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β-PEROXYPROPIOLACTONES FROM CYCLOPROPANONE CYANOHYDRINS AND THEIR NOVEL REARRANGEMENT[1]

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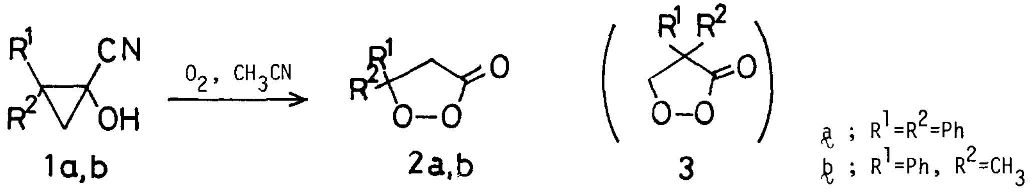
Abstract: Air oxidation of cyclopropanone cyanohydrins produced β-peroxypropiolactones (2). The 3,3-diphenyl-substituted-2 was decomposed readily by the catalysis of silica gel to yield α-phenoxystyrene quantitatively.

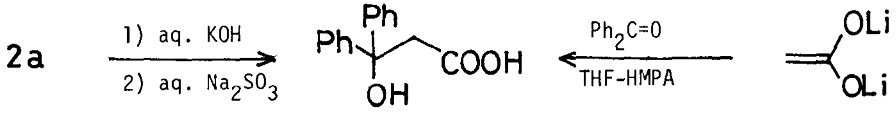
In addition to a limited number of hitherto reported synthetic access to β-peroxypropiolactones[2,3,4] that are gathering current theoretical and mechanistic dispute on diradical chemistry, we first present a novel method which comprises the air oxidation of cyclopropanone cyanohydrins. We also report a silica gel-catalyzed novel rearrangement of the peroxylactones that decarboxylate in a different way from their well-established thermolytic and photolytic transformations.

When an acetonitrile solution of 2,2-diphenylcyclopropanone cyanohydrin (1a)[5] was stirred under the atmospheric conditions at 50 °C for 12 h, 3,3-diphenyl-β-peroxypropiolactone (2a)[6] was formed and isolated in 52% yield. The yield was improved to 61% in the presence of silver nitrate (AgNO$_3$).



1a,b 2a,b 3

a ; R^1=R^2=Ph
b ; R^1=Ph, R^2=CH$_3$



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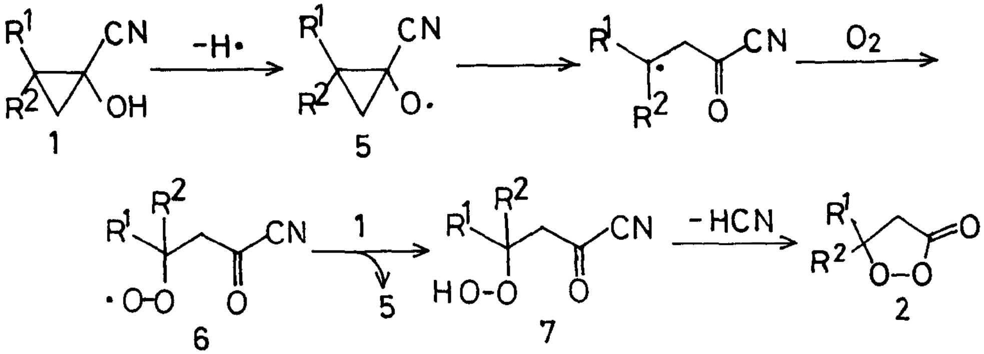
The ^{1}H NMR spectrum of 2a was characteristic of the presence of ring methylene protons appearing at δ 3.69, the IR spectrum shows ν(C=O) at 1800 cm^{-1}, and mass spectrum as well as elemental analysis was consistent with the peroxylactone structure 2a (or 3). The iodometric titration proved that it contains a peroxide linkage.[7] Since two structures 2a and 3 can be drawn from these spectral data, we carried out the following chemical transformation for structure determination. The peroxide was hydrolyzed in ethanol by aqueous potassium hydroxide followed by the workup with aqueous sodium sulfite to give 3-hydroxy-3,3-diphenylpropionic acid (4).[8] This acid was independently synthesized from acetic acid dianion and benzophenone.

Similar air oxidation of 2-methyl-2-phenylcyclopropanone cyanohydrin (1b,[5] a mixture of isomers) in acetonitrile proceeded smoothly in the presence of AgNO$_3$ to give the corresponding peroxypropiolactone 2b in 50% yield.[9] The NMR and IR spectra of 2b were identical with those reported.[3] In the absence of AgNO$_3$, however, 1b unreacted.

The mechanistic verification of the oxidation was carried out. The addition of 2,6-di-t-butyl-p-cresol (DTBPC, 0.1 mol equiv) to the reaction mixture of 1a resulted in the exclusive recovery of 1a even under the presence of AgNO$_3$. Heating of an acetonitrile solution of 1a under a nitrogen stream also resulted in the recovery of 1a.[10] These findings adduce firm evidences for the oxidation of 1a to proceed through a radical chain mechanism.

On the basis that the hydroxy hydrogen of cyclopropanols can be easily abstracted by free radicals,[11] a possible mechanism for the present oxidation is shown in Scheme 1. The hydrogen abstraction on 1 gives cyclopropyloxy

Scheme 1



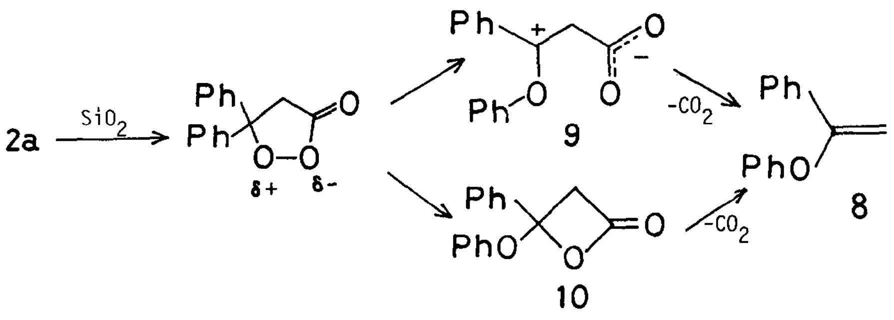
radical **5** which, after undergoing a ring-opening, reacts with oxygen to generate peroxyradical **6**. Radical **6** abstracts a hydrogen atom from **1** to form hydroperoxyacyl cyanide **7**. The ring-closure of hydroperoxide **7** gives the final product **2**.

Greene and coworkers prepared **2b** by the reaction of 3-hydroxy-3-phenylbutyric acid with hydrogen peroxide but they commented that the procedure was dangerous.[3] In contrast, our airoxidation procedure seems to be a much safer one.

Peroxypropiolactone **2a** is a thermally stable compound at an ambient temperature even under prolonged storage. However, when it was treated with silica gel in cyclohexane at an ambient temperature for 5 h α-phenoxystyrene (**8**)[12] was formed in 96% yield, but benzyl phenyl ketone which is one of the anticipated products according to the thermolysis mechanism as proposed by Adam[13] was not detected. In contrast, a carbon tetrachloride solution of **2a** heated in the absence of silica gel at 100 °C for 6 h gave **8** only in 19% yield.

This catalytic decomposition of **2a** seems to present a novel type of rearrangement of β-peroxypropiolactones. Extensive investigations[13,14] of the mechanistic features of the decomposition of β-peroxypropiolactones proved that, in thermolysis and photolysis,[13] the only migration mode of substituent observed was from 3- to 2-position of the peroxylactone. However, the present silica gel-catalyzed decomposition involves the phenyl shift from 3-position to the adjacent oxygen atom. Scheme 2 shows a mechanism for the rearrangement of **2a** to **8**. By the acid-catalysis of silica gel[15] at an electronegative oxygen, the positive counterpart of the peroxide linkage induces the Criegee-type[16] migration of a phenyl group, and the zwitterion **9** or β-lactone intermediate **10**, thus formed, undergoes decarboxylation to yield the final product α-phenoxystyrene (**8**).

Scheme 2



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(1) Ketene Equivalents, No. 10. For No. 9 see ref 5.

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(3) Greene, F. D.; Adam, W.; Knudsen, G. A. *J. Org. Chem.* **1966**, *31*, 2087.

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(6) **2a**: viscous oil; ^{1}H NMR ($CDCl_3$) δ 3.69 (2 H, s), 7.3-7.5 (10 H, m); IR (liquid film) 3060 (w), 1800 (s), 1460 (m), 1010 (m), 700 (s) cm^{-1}; mass spectrum, *m/z* (rel. intensity) 240 (M$^+$, 11), 196 (26), 182 (31), 105 (100), 94 (81), 77 (68); Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.68; H, 5.07.

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(9) 2-Phenylcyclopropanone cyanohydrin (**1c**) also underwent the airoxidation but acetophenone was formed instead of the intermediately produced peroxylactone.

(10) A trace amount of **2a** (3%) was formed besides the recovery of **1a**.

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(12) **8**: viscous oil; ^{1}H NMR ($CDCl_3$) δ 4.44 (1 H, d, *J* = 2.4 Hz), 5.04 (1 H, d, *J* = 2.4 Hz), 6.8-7.8 (10 H, m); IR (liquid film) 1630 (m), 1600 (m), 1495 (m), 1285 (m), 1220 (s) cm^{-1}; mass spectrum, *m/z* (rel. intensity) 196 (M$^+$, 35), 105 (35), 103 (74), 94 (100), 77 (34); Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.78; H, 6.22.

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