presented here are of recent origin.

[2] Research Corporation grant, 1952.

[3] Deceased August 10, 1949.

[4] P. Sabatier and J. B. Senderens, *Compt. rend.*, **140**, 482 (1905).

[5] G. Mignonac, *ibid.*, **171**, 114 (1920).

[6] J. von Braun, G. Blessing and F. Zobel, *Ber.*, **56**, 1988 (1923).