Anal. Calcd. for $C_{10}H_{18}O_5$: C, 55.5; H, 7.5; sapon. equiv., 108. Found: C, 55.6; H, 7.5; sapon. equiv., 109.

The infrared spectrum showed ester carbonyl absorption at 5.71μ and no unsaturation at 6.07μ (characteristic of the starting material).

A 2-g. sample of epoxy diester was shaken for 1 hr. with 25 ml. of concd. aqueous ammonium hydroxide to give 1.3 g. of 3-methyl-2,3-epoxy-2-carbamylbutyramide (VII), m.p. 250–251° (dec.; placed on block at 225°). Recrystallization from hot water gave material with m.p. 251–252° dec.

EMERYVILLE, CALIF.

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.]

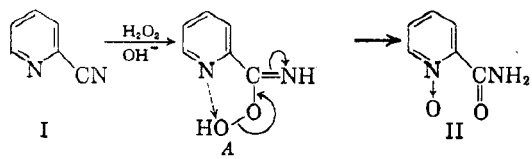
Reactions of Hydrogen Peroxide. IX. Oxidation of Cyanopyridines

GEORGE B. PAYNE

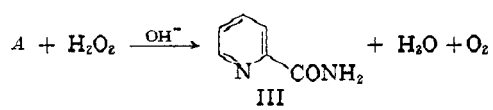
Received April 20, 1960

Reaction of the three isomeric cyanopyridines with hydrogen peroxide was carried out at *p*H 7.5–8. The 2- and 3-isomers gave the corresponding amide 1-oxides in 70 and 44% yields, respectively. The 4-isomer, on the other hand, gave the simple amide as the major product in 45% yield. These results are discussed from the point of view of reaction mechanism.

2- and 4-Cyanopyridines. It was expected, on the basis of the facile oxidation of pyridine by benzonitrile–hydrogen peroxide at *p*H 8,[1] that 2-cyanopyridine (I) might react with hydrogen peroxide under controlled conditions to give 2-picolinamide-1-oxide (II). It was felt that the reaction would probably proceed *via* a cyclic intermediate (*A*) similar to that postulated for the oxidation of acrylonitrile by hydrogen peroxide[2]:

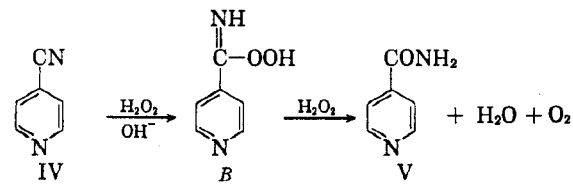


When I was treated with one mole of hydrogen peroxide at *p*H 7.5–8, 96% of the theoretical amount of oxidant was consumed in 2 hours at 35–40°. Only 2 mole % of oxygen was evolved; this indicated that very little of the following type of amide hydrolysis was occurring[3]:



Investigation of the reaction mixture did, indeed, lead to II as the only product isolated (70% yield).

When 4-cyanopyridine (IV) was substituted for the 2-isomer, it was found to react at approximately the same rate.[4] In contrast, however, 1.36 molar equivalents of hydrogen peroxide were consumed and a substantial oxygen evolution indicated a large amount of Radziszewski reaction to be occurring:



From the reaction mixture, V was isolated in 45% yield. Also secured was a 4% yield of the corresponding 1-oxide. The latter undoubtedly was formed by *intermolecular* oxidation-hydration (see below).

This striking difference in the nature of products derived from 2- and 4-cyanopyridines is taken as evidence in support of the intramolecular reaction postulated for the 2-isomer.

3-Cyanopyridine. The reaction of 3-cyanopyridine with strongly alkaline hydrogen peroxide has been studied at some length.[5] There the only product isolated was nicotinamide, in a maximum yield of 19%. This low figure was most likely due to the formation of a substantial amount of the corresponding 1-oxide, but the possibility of isolating the latter product was apparently not realized at that time.

When the 3-isomer (VI) was treated with hydrogen peroxide at *p*H 7.5–8, the reaction proceeded at a slightly slower rate than that found for the other isomers. Nicotinamide 1-oxide (IX) was obtained in 44% yield and no other pure product was isolated. IX was felt to be formed by an inter-

(1) G. B. Payne, P. H. Deming, and P. H. Williams, *J. Org. Chem.* 26, 659 (1961).

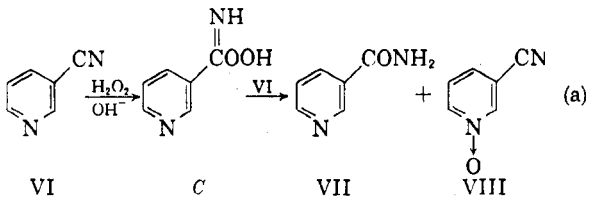
(2) G. B. Payne and P. H. Williams, *J. Org. Chem.* 26, 651 (1961).

(3) Nitrile hydrolysis by hydrogen peroxide to give amide, water, and oxygen is called a Radziszewski reaction. *Cf.* B. Radziszewski, *Ber.* 17, 1289 (1884).

(4) Substituents at the 2- and 4-positions in the pyridine ring usually exhibit similar reactivity. See H. S. Mosher in *Heterocyclic Compounds*, Vol. 1, John Wiley and Sons, Inc., New York, 1950, p. 402.

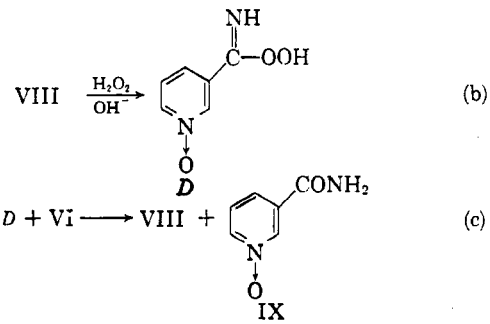
(5) A. George and P. Bachmann, *Helv. Chim. Acta* 26 361 (1943).

molecular process, as an intramolecular reaction would appear to be excluded on steric grounds[6]:



(a)

VI C VII VIII



(b)

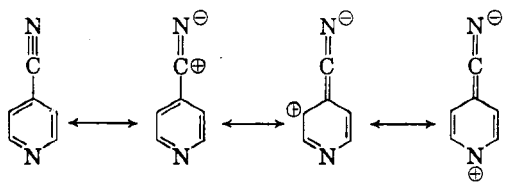
(c)

$$C + VII \longrightarrow IX + VII \quad (d)$$

$$D + VII \longrightarrow 2\ IX \quad (e)$$

As can be seen, the observed product (IX) may be formed in several different ways. A more detailed study of the reaction is needed in order to determine the dominant path by which it is produced.

Failure of the 4-isomer to undergo a significant amount of intermolecular reaction (similar to that postulated above) is best explained as follows: the electron withdrawing effect of the 4-cyano group tends to decrease the basicity of the ring nitrogen (relative to pyridine); this makes it



less susceptible to attack by an electrophilic peroxycarboximidic acid intermediate.

The ring nitrogen of the 2-isomer would also be expected to be less basic because of the adjacent cyano group.[4] In that case, however, the opportunity for intramolecular reaction would be vastly more important.

EXPERIMENTAL

All melting points are uncorrected.

Reaction of 2-cyanopyridine with hydrogen peroxide. A solution of 52 g. (0.50 mole) of 2-cyanopyridine (Aldrich Chemical Company, redistilled, b.p. 71°/2–3 mm.) in 300 ml. of methanol was stirred at 35–40° while adding 0.50 mole of 50% hydrogen peroxide over 1 hr. at *p*H 7.5–8 (meter *p*H of 9.5). At the end of an additional hour, 96% of the peroxide had been consumed along with 0.05 mole of alkali; 0.01 mole of oxygen had been evolved, as determined by a wet test meter.

After standing overnight at room temperature the mixture was chilled thoroughly to precipitate 30 g. of picolinamide 1-oxide, m.p. 159–160° (lit.[7] m.p. 161°). A second crop was secured by concentration to a viscous residue, followed by recrystallization from methanol. It weighed 18 g., m.p. 155–157°. The combined yield on both crops was 70%.

A 6.9-g. sample (0.050 mole) of the first crop was *hydrogenated* on a bottle shaker at 50 p.s.i.g. and room temperature using 100 ml. of ethanol as solvent and 1.0 g. of 5% palladium on charcoal catalyst. In 0.5 hr., 1.08 molar equivalents of hydrogen had been absorbed and the uptake was then very slow. The mixture was warmed to 50° and filtered to remove catalyst. Concentration followed by crystallization gave picolinamide, m.p. 105–106° (lit.[8] m.p. 107°).

Oxidation of 3-cyanopyridine. The reaction was carried out as above using 52 g. (0.50 mole) of 3-cyanopyridine (Aldrich, recrystallized, m.p. 49–50°). One hour after completion of the peroxide addition, 0.40 mole of peroxide had been consumed along with 0.06 mole of alkali; 0.04 mole of oxygen had been evolved. An additional 0.10 mole of peroxide was added over 20 min. and the reaction was continued for 3.5 hr. longer. At that time a total of 0.50 mole of peroxide had been consumed, 0.08 mole of caustic used, and 0.05 mole of oxygen evolved.

After standing overnight at room temperature the mixture was again titrated for peroxide; only 0.05 mole remained (0.55 mole total consumption). The solid which had precipitated during the reaction was collected by filtration, washed with methanol, and dried. It weighed 30 g., m.p. 283–284° dec. in agreement with the literature value[7] for *nicotinamide 1-oxide*. The yield of first crop was 44% based on nitrile charged.

The filtrate was concentrated to a residue and this was dissolved in 250 ml. of boiling methanol. Filtration effected the removal of 6 g. of insoluble salt and the filtrate was concentrated to a volume of 125 ml. and chilled to give a second crop of crude 1-oxide weighing 2.5 g., m.p. *ca.* 250°.

A 6.9-g. sample (0.050 mole) of purest 1-oxide was *hydrogenated* as above, except that water was used as solvent. After 17 min., 1.12 molar equivalents of hydrogen had been absorbed and the rate of uptake was then less than 25% of the initial. After filtration to remove catalyst, the filtrate was concentrated to a solid residue. Recrystallization from ethanol gave 3.6 g. of nicotinamide, m.p. 127–128° (lit.[9] m.p. 128.5–129.5°).

Oxidation of 4-cyanopyridine. The reaction was carried out as described for the 3-isomer using 4-cyanopyridine (Aldrich, recrystallized, m.p. 78–78.5°). At the end of 2 hr., essentially all of the peroxide had been consumed, 0.07 mole of alkali utilized, and 0.15 mole of oxygen evolved. Another 0.25 mole of peroxide was added dropwise over 45 min., and 1 hr. later 0.08 mole of peroxide remained. The reaction was essentially complete at that time, as only 0.01 mole more peroxide was consumed after 2 hr. longer. Total oxygen evolution amounted to 0.21 mole; alkali used was 0.09 mole.

The mixture was concentrated to constant weight under vacuum and the resulting residue was dissolved in 300 ml. of boiling ethanol. Six grams of insoluble salt were removed by filtration and the filtrate concentrated to a constant weight of 57 g., m.p. 130–150°. Recrystallization from 170 ml. of water gave 27 g. (45%) of isonicotinamide, m.p.

(6) A study of models showed the hydroxyl group of the peroxycarboximidic acid intermediate to be too far removed from the ring nitrogen to allow the operation of a cyclic mechanism.

(7) M. Shimizu, T. Naito, G. Ohta, T. Yoshikawa, and R. Dohmoir, *J. Pharm. Soc. Japan* **72**, 1474 (1952); *Chem. Abstr.* **47**, 8077 (1953).

(8) H. Meyer, *Rec. trav. chim.* **44**, 324 (1925).

(9) A. Galat, *J. Am. Chem. Soc.* **70**, 3945 (1948).

154–155° (lit.[8] m.p. 152–154°). Filtrate from this operation was concentrated to a solid residue. Recrystallization from methanol gave 1.7 g. (4%) of isonicotinamide 1-oxide, m.p. 298–300° dec. (lit.[7] m.p. 303° dec.).

Anal. Calcd. for $C_6H_6N_2O_2$: C, 52.2; H, 4.4; N, 20.3. Found: C, 52.6; H, 4.7; N, 19.7.

EMERYVILLE, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

The Chromic Acid Oxidation of Tetraarylethylenes[1]

WILLIAM A. MOSHER, FREDERICK W. STEFFGEN, AND PETER T. LANSBURY[2]

Received June 15, 1960

The oxidation of tetraphenylethylene (I) with diacetyl chromate (chromium trioxide in acetic anhydride) gives high yields of benzpinacol carbonate (III) in addition to tetraphenylethylene oxide (II) and benzophenone. A variety of other tetraarylethylenes have been oxidized to cyclic carbonates by this reagent, thus making available compounds which cannot be prepared from the glycols by normal methods. The reaction is not stereospecific when *cis* and *trans* forms of an olefin are oxidized. A mechanism for these oxidations is proposed, wherein the carbonate arises from the reaction of the intial olefin–chromic acid complex with a source of acetate ion, followed by the formation of an intermediate ketene acetal, which undergoes further oxidation. Tetraphenylethylene oxide was isolated from permanganate oxidation of I, this being the first example of the formation of an epoxide by olefin oxidation with this reagent. Infrared spectral data on a number of new cyclic carbonates are presented.

Much attention has recently been given to the mechanisms of chromic acid oxidation of organic compounds.[3] Of the various types of substrates studies, the isolated double bond has been somewhat overlooked and considerable disagreement seems to exist on the manner in which chromic acid attacks the olefinic linkage. Hickinbottom and his co-workers[4] have studied the nature of products obtained from aliphatic olefins by oxidation with chromium trioxide in aqueous sulfuric acid and in acetic anhydride; they propose electrophilc attack of chromium trioxide at the negative end of the double bond, followed by reaction with water (in the aqueous oxidations only) to give the conjugate acid of an epoxide, from which subsequent product-forming paths can be formulated. In acetic anhydride medium the epoxides were isolatable.[4] Zeiss and Zwanzig[5] have alternatively suggested a cyclic chromate ester to explain the absence of rearrangement products in the oxidation of 1-methyl-α-fenchene to camphor. Hickinbottoms's objections[4] to the Zeiss mechanism were its alleged inability to explain the formation of 1,4-enediones upon oxidation of terpenoid β,γ-unsaturated alcohols,[6] and the difference between chromic acid oxidation of olefins and the attack on alkenes by osmium tetroxide[7] or potassium permanganate,[8] both of which have been shown to proceed *via* cyclic ester intermediates. With regard to the first contention, regarding oxidation of unsaturated carbinols, Nichols and Schipper[9] showed that the chromic acid oxidation of ricinoleic acid to *trans*-9,12-dioxo-10-octadecenoic acid does not proceed *via* the β,γ-epoxide, which might have arisen from a cyclic chromate ester. However, the claim that chromic acid and permanganate oxidize to different products is not entirely valid. In the present work we report the first case of the isolation of an epoxide as product from a permanganate oxidation (*vide infra*). Moreover, Wiberg[10] has demonstrated the mechanistic similarity of these two reagents in the oxidation of benzaldehyde. Wiberg has also pointed out that the actual form of chromium trioxide in solution may change with the solvent and that this factor can lead to different types of products.[11]

The present study was undertaken in order to consider more closely the initial mode of attack by chromic acid upon an isolated double bond. Tetraphenylethylene (I) was chosen as a model compound for this investigation because the absence of vinylic and allylic hydrogens reduces potential complexities which might arise from allylic attack or further oxidation of rearranged primary products. Behr[12] reported the oxidation of I in boiling, glacial acetic acid and claimed that tetraphenylethylene oxide (II) was the major product,

(1) Presented in part at the 135th meeting of the American Chemical Society, Boston, Mass., April, 1959.

(2) Present address: Department of Chemistry, University of Buffalo, Buffalo 14, N. Y.

(3) W. A. Waters, *Quart. Revs.*, 12, 277 (1958), and references cited therein.

(4) M. A. Davis and W. J. Hickinbottom, *J. Chem. Soc.*, 2205 (1958), and earlier papers in the series.

(5) H. H. Zeiss and F. R. Zwanzig, *J. Am. Chem. Soc.*, 79, 1733 (1957).

(6) D. H. R. Barton, N. J. Holness, K. H. Overton, and W. J. Rosenfelder, *J. Chem. Soc.*, 3751 (1952).

(7) R. Criegee, *Annalen*, 522, 75 (1936).

(8) K. B. Wiberg and K. A. Saegebarth, *J. Am. Chem. Soc.*, 79, 2822 (1957).

(9) J. Nichols and E. Schipper, *J. Am. Chem. Soc.*, 80, 5705 (1958).

(10) K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, 80, 3022 (1958).

(11) K. B. Wiberg, Abstracts of the 16th National Organic Symposium, Seattle, Wash., July, 1959, pp. 105–106.

(12) A. Behr, *Ann.*, 5, 277 (1872).