Peroxyacetyl Nitrate. A Novel Reagent for Oxidation of Organic Compounds

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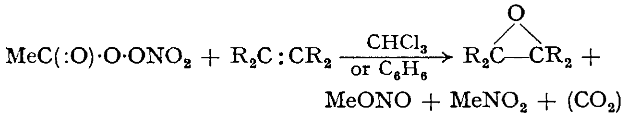
Summary The reaction of peroxyacetyl nitrate with olefins yields epoxides, nitromethane, and methyl nitrite, the latter two products possibly arising from free-radical intermediates.

PEROXYACETYL NITRATE (PAN)† (an important air pollutant in photochemical smog[3] which produces deleterious effects on plants, animals, and man[4]) reacts with simple olefins quantitatively in solution to give the corresponding epoxides:



$$\mathrm{MeC(:O){\cdot}O{\cdot}ONO_2 + R_2C:CR_2 \xrightarrow[\text{or } C_6H_6]{CHCl_3} R_2\overset{O}{C-C}R_2 + MeONO + MeNO_2 + (CO_2)}$$

Methyl nitrite[5] and nitromethane are formed in approximately equal amounts and account for 70—90% of the reacted PAN. The Table gives the half-lives of PAN with the olefins studied. The relative reactivities parallel those observed for the epoxidation using peroxy-acids.[6]

The reaction appears to produce free radicals. The formation of methyl nitrite in the reaction of an excess of PAN with acenaphthylene was followed by n.m.r. spectroscopy. Initially the CH_3ONO signal appears as an emission rather than an absorption peak, a phenomenon which has been attributed to chemically induced dynamic nuclear polarization and which is often associated with rapid radical reactions in solution.[7] PAN reacts with either *cis*- or *trans*-stilbene to give only (>95%) *trans*-stilbene oxide and with either *cis*- or *trans*-but-2-ene to give predominantly (*ca.* 75%) *trans*-butene oxide. In both cases the excess olefin is isomerized, *cis*-stilbene to the *trans*-isomer and either *cis*- or *trans*-butene to a predominantly *trans*-mixture. The olefin isomerizations are also readily effected by adding a small amount of nitrogen dioxide ($2\mathrm{M}$-N_2O_4 in $CDCl_3$) to solutions of the olefins. The following reaction sequence accounts for these observations;

TABLE

Relative reactivity of PAN with olefins

Olefin	$t\frac{1}{2}$ (min.)[a]
2,3-dimethylbut-2-ene	10
2-methylbut-2-ene	12
but-2-ene (*cis* or *trans*)	23
2,3-dimethylbut-1-ene	50
cyclohexene	30
acenaphthylene[b]	9
stilbene (*cis* or *trans*)	16

[a] Time required for one-half of the PAN to be consumed when a two-fold molar excess of the olefin had been added to *ca.* 0·1M-solutions of PAN in $CDCl_3$. Reactions were monitored by n.m.r. spectroscopy.

[b] 50% yield of epoxide, very low yield of methyl nitrite and nitromethane.

$$\mathrm{PAN + olefin \rightarrow epoxide + CH_3COO\cdot + NO_2}$$
$$\mathrm{CH_3COO\cdot \rightarrow CH_3\cdot + CO_2}$$
$$\mathrm{NO_2 + CH_3\cdot \rightarrow CH_3NO_2 \text{ and } CH_3ONO}$$
$$\mathrm{NO_2 + olefin \rightarrow NO_2 + isomerized\ olefin}$$

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† PAN is violently explosive when condensed as a pure liquid.[1] In the gas phase or dilute solution it slowly decomposes with a half-life of several days. It is prepared according to published procedures.[2] We are grateful to Dr. O. C. Taylor, University of California Statewide Air Pollution Research Center for making available the PAN used in this work.

confirmation of this scheme, however, awaits the results of further experiments.

Acenaphthylene oxide is unstable to acidic conditions and a successful synthesis has been reported only recently.[8] The preparation of this epoxide using PAN suggests the potential utility of PAN as a nonacidic epoxidizing agent where neither starting material nor products are acidic. On the other hand, reactions using PAN may be complicated by competing free-radical reactions such as the isomerization described above.

Our current results of the reaction of PAN with methanethiol indicate that for each mole of PAN consumed at least two moles of thiol are oxidized to the disulphide. In the most rapid reaction so far observed ($t_{\frac{1}{2}} < 1$ min.), PAN converts one mole of dimethyl sulphide into the corresponding sulphoxide.

This work was supported by the National Air Pollution Control Administration, U.S. Public Health Service. One of us (K.R.D.) acknowledges an Air Pollution Special Postdoctoral Fellowship.

(*Received, July 27th,* 1970; *Com.* 1233.)

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