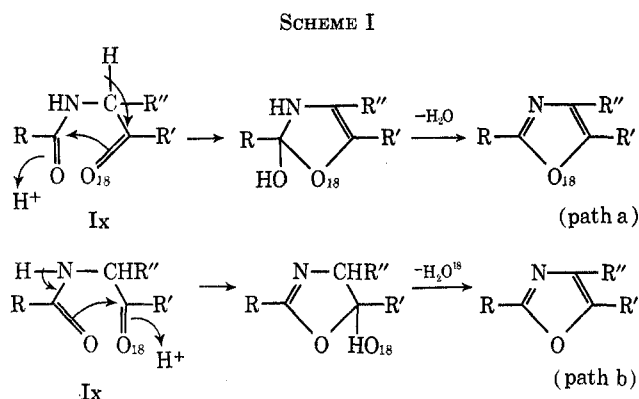able pathways which may be considered in viewing the mechanism of this reaction. These alternative routes, summarized in Scheme I, differ in the nature of the ox-

SCHEME I

(path a)

(path b)

ygen atom incorporated into the oxazole, *i.e.*, ketone oxygen (path a) *vs.* amide oxygen (path b). We sought to differentiate between these two possibilities using oxygen-18 tracer methods in conjunction with high-resolution mass spectrometry.

For these studies, we prepared α-benzamidopropiophenone[5,6] (Ix) with an oxygen-18 label in the keto portion of the molecule, and, in a second case (Iy),

with an oxygen-18 label in the amide carbonyl group.

To incorporate the labeled oxygen into Ix, the keto amide was allowed to equilibrate with 30% $H_2^{18}O$ in anhydrous THF with no catalyst present.[7] It is well known that under these conditions the ketone oxygen undergoes rapid exchange with the labeled water while the amide oxygen undergoes no exchange.[8] Mass spectrometric analysis indicated 26.7 ± 0.5% label in the keto oxygen. Cyclization with concentrated sulfuric acid afforded 2,5-diphenyl-4-methyloxazole,[6] the mass spectrum of which showed 0.2 ± 0.5% label present, thereby indicating that the amide oxygen is incorporated, and the ketone oxygen expelled in the formation of the oxazole, in accord with path b.

In an independent proof of mechanism, α-amino-propiophenone[5] was allowed to react with O-18 enriched benzoyl chloride[9] (from *ca.* 9.5% doubly labeled benzoic acid), yielding Iy with 9.6 ± 0.5% ^{18}O in the amide oxygen. Cyclization as above gave 2,5-diphenyl-4-methyloxazole containing 9.7 ± 0.5% oxygen-18 as shown by mass spectrometric analysis. These results clearly show that in this case the amide oxygen is retained in the product, again in accord with pathway b.[10]

(5) L. Behr-Bregowski, *Ber.*, **30**, 1521 (1897).

(6) J. Lister and R. Robinson, *J. Chem. Soc.*, **101**, 1297 (1912).

(7) A. Murray and D. Williams, "Organic Syntheses with Isotopes," part III, Interscience, New York, N. Y., 1958, p 1887.

(8) W. H. Mears and H. Sobotka, *J. Amer. Chem. Soc.*, **61**, 880 (1939).

(9) Reference 7, pp 1870–1871.

(10) This is the pathway favored by Paquette in picturing the mechanism of oxazole formation by the cyclization of α-acylamino ketones. See L. Paquette, "Principles of Modern Heterocyclic Chemistry," W. A. Benjamin, New York, N. Y., 1968, p 191.

Experimental Section

Ketone-^{18}O-Labeled α-Benzamidopropiophenone (Ix).—α-Benzamidopropiophenone[5,6] (1.00 g, 3.96 mmol), 30% $H_2^{18}O$ (0.10 ml), and 5 ml of tetrahydrofuran (distilled from lithium aluminum hydride) were refluxed for 1.5 hr. The solvent was removed *in vacuo* and the labeled keto amide was recrystallized from diethyl ether, mp 103–104° (lit. mp 104–105°[6]). The high-resolution mass spectrum shows the parent peak (*m/e* 253) with a P + 2 peak indicating an ^{18}O enrichment of 26.7 ± 0.5%.

Amide-^{18}O-Labeled α-Benzamidopropiophenone (Iy).—Amino-propiophenone stannic chloride[5] (1.82 g, 2.89 mmol of amino ketone) was suspended in 18 ml of water with stirring and ice-bath cooling. Benzoyl-^{18}O chloride[9] (1.21 g, 8.65 mmol) of *ca.* 9.5% enrichment and aqueous potassium hydroxide (5.50 g in 8 ml) were added successively, and the mixture was stirred for 0.5 hr. Ether extraction followed by drying over anhydrous magnesium sulfate, filtration, and removal of solvent yielded 0.60 g (82%) of Iy, mp 104–105°, tlc behavior identical with Ix. The high-resolution mass spectrum shows the parent peak (*m/e* 253) with a P + 2 peak having 9.6 ± 0.5% enrichment in ^{18}O.

2,5-Diphenyl-4-methyloxazole. A.—A 0.3-g portion of ketone-labeled α-benzamidopropiophenone (Ix) was added to 3 ml of concentrated sulfuric acid with stirring. After 10 min, copious quantities of water were added to the reaction mixture until the milky white product was completely precipitated. The 2,5-diphenyl-4-methyloxazole was collected by filtration and recrystallized from petroleum ether (bp 30–60°) to yield 0.20 g (72%), mp 80–81° (lit. mp 82°[6]). The high-resolution mass spectrum shows the parent peak (*m/e* 235) with a P + 2 peak having 0.2 ± 0.5% ^{18}O enrichment.

B.—A 0.5-g portion of amide-labeled α-benzamidopropiophenone (Iy) was cyclized as described previously for Ix. The oxazole obtained (81%, mp 81–82°) was analyzed by high-resolution mass spectroscopy. The parent peak (*m/e* 235) had a P + 2 peak showing an ^{18}O enrichment of 9.7 ± 0.5%.

The Reaction of Trityloxyamine with Lead Tetraacetate

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Considerable interest continues to be expressed in the generation of *O*-nitrene intermediates, although rarely has their existence been substantiated by the weight of experimental evidence.[1] A notable exception may be cited in the work of Brois,[2] who successfully trapped methoxynitrene with tetramethylethylene during the lead tetraacetate (LTA) oxidation of methoxyamine. Recently the oxidation of several *O*-arylalkyl-hydroxylamines with LTA has been studied by Carey[3] and Partch.[4] The suggestion by the latter author that such oxidations may involve the intermediate unstable hyponitrite esters as well as the actual isolation

(1) J. Boyer and J. Woodyard, *J. Org. Chem.*, **33**, 3329 (1968); A. Hassner, R. Wiederkehr, and A. Kascheres, *ibid.*, **35**, 1962 (1970).

(2) S. Brois, *J. Amer. Chem. Soc.*, **92**, 1079 (1970).

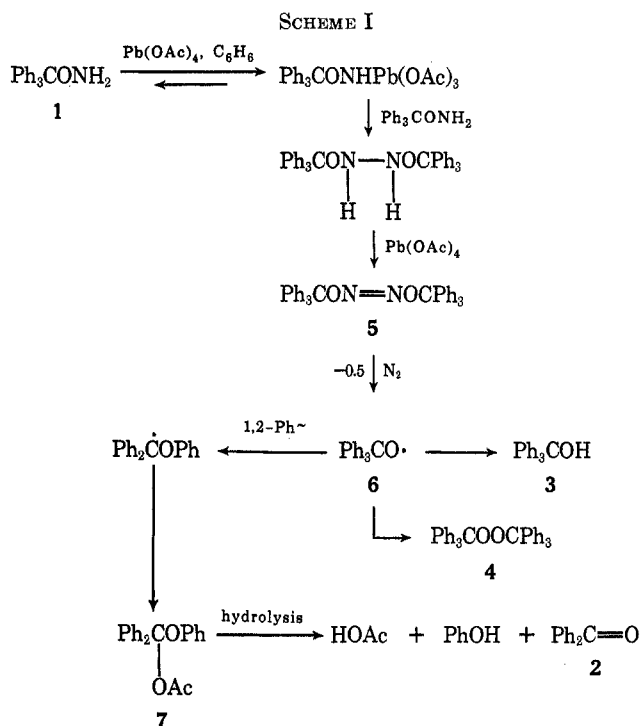(3) F. Carey and L. Hayes, *J. Amer. Chem. Soc.*, **92**, 7613 (1970).

(4) R. Partch, B. Stokes, D. Bergman, and M. Budnik, *Chem. Commun.*, 1504 (1971).

of such a hyponitrite ester in the oxidative bromination of ethoxyamine[5] prompts the report herein of the results regarding the LTA oxidation of the recently[6] prepared trityloxyamine (1).

When a mixture of 1 and LTA was stirred in anhydrous benzene for 1 hr at room temperature followed by the usual work-up, vpc analysis revealed the presence of benzophenone (12%) and triphenylcarbinol (75%). That the benzophenone (2) did not derive from the decomposition of triphenylcarbinol (3) under vpc conditions was indicated by the appearance of the absorption band at 1667 cm^{-1} in the infrared spectrum of the crude reaction mixture prior to work-up. In a related experiment, the crude reaction mixture was simply filtered from the precipitated inorganic salts and after removal of the solvent the residue was chromatographed without any prior aqueous work-up. Initial elution yielded a mixture of 2 (12%) and triphenylmethyl peroxide (4) (8%) while further elution yielded 3 (71%). Triphenylmethyl peroxide (4) was identified by a comparison of its melting point and infrared spectrum with those of an authentic sample.[7] That 3 is not derived *via* a concerted fragmentation–recombination pathway from hydrolysis of trityl acetate was substantiated by two experimental observations. First, control experiments demonstrated the stability of an authentic sample of trityl acetate[8] under the work-up conditions; second, the attempt to trap the possible trityl carbonium ion intermediate when the reaction was conducted in the presence of excess added sodium azide was unsuccessful.[9]

A final and mechanistically significant experiment was conducted at Dry Ice–acetone temperature in the presence of 2,3-dimethylbutadiene in an attempt to trap the oxynitrene intermediate from 1. The latter was completely unsuccessful; however, triphenylmethyl peroxide (4) (85%) was successfully isolated. The mechanistic significance of the isolation of 4 in high yield at −78° is that it offers the first reported experimental evidence that the postulated[3,4] precursor to the formation of alcohols from LTA and O-substituted hydroxylamines is an oxy radical (RO·) 6. It is therefore suggested that the observed products arise from the homolytic decomposition of the presumably very unstable[10] hyponitrite ester[7] 5 to yield the trityloxy radical 6 [it is worth mentioning that the reaction of trityl chloride and silver hyponitrite in benzene was demonstrated by Spielman[7] to produce nitrogen and triphenylmethyl peroxide (4), the latter arising from the decomposition of the unstable intermediate hyponitrite ester 5]. The trityloxy radical 6 may either couple to produce 4, abstract hydrogen to give 3, or suffer carbon-to-oxygen phenyl migration[11] to yield

the labile ketal acetate (7) known to hydrolyze to 3, phenol, and acetic acid (Scheme I).

SCHEME I

(5) L. Seed, British Patent 795,824 (1959); *Chem Abstr.*, **53**, 219*f* (1959).
(6) W. B. Lutz, *J. Org. Chem.*, **36**, 3835 (1971).
(7) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1955, p 81; M. A. Spielman, *J. Amer. Chem. Soc.*, **57**, 1117 (1935).
(8) M. Gomberg, *Chem. Ber.*, **35**, 1835 (1902).
(9) I. Necsoiu and C. D. Nenitzescu, *Chem. Ind. (London)*, 377 (1960).
(10) For general references to hyponitrite chemistry see M. Hughes, *Quart. Rev.*, **22**, 1 (1968); J. Boyer and J. Woodyard, *J. Org. Chem.*, **33**, 3329 (1968); J. Cooley, M. Mosher, and M. Khan, *J. Amer. Chem. Soc.*, **90**, 1867 (1968).
(11) W. H. Starnes Jr., *J. Amer. Chem. Soc.*, **90**, 1807 (1968); P. D. Bartlett and J. D. Cotman Jr., *ibid.*, **72**, 3095 (1950); R. O. C. Norman and R. A. Watson, *J. Chem. Soc.*, 184 (1968); M. S. Kharasch, A. C. Poshkus, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **16**, 1485 (1951); M. S. Kharasch, A. Fono, and W. Nudenberg, *ibid.*, **15**, 763 (1950).

Experimental Section

All melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Spectracord infrared spectrophotometer. The nmr spectra were determined with a Varian A-60 instrument. Gas chromatographic analyses were performed on an F & M Scientific Model 720 dual column temperature programmed gas chromatograph.

Trityloxyamine (1) was prepared according to the procedure of Lutz:[6] mp 80–82° (lit.[6] mp 83–85°); ir (CCl$_4$) 3320 and 3240 cm^{-1}; nmr (CCl$_4$) τ 2.6–3.2 (m, 15 H), 5.4 (s, 2 H).

Reaction of LTA with Trityloxyamine (1).—Into a 300-ml three-necked round-bottom flask equipped with a dropping funnel, reflux condenser, and magnetic stirrer was placed 4.90 g (0.01 mol) of LTA. The system was evacuated for 2 hr on a vacuum pump, after which 100 ml of sodium-dried benzene was introduced. The entire reaction was conducted under a nitrogen atmosphere. After the dropwise addition of a solution of 1 (2.75 g, 0.01 mol) in benzene (100 ml), the reaction mixture was stirred at room temperature[12] for 1 hr. The mixture was filtered and the benzene solution was washed with ethylene glycol, water, aqueous sodium carbonate, and water and dried (MgSO$_4$). Removal of the benzene under vacuum followed by treatment of the residue with CCl$_4$ yielded 1.95 g (0.0075 mol, 75%) of 3, mp 158–160°, undepressed by admixture with an authentic sample, ir (KBr) 3480 and 3610 cm^{-1}.

In a second run, the benzene solution was concentrated to 10 ml and aliquots were subjected to vpc analysis (2 ft × 0.25 in. UC-W 98 silicone gum rubber column at 230°). Two peaks were observed; the first corresponded to 2 (12%) and the second to 3 (75%). The assignments were confirmed by selective peak enhancement upon coinjection with authentic samples. In addition the first peak 2 was collected, ir (CCl$_4$) 1667 cm^{-1}.

In another experiment, 1 (350 mg, 1.25 mmol) was treated with LTA in the presence of a 100-fold molar excess of sodium azide. The reaction mixture was not subjected to any work-up, but was filtered, the benzene was removed, and the residue was dissolved in benzene (5 ml) and chromatographed on 50 g of neutral alumina. Elution with 50% (v/v) hexane–benzene yielded a solid mixture of 2 and 4. The solid mixture was washed with cold ether and the insoluble portion was filtered, yielding 50 mg (0.096

mmol, 8%) of **4**, mp 179–181°, ir (KBr) 1155 and 874 cm^{-1}. Removal of the ether yielded approximately 27 mg (0.15 mmol, 12%) of **2**, ir (CCl$_4$) 1667 cm^{-1}. Finally, elution with benzene gave 247 mg (0.95 mmol, 71%) of **3**, mp 158–160°.

In a final experiment a magnetically stirred mixture consisting of 13.1 g (0.16 mol) of freshly distilled 2,3-dimethylbutadiene,[13] 4.87 g (0.01 mol + 10% excess) of LTA from which the acetic acid had previously been removed *in vacuo*, and 36 ml of methylene chloride was immersed in a Dry Ice–acetone bath and maintained under a nitrogen atmosphere. A solution of 2.75 g (0.01 mol) of **1** in 25 ml of methylene chloride was then admitted dropwise during a period of 30 min. The brown reaction mixture was stirred for 1 hr, at the end of which time the color had entirely discharged. Work-up of the reaction mixture in the usual aqueous fashion, followed by the removal of the solvent and excess 2,3-dimethylbutadiene *via* rotary evaporator, yielded as the major product 2.20 g (0.0043 mol, 85%) of a crystalline white solid, mp 179–183°. The white solid exhibited the same melting point behavior noted with authentic trityl peroxide,[7] and, analogously, was also insoluble in either cold benzene or cold ether but readily soluble in cold concentrated sulfuric acid. In the latter solvent, an orange-red solution resulted. The spectral (ir, nmr) properties of the product were identical with those of authentic trityl peroxide.[7] Recrystallization of the solid from benzene–chloroform gave the analytical sample.

Anal. Calcd for C$_{38}$H$_{30}$O$_2$: C, 88.00; H, 5.79. Found: C, 87.51; H, 6.02.

Registry No.—**1**, 31938-11-1; **2**, 119-61-9; **3**, 76-84-6; **4**, 596-30-5; LTA, 546-67-8.

(13) C. F. H. Allen and A. Bell, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 312.

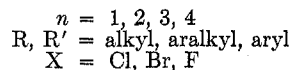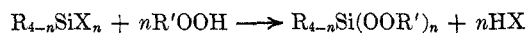### Amine–Hydroperoxide Adducts. Use in Synthesis of Silyl Alkyl Peroxides

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Silyl alkyl peroxides (compounds containing one or more Si–O–O–C bonds) were first reported by Buncel and Davies in 1956.[1] Subsequently, a number of publications were released concerning the preparation and characterization.[2–5]

The general method for the preparation of silyl alkyl peroxides involves reaction of an alkyl, aryl, or aralkyl hydroperoxide with a chlorosilane.

$$R_{4-n}SiX_n + nR'OOH \longrightarrow R_{4-n}Si(OOR')_n + nHX$$

$$n = 1, 2, 3, 4$$
$$R, R' = alkyl, aralkyl, aryl$$
$$X = Cl, Br, F$$

Such reactions are usually carried out in an inert solvent in the presence of an acid acceptor, pyridine for instance. Much lower yields result in the absence of acid acceptors.[2]

A less frequently used method involves the condensation of trimethylsilyl alkyl amines with *tert*-butyl hydroperoxide. A 20% yield of trimethyl(*tert*-butylperoxy)-silane has been reported.[5]

Generally speaking, there are two drawbacks to these

methods: (1) the yields are fairly low, especially for silyl alkyl peroxides containing more than one peroxy group; (2) the silyl alkyl peroxides made must be purified by distillation or other suitable means subsequent to the preparation step.

Results and Discussion

Synthesis by the Amine–Hydroperoxide Adduct Method.—The amine–hydroperoxide adduct synthesis of silyl peroxides requires two steps: (1) preparation of the amine–hydroperoxide adduct; (2) reaction of the adduct with chlorosilane in an inert solvent. Preparation of the adduct is carried out by mixing stoichiometric amounts of a suitable amine and the hydroperoxide in an inert solvent.[6] Assuming that the proper solvent has been selected, the crystalline adduct separates and can be collected by filtration.

Not all amines form adducts with hydroperoxides. For the majority of our work we have used 1,4-diazabicyclooctane (Dabco). The selection of Dabco resulted when other amines examined failed one or more of the following criteria: (1) the adduct must be a solid at the reaction temperature; (2) the solid adduct should be fairly insoluble in the solvent of choice; (3) the amine should not be oxidized by any of the reactants or products.

Primary and secondary amines were largely ruled out by 3. The convenience of operating at ambient temperatures, or slightly above, eliminated those amines which gave insoluble adducts only at lower temperatures.

No compromises were required when Dabco was used as the adduct amine. Both nitrogens of Dabco are involved and the resulting adduct contains 2 mol of hydroperoxide/mol of Dabco. The same solvent used for adduct preparation may be used for the halosilane reaction. The reaction is exothermic and usually complete within minutes. Once the Dabco hydrochloride is removed by filtration, solvent evaporation produces very pure silyl alkyl peroxide.

Hexamethylenetetramine (Hexa) also formed solid *tert*-butyl or cumyl hydroperoxide adducts. Unlike Dabco, only one nitrogen was involved in the Hexa adduct. When treated with halosilanes, poor yields, typically below 50%, of silyl alkyl peroxides were obtained. Reasoning that the remaining nitrogens were involved, calcium chloride was introduced into the reaction medium prior to the addition of halosilane to complex and nitrogens not involved in adduct formation. Under these conditions, high yields of product were obtained. Other metal salts (Ba^{2+}, Mg^{2+}) capable of complexing nitrogen were used successfully. Metals which did not complex had no effect.

Tables I–IV list the silyl alkyl peroxides prepared using the amine–hydroperoxide adduct technique. For convenience they are grouped according to the number of alkylperoxy substituents on silicon. References are given, where available, to those compounds appearing in the literature previously along with their reported yields.[7–9]

(1) E. Buncel and A. G. Davies, *Chem. Ind. (London)*, 1052 (1956).

(2) A. G. Davies and E. Buncel, British Patent 827,366 (Feb 3, 1960).

(3) H. Jenkner, U. S. Patent 2,997,497 (Aug 22, 1961).

(4) G. Sosnovsky and J. H. Brown, *Chem. Rev.*, **66**, 529 (1966).

(5) R. A. Pike and L. H. Shaffer, *Chem. Ind. (London)*, 1294 (1957).

(6) A. A. Oswald, U. S. Patent 3,236,850 (Feb 22, 1966).

(7) A. K. Litkovets and T. I. Yurzhenko, *Dokl. Akad. Nauk SSSR*, **142**, 1316 (1962).

(8) T. I. Yurzhenko and A. K. Litkovets, *ibid.*, **136**, 1361 (1961).

(9) E. Buncel and A. G. Davies, *J. Chem. Soc.*, 1550 (1958).