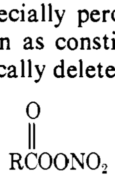
Facile Preparation of Peroxyacyl Nitrates

Sir:

"Peroxyacyl nitrates" (**1**)—generally accepted to be acyloxy nitrates[1]—and especially peroxyacetyl nitrate (PAN) (**1**, R = Me) are known as constituents of photochemical smog, producing biologically deleterious effects.[2]

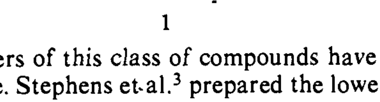


$\mathrm{R\overset{\overset{O}{\|}}{C}OONO_2}$

1

Few members of this class of compounds have been synthesized per se. Stephens et al.[3] prepared the lower alkyl derivatives of **1** (R = Me, Et, *n*-Pr) via vapor-phase photolysis of the corresponding alkyl nitrite RCH_2ONO with oxygen, or through photolysis of very dilute mixtures of a symmetrical olefin with NO_x in oxygen (air). Alternatively, the dark reaction of the appropriate aldehyde with $NO_2 + O_3$ (or with N_2O_5) can be utilized, again at low concentration levels (up to a few tenths of a per cent), in a flow system.[4] Peroxybenzoyl nitrate (PBzN) (**1**, R = Ph) has similarly been prepared by Heuss and Glasson[5] in a static system; a simple flow system can also be applied in that case.[6] These rather laborious gas-phase techniques, however, result in low production rates of, at best, a few mmol/hr. Moreover, when R is large, the low volatility of reactant and product will cause additional problems. These, then are serious drawbacks met in preparative scale synthesis of type **1** compounds with large variations in R.

Our interest in **1**[6,7] led us to look for better alternatives. We now wish to report the convenient synthesis of **1** in liquid-phase systems, starting from the corresponding (per)acid **2** (eq. 1). Method A uses 1 molar equiv of dinitrogen pentoxide[8] in a suitable solvent, such as dry methylene chloride, at −40 to −10°. As the reaction proceeds, N_2O_5 goes into solution, within 30 min. After 0.5–1 hr the mixture is treated with ice-cold water (three times) and the organic layer dried on $MgSO_4$, while kept at ca. −20°. Isolation is achieved by adding 0.5–1 g of neutral silica, removal of the solvent in vacuo at 0°, and transfer of the adsorbed residue to a silica column (ca. 7 × 1 cm, equipped with a cooling mantle). Chromatography (at 0°, elution with *n*-pentane or 1:10 CH_2Cl_2:pentane for **1**, R = *p*-nitrophenyl[9]) leads to **1** as the first (peroxidic) product, its elution being easily checked via spot tests.[12] Method B involves standard laboratory chemicals: 1 equiv of 100% nitric acid plus 1 equiv of SO_3 (as 60% SO_3 in H_2SO_4). To the peracid (ca. 5 mmol scale) in a 100-ml three-necked flask (stirrer, thermometer drying tube, N_2 atmosphere) 10–15 ml of dry *n*-pentane is added. After cooling the HNO_3 and oleum are also added and the two-layer system is stirred for ca. 3 hr. Work-up is as described above.



(1)

Table I shows that yields are acceptable (20–60%); these figures may well be subject to improvement, e.g., by reducing losses during chromatography. Both aliphatic and aromatic derivatives can be obtained; the scope of the present method, likely, is as wide as that for peracid synthesis. Stephens has reported[4] that a standard nitration mixture of nitric and sulfuric acids, when treated with peracetic acid, produced some PAN; this reaction was stated to be of theoretical interest only.

The *mechanism* may well be simply an exchange of H^+ for NO_2^+ (eq 2), Z^- being NO_3^- for method A and

$$RCO_2O^-,\ H^+ + NO_2^+,\ Z^- \longrightarrow 1(+HZ) \qquad (2)$$

HSO_4^- for method B. One may further conclude that **1** is sufficiently stable to strong proton acids; i.e. there is no need for adding bases, which, inter alia, may entail decomposition of **1** (vide infra).

All type **1** compounds prepared thus far show the expected properties; they have a "clean linen" smell and may cause eye irritation. The mass spectra (AEI-MS 902, 70 eV, direct inlet system) all reveal parent peaks together with the important ions CO^+, NO^+, CO_2^+, NO_2^+, R^+, and RCO^+ (cf. data for PAN and PBzN[5]). The ir spectra also show characteristic absorptions.[5]

Although the biological effects of PAN (**1**, R = CH_3) have been investigated in some detail, little of its "normal" (organic) chemistry has been reported.[2,15] As peroxyacyl nitrates **1** now can be considered as readily accessible, if not ordinary molecules, they can be investigated in a systematic fashion, including consideration of structural effects. The danger of explosion—which allows handling of PAN and of PPN (**1**, R = Et) as a highly diluted gas (N_2 or air) only—can be reduced by resorting to higher aliphatic homologues instead (e.g., R = *n*-C_6H_{13} or stearyl). A reasonable degree of thermal stability and resistance to solvolysis in water or

Table I. Preparation and Some Physical Properties of 1

R in RCO_3H	Method[a]	Yield (%)[b]	Mp (°C)	Ir data[c] (cm^{-1})
1-*n*-Pentyl[d]	A	27		
	B	40	<−20	1820; 1730; 1295 (T)
Phenyl[e]	A	20	<−20	1795; 1730; 1295 (P)
m-Chlorophenyl[f]	A	56	ca. −15	
	B	40		1800; 1735; 1300 (P)
p-Nitrophenyl[g]	A	18	43	1800; 1740; 1295 (T)
β-Naphthyl[g,h]	A	21	64–65	1790; 1730; 1295 (C)

[a] See text. [b] Isolated product; purity checked by TLC, by iodometric titration, and/or by conversion with MeO^-–MeOH into RCOOMe and GLPC analysis. [c] Key: P = pure material, T = carbon tetrachloride, C = in carbon disulfide. [d] Prepared according to ref 13, using 30% H_2O_2 plus oleum rather than—unavailable—60% H_2O_2–water. Stoichiometry based on RCO_3H content (ca. 65%). [e] See A. I. Vogel, "Text-Book of Practical Organic Chemistry", Longmans, Green and Co., New York, N.Y., 1970. [f] From Aldrich Chemicals. [g] Via acid chloride + Na_2O_2, see ref 14. [h] Mp 174–176°.

alcohols (we observe a half-life of ca. 4 hr for **1**, R = Ph, in methanol at room temperature) also provide an attractive basis for further investigation.

Our preliminary results confirm the impression[2,15] that type **1** compounds can take part in a great variety of reactions, including free-radical processes, nucleophilic displacements and oxidation-reduction phenomena.

Thus, 0.1 *M* methanolic solutions of **1** react instantaneously (cf. ref 15b) with methanolate solution, the corresponding methyl esters being formed quantitatively. From competitive reactions involving **1**, R = *m*-chlorophenyl, and **1**, R = Ph, and using small proportions of CH_3ONa in methanol, it is found that the relative rate (m-Cl/H) ≈ 2.0 at 20°. The reaction with methanol-pyridine takes several minutes to reach completion and is also more selective. Finally, the high reactivity with 0.2 *M* methanolic thioanisole (50% conversion of **1**, R = Ph in ca. 2 min) is noteworthy by comparison with sulfides in reaction with other peroxy compounds, such as acylperoxides,[16] which are formally analogs of **1**. This is in line with expectations in considering the relative leaving group facility of NO_3^- and RCO_2^- in nucleophilic displacements.

Our investigations as regards preparation and properties of **1** are being continued.

References and Notes

(1) R. D. Harcourt and D. P. Kelly, *Environ. Sci. Technol.*, **8**, 675 (1974).

(2) See, for instance, P. H. Wendschuh, C. T. Pate, and J. N. Pitts, Jr., *Tetrahedron Lett.*, 2931 (1973), and references cited there.

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(9) Cf. the conversion of hydroperoxides ROOH with N_2O_5 to give $ROONO_2$, documented recently for R = Me[10] or *t*-Bu,[10] and for R = CF_3.[11]

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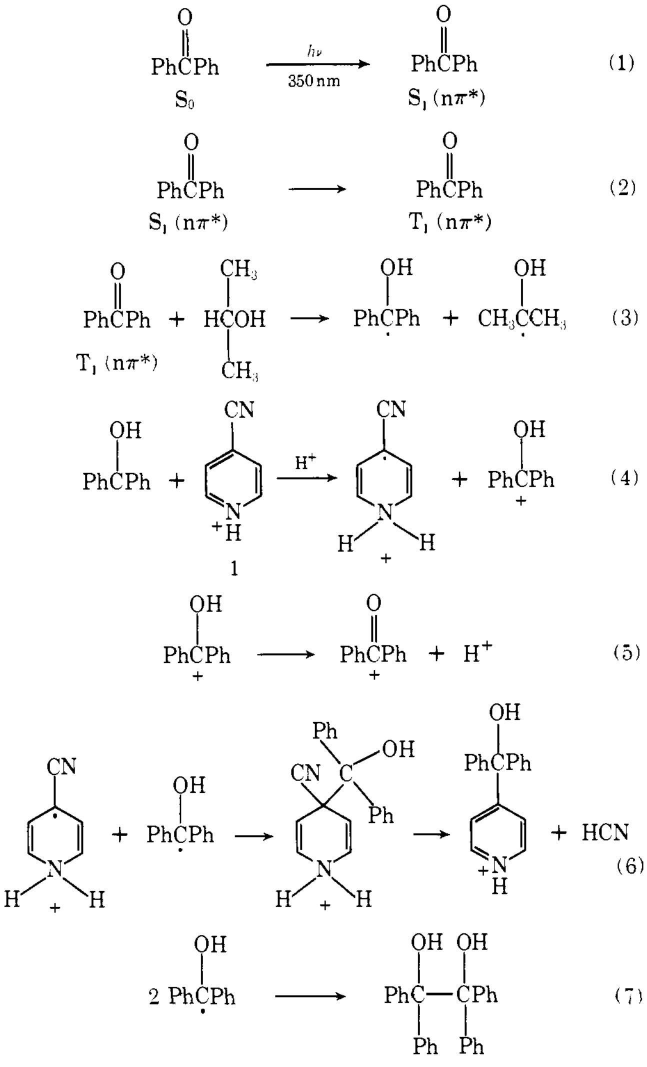
The Photoinitiated Electron Transfer-Substitution Reaction of Diphenyl Ketyl with Protonated 4-Cyanopyridine

Sir:

Recent findings have demonstrated that substituent effects can dramatically alter the course of homolytic substitution reactions of protonated heteroaromatic bases. For example, reactions of radicals with pyridines containing electron withdrawing substituents in the 4 position, in acid solution, form products of addition to the 2 position in better yield and with higher selectivity than is found with pyridine itself under the same conditions.[1] This high sensitivity to substituent effects has been explained in terms of a transition state similar to a charge-transfer complex in which a positive charge develops on the attacking radical.[2] Nucleophilic π type radicals, such as benzyl, in which the incipient positive charge can best be stabilized do, in fact, produce the highest yields of substitution products.

Scheme I



We would now like to report a novel $\mathrm{S_R}$ reaction of protonated 4-cyanopyridine (**1**) in which substitution occurs in the 4 position, resulting in the displacement of the cyano group. This reaction is best explained (Scheme I) by an electron transfer from the π type diphenyl ketyl radical to the 4-cyanopyridinium ion in 1 *M* sulfuric acid in aqueous 2-propyl alcohol (1:3). The donor radical is conveniently produced photochemically by the well-known process of hydrogen atom abstraction by the T ($n\pi^*$) state of benzophenone.[3,4] The reaction mixtures were degassed by four successive freeze-vacuum-thaw cycles and the irradiations were carried out under nitrogen in a Model RPR-100 Rayonet photochemical reactor at 350 nm using quartz reaction vessels.[5,6] Three of the major products formed in the reaction are diphenyl(4-pyridyl)carbinol (**2**), mp 235.5-236.5 (7.2% yield) (lit.[7] 235°), 4-benzhydrylpyridine (**3**), mp 123-124° (18.7% yield) (lit.[7] 125°), and benzopinacol (**4**).[8] Another product for which no structure has yet been assigned has a molecular weight of 348 by mass spectroscopy and melted at 146.5-147° (2% yield). This compound contains cyano, isopropyl, and benzhydrol groups and is apparently the result of two radical substitution reactions of the same pyridine ring.

Five additional basic compounds (approximately 60% yield) were isolated from the reaction mixture in semipure