time of 15 min, gave an acceptable elemental analysis, and was identical in all respects with the material isolated previously. A small peak (*ca.* 2%) with retention time of 17 min was also isolated and shown by pmr spectra to be **diethyl *cis*-β-chlorovinylphosphonate** (*cis*-3); infrared spectrum: 2998 m, 2950 w, 2915 w, 1585 m, 1484 w, 1449 w, 1398 w, 1374 w, 1323 w, 1263 s, 1173 m, 1105 m, 1030 s, 970 s, 864 w, 829 w, 790 w, and 749 w cm^{-1}.

Anal. Calcd for $C_6H_{13}ClO_3P$: C, 36.25; H, 6.09; P, 15.60. Found: C, 36.51, 36.44; H, 6.19, 6.21; P, 15.88.

A Cyclic Peroxy Ester, β-Methyl-β-phenyl-β-peroxypropiolactone[1]

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The synthesis, properties, and thermal decomposition of the novel peroxygen compound, β-methyl-β-phenyl-β-peroxypropiolactone, are described. The peroxylactone may be prepared by acid-catalyzed reaction of hydrogen peroxide and the hydroxy acid. Decomposition in carbon tetrachloride at 134° affords propiophenone (70%), benzyl methyl ketone (15%), acetophenone (5%), and α-phenylpropionaldehyde (1.5%). Two possibles species, α-methylstyrene oxide and α-methoxystyrene, have been excluded as products or as precursors of the major products; the oxide, however, may be the precursor of the 1.5% of aldehyde observed. Decomposition is first order in peroxylactone and is insensitive to oxygen or azobisisobutyronitrile (ΔH^*, 31.5 kcal/mole; ΔS^*, −0.3 cal/mole per degree). Possible modes of decomposition of the peroxylactone are discussed.

A number of points of interest are associated with the incorporation of the oxygen–oxygen bond in a cyclic system. Such systems may serve as precursors of a variety of biradicals. Secondly, the constraint such systems place on the oxygen–oxygen bond may lead to marked changes in chemical behavior in comparison with acyclic analogs (*e.g.*, phthaloyl peroxide).[3] It was thus of interest to us to examine the chemical consequences of incorporation of the oxygen–oxygen bond in a cyclic perester. This paper reports the synthesis and study of the thermal decomposition of the first example of this class, β-methyl-β-phenyl-β-peroxypropiolactone (1).

Results

The peroxylactone, 1, was prepared by reaction of hydrogen peroxide with β-hydroxy-β-phenylbutyric acid in ether, catalyzed by concentrated sulfuric acid. The structure proof of the peroxylactone, obtained as a low melting solid, is based on spectral and analytical data summarized in the Experimental Section. The carbonyl band in the infrared is at 1810 *vs.* 1750 cm^{-1} for acyclic per esters, a difference somewhat greater than that observed between esters and γ-lactones. The peroxylactone may be titrated by iodometric analysis, does not appear to be shock sensitive, and has thermal stability comparable with that of *t*-butyl peracetate.[4]

Thermal Decomposition.—Decomposition of the peroxylactone in carbon tetrachloride (degassed, sealed tubes) afforded four products, propiophenone, benzyl methyl ketone, acetophenone, and α-phenylpropionaldehyde, analyzed by vpc and identified by collection and comparison with authentic samples. Product studies were made at two temperatures and at two initial concentrations. At 134°, the four principal products account for 93–95% of the peroxylactone.

Table I

Products of the Thermal Decomposition of β-Methyl-β-phenyl-β-peroxypropiolactone in Carbon Tetrachloride

Products	Yield, % 107°[a,b]	134°[a,b]	134°[b,c]
$C_6H_5COCH_3$	8.0, 7.9	5.7, 5.6	5.1, 5.1
$C_6H_5CH(CH_3)CHO$	<0.5, <0.5	1.5, 1.5	1.5, 1.5
$C_6H_5CH_2COCH_3$	9.7, 10.8	15.2, 14.9	15.8, 15.7
$C_6H_5COCH_2CH_3$	63.6, 63.0	71.2, 70.0	72.1, 70.7

[a] Initial peroxylactone, 0.0546 *M*; pyridine, 0.1 *M*. [b] Two separate runs. [c] Initial peroxylactone, 0.0254 *M*; pyridine, 0.1 *M*.

Kinetics.—A series of experiments was made to ascertain the principal mode of decomposition of the peroxylactone. The rate of decomposition in carbon tetrachloride alone was close to first order. Excellent first-order behavior was observed upon the inclusion of pyridine, which consequently was also employed in the product studies described above. The rate of disappearance of peroxylactone was unaffected by glass wool, oxygen, or azobisisobutyronitrile (present in severalfold excess over the peroxylactone) indicating the unimportance of surface catalysis or induced decomposition under the conditions of this study. Only a slight increase in rate was observed upon decomposition of peroxylactone in the presence of 0.01 *M* trifluoroacetic acid.

The rate of decomposition was measured over a ninefold variation in initial concentration of peroxylactone and at three temperatures. The results are summarized in Table II.

Table II

Decomposition of β-Methyl-β-phenyl-β-peroxypropiolactone in Carbon Tetrachloride

Temp, °C	Peroxylactone, $M \times 10^2$	$k_1 \times 10^5$ sec^{-1}
126	1.10	4.59 ± 0.05
126	4.86	5.19 ± 0.04
126	9.75	5.15 ± 0.13
134	1.06[a]	9.71 ± 0.08
134	1.03[a]	9.54 ± 0.09
106.8	1.02[a]	0.565 ± 0.005

[a] Pyridine, 0.02 *M*.

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(1) Supported in part by a grant from the Sloan Foundation and from the Petroleum Research Fund PRF No. 1291-B5 (W. A.)

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(3) F. D. Greene and W. W. Rees, *J. Am. Chem. Soc.*, **80**, 3432 (1958); **82**, 893 (1960).

(4) See Table I in P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

The activation parameters calculated from these data are ΔH^*, 31.5 kcal/mole, and ΔS^*, -0.3 cal/mole per degree (for di-*t*-butyl peroxide, ΔH^*, 37.8, and ΔS^*, 13.8; for *t*-butyl peracetate, ΔH^*, 38, and ΔS^*, 17).[4]

Discussion

The results of the kinetic studies indicate that peroxylactone disappears by unimolecular decomposition. The two major products, propiophenone **2** and benzyl methyl ketone **3**, correspond to a loss of carbon dioxide from **1** and skeletal rearrangement, with an apparent fivefold preference for methyl *vs.* phenyl migration (Chart I). In view of the rarity of radical rearrangements[5] and the usual preference for phenyl *vs.* alkyl migration,[5,6] this aspect appeared to be of special interest. Several reasonable routes from **1** to **2** and **3** are possible (Chart II).

CHART I

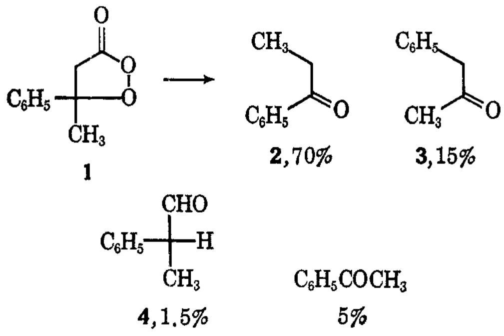
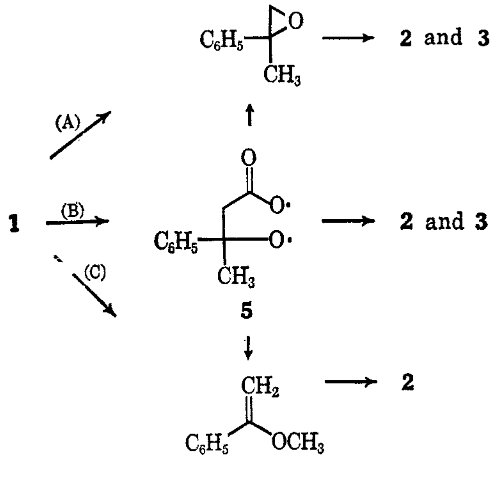


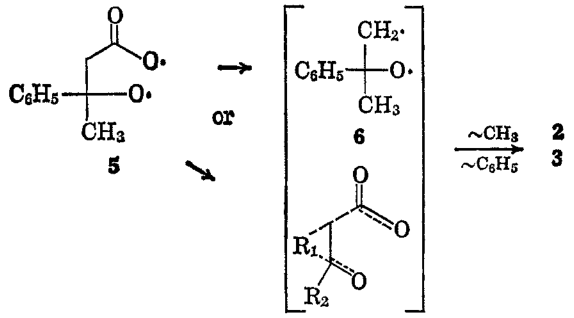
CHART II



The intermediacy of α-methylstyrene oxide (path A) is considered to be unimportant in that the yields of **2** and **3** are not altered upon decomposition of peroxylactone in the presence of authentic epoxide. It is possible that conversion of diradical **5** to α-methylstyrene oxide might afford the oxide with such an excess of energy that immediate rearrangement to products ensues. Such phenomena are known in the gas phase;[7] occurrence in this reaction (liquid phase) seems less likely. In any event, this route would not appear to be an adequate explanation for the formation of **2** and **3** since thermal decomposition of the epoxide (200°) affords α-phenylpropionaldehyde.[8] The 1.5% of this aldehyde isolated from decomposition of peroxylactone may arise from α-methylstyrene oxide.

The intermediacy of α-methoxystyrene (path C) may also be excluded although the evidence is less direct. α-Methoxystyrene is unstable in carbon tetrachloride at 134°. The products of reaction, however, have different vpc retention times from those of the products of decomposition of peroxylactone. Upon heating a carbon tetrachloride solution containing both the peroxylactone and α-methoxystyrene, products are observed with retention times different from those of decomposition of either reactant alone, and the yields of the usual products of decomposition of peroxylactone are greatly diminished. These results are suggestive of a reaction between α-methoxystyrene and peroxylactone, possibly of a type related to previous examples of olefin–peroxide reactions.[9]

With the exclusion of paths A and C the most probable route to products **2** and **3** would appear to be *via* path B (or a more synchronous version of it). The species **5** would be expected to be capable of rapid decarboxylation and of fragmentation characteristic of alkoxyl radicals. One might expect decarboxylation to precede or to be synchronous with cleavage of the methyl (or phenyl) group. The expectation is based on (a) the extensive experimental data concerning capture of alkoxyl radical intermediates[10] *vs.* the difficulty in capture of aliphatic carboxylate radicals;[11] (b) thermochemical and activation data for fragmentation of alkoxyl radicals[12] such as cumyloxy *vs.* exothermicity for decarboxylation of aliphatic carboxylate radicals.[13]



The migration of a substituent in **6** (or **5**) may be viewed both as a migration *to* a radical (or incipient radical) site and as an ejection of a radical *from* a location at which a carbon to oxygen bond is changing to a carbonyl group. Alkoxyl fragmentation reactions have been studied in detail.[10,14] Fragmentation of

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[5] C. Walling in P. de Mayo, "Molecular Rearrangements," Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 7.

[6] See C. Ruechardt, *Chem. Ber.*, **94**, 2599 (1961), and references cited therein; C. Ruechardt and R. Hecht, *ibid.*, **98**, 2460, 2471 (1965); C. Ruechardt and H. Trautwein, *ibid.*, **98**, 2478 (1965).

[7] *E.g.*, H. M. Frey, *Trans. Faraday Soc.*, **58**, 516 (1962); see also J. A. Bell, *Progr. Phys. Org. Chem.*, **2**, 1 (1964).

[8] (a) S. Danilow and E. Venus-Danilowa, *Ber.*, **60**, 1062 (1927); (b) see Control Experiments on α-methylstyrene oxide in the present paper.

[9] F. D. Greene, W. Adam, and J. E. Cantrill, *J. Am. Chem. Soc.*, **83**, 3461 (1961), and references cited therein.

[10] (a) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959); (b) C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964).

[11] D. F. DeTar and R. C. Lamb, *ibid.*, **81**, 122 (1959).

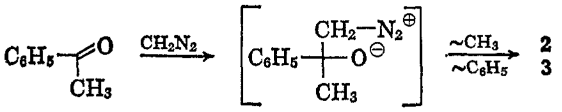
[12] See ref 10a, pp 262, 276.

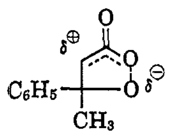
[13] L. Jaffe, E. J. Prosen, and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957). [For information on benzoate radical, see J. C. Bevington and J. Toole, *J. Polymer Sci.*, **28**, 413 (1958).]

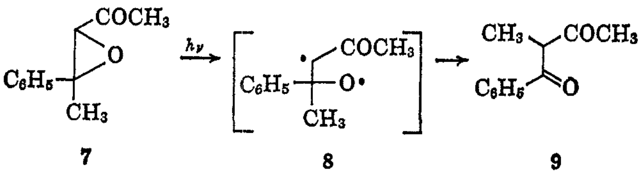
[14] (a) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1193 (1962); (b) F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963).

the cumyloxy radical results primarily in cleavage of the methyl group.[15] As noted earlier, radical rearrangements are rare, particularly the migration of aliphatic groups [5] For cases in which alkyl and aryl migration in a radical system may be compared [*e.g.*, $C_6H_5C(CH_3)_2$–$CH_2\cdot$] phenyl migration appears to be greatly favored.[5,6] Thus, the preferential migration of methyl *vs.* phenyl in the peroxylactone decomposition is suggestive that the dominant factor for migratory aptitude here is bond breaking at the migration origin. The present data do not provide a distinction between strict intramolecular 1,2-alkyl migration *vs.* fragmentation and cage recombination. The relative importance of product **3** in comparison with the absence of phenyl cleavage in cumyloxy radical[15] is, perhaps, more in accord with the former than the latter interpretation.

It is also of interest to compare the present case with two others: a structurally related ionic reaction and a photochemical reaction. In the former, addition of diazomethane to acetophenone (or deamination of 2-hydroxy-2-phenylpropylamine) results in a fifteenfold preference for phenyl migration *vs.* methyl.[16a] The observed fivefold preference for methyl *vs.* phenyl migration in the peroxylactone case is thus not in accord with possible transition states involving charge separation of the following type. The photochemical reaction comes from a preliminary report in which the β diketone **9** is the major product (25% yield) of irradiation of epoxy ketone **7**.[16b] Preferential migration of methyl in a species of diradical character such as **9** may be indicated.







7 **8** **9**

A final point of interest is associated with the formation of acetophenone from decomposition of the peroxylactone (5% yield at 134°). This may arise by ejection of the fragment of composition CH_2CO_2 (corresponding to an α-lactone) from **5** or, possibly, directly from **1**.[17]

Experimental Section

β-Hydroxy-β-phenylbutyric acid was obtained from the corresponding ester[18] by alkaline hydrolysis in 60% yield, mp 72–74° (lit. mp 71–72°).

β-Methyl-β-phenyl-β-peroxypropiolactone (Caution).[19]—To a stirred solution of 1.8 g (0.01 mole) of β-hydroxy-2-phenylbutyric acid in 10 ml of ether (reagent grade) cooled to 0° was slowly added 5 ml of 90% hydrogen peroxide. After a few minutes, 3 drops of concentrated sulfuric acid was added and stirring was continued for 30 min at 0°. The cooling bath was lowered from the flask and the flask was left at room temperature (stoppered) for 20 hr. To the solution was added saturated aqueous ammonium sulfate solution (20 ml), the mixture was transferred to a separatory funnel, and the ether layer was washed (15 ml of H_2O, two 15-ml portions of 5% aqueous $KHCO_3$, 15 ml of saturated aqueous NH_4SO_4, 15 ml of 1% aqueous KOH, and 15 ml of H_2O) and then dried ($MgSO_4$). Evaporation gave a colorless oil which was passed through a short column of Florisil eluting with ether. Three recrystallizations at −50° from a 1:1 ether–hexane mixture yielded 1.16 g (65%) of colorless crystals: mp 28–29°; purity, 99.5% by iodometric analysis.[20]

Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66; mol wt, 178. Found: C, 67.28; H, 5.84; mol wt, 175 (osmometer).

The compound shows singlet peaks in the nmr (in CCl_4) at δ 1.73, 3.22, and 7.52 of area ratio 3:2:5 assigned to the methyl, methylene, and phenyl hydrogen atoms of the peroxylactone. In the infrared (in CCl_4) the compound shows absorption at 3080 (w), 3060 (w), 3025 (w), 2980 (w), 2925 (w), 1810 (vs), 1490 (w), 1445 (w), 1425 (w), 1370 (w), 1300 (w), 1270 (m), 1205 (m), 1185 (w), 1170 (w), 1140 (w), 1080 (w), 1060 (w), 1050 (w), 1025 (w), 950 (w), 910 (w), 870 (w), 860 (w), and 695 (s) cm^{-1}.

α-Methylstyrene oxide was prepared from 1-chloro-2-phenyl-2-propanol[21] by the action of ethanolic sodium ethoxide:[22] bp 66–68° at 4 mm (lit. 85–88 at 17 mm); nmr, δ 1.68 (singlet, 3 H, CH_3), 2.76 (quartet, 2 H, CH_2), 7.48 (5 H, C_6H_5); infrared, identical with that of Patterson.[23]

α-Methoxystyrene.—1-Iodo-2-methoxy-2-phenylethane was prepared following a procedure reported for the *p*-ethyl derivative.[24] The product was converted to α-methoxystyrene by methanolic sodium methoxide:[25] bp 91–93° at 22 mm (lit. bp 88–89° at 20 mm).

Thermal Decomposition of the Peroxylactone.—To a dried, constricted test tube was added a solution of 0.0486 g (0.273 mmole) of peroxylactone in 5 ml of carbon tetrachloride (reagent grade, distilled from P_2O_5) to which pyridine (freshly distilled from barium oxide) had been added to a concentration of 0.1 *M*. The test tube was degassed, sealed under vacuum, and heated at 134° for 14 hr (7 half-lives). Vapor phase chromatography on a Dow-Corning 200 (15%) and Carbowax 1540 (3%) Chromosorb P (base-washed) column (hereafter referred to as column A) at 107°, 15 psi of helium pressure, showed peaks at retention times (relative to *p*-bromotoluene = 1.00) of 1.54, 1.70, 2.24, and 2.4. Samples of each peak were collected; they were identical in infrared spectra and retention times with acetophenone, α-phenylpropionaldehyde, benzyl methyl ketone, and propiophenone, respectively. Analysis was also made on an XF 1150 (11%) and Carbowax 20M (5%) Chromosorb W (base-washed) column (column B) at 131° and 16 psi of helium. The chromatogram again showed four peaks, corresponding to acetophenone, α-phenylpropionaldehyde, benzyl methyl ketone, and propiophenone, shown by collection and identity of infrared spectra and retention times with authentic samples.

Quantitative analysis[26] of the product mixture was made on column A with *p*-bromotoluene as internal standard. The results are summarized in Table I.

Rate of Reaction.—Solutions of the peroxylactone, *ca.* 0.01 *M*, and pyridine[27] (freshly distilled from barium oxide), *ca.* 0.02

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[15] M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **16**, 105 (1951).

[16] (a) H. O. House, E. J. Grubbs, and W. F. Gannon, *J. Am. Chem. Soc.*, **82**, 4099 (1960); (b) H. E. Zimmerman, B. R. Cowley, C. Y. Tseng, and J. W. Wilson, *ibid.*, **86**, 947 (1964).

[17] For an example of a reaction (photochemical) in which another five-membered ring, a pyrazoline, decomposes by two paths (loss of N_2 to form a cyclopropane and loss of CH_2N_2 to form an olefin), see K. L. Rinehart, Jr., and T. V. Van Auken, *ibid.*, **82**, 5251 (1960).

[18] J. A. Reid and E. E. Turner, *J. Chem. Soc.*, 3365 (1949); M. H. Palmer and J. A. Reid, *ibid.*, 931 (1960).

[19] Mixtures of high concentration hydrogen peroxide and ether are potentially of great hazard ("Hydrogen Peroxide," E. I. du Pont de Nemours and Co., Wilmington, Del.).

[20] A modification of the procedure of C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950). The modified procedure is described under Rate of Reaction.

[21] M. Tiffeneau, *Ann. Chem.*, [8] **10**, 176 (1907).

[22] A. Klages, *Ber.*, **38**, 1969 (1905).

[23] W. A. Patterson, *Anal. Chem.*, **26**, 823 (1954).

[24] K. B. Wiberg, T. M. Shryne, and R. R. Kintner, *J. Am. Chem. Soc.*, **79**, 3160 (1957); see also M. Tiffeneau, *Compt. Rend.*, **145**, 811 (1901).

[25] S. Winstein and L. L. Ingraham, *J. Am. Chem. Soc.*, **77**, 1738 (1955).

[26] See ref 14b, p 63.

[27] See Kinetics section under Results.

M, were prepared in carbon tetrachloride (reagent grade); 5-ml aliquots were transferred to constricted Pyrex tubes (previously washed in an alkaline soap solution, thoroughly rinsed, and dried), degassed, sealed, and placed in the thermostat. The rate of reaction was followed by iodometric analysis for peroxide.[20] An aliquot of 4.0 ml of reaction solution was placed in a 125-ml glass-stoppered erlenmeyer flask. The carbon tetrachloride was removed by a gentle stream of purified nitrogen gas. (Control experiments showed that peroxylactone was not lost by this procedure.) Acetone (15 ml of reagent grade) was added and the solution was degassed by powdered Dry Ice. Sodium iodide (1 g) and 10% aqueous hydrochloric acid (3 ml) were added and the flask was stoppered. After 10 min in the dark, 25 ml of distilled water was added, and the liberated iodine was titrated with 0.01 *N* thiosulfate solution to the disappearance of the iodine color. Frequent blank determinations were made but were always 0. Analysis by a number of the previously published methods for analysis of peroxides gave less satisfactory results. Scatter in the kinetic data observed in early runs was eliminated (and the over-all rate somewhat reduced) by the inclusion of pyridine, at *ca.* 0.02 *M*.

The rate of disappearance of peroxylactone was unaffected by oxygen, glass wool, or added azobisisobutyronitrile. The kinetic data are summarized in Table II.

Control Experiments. A. α-Methylstyrene Oxide.—Subjection of the epoxide to vpc analysis affords a single peak. Retention times of epoxide and α-phenylpropionaldehyde differ only slightly (61.8 and 60.8) on the columns used for product analyses. The hot wire of the vpc detector rearranges the epoxide to the aldehyde.

A solution of the epoxide, 0.0496 *M* in carbon tetrachloride containing 0.1 *M* pyridine, was degassed, sealed, and heated for 14 hr at 134°. The infrared spectrum of the reaction mixture was largely that of the epoxide plus a small amount of α-phenylpropionaldehyde. Analysis by vpc on column A at 107°, 15 psi of helium, showed small peaks (relative to *p*-bromotoluene = 1.00) at 1.42 and 2.38, and a major peak at 1.73 (starting material, 85%). The small peaks at 1.42 and 2.38 are not present in the peroxylactone decomposition and were not further investigated.

Subjection of the epoxide to the above conditions, omitting pyridine, resulted in conversion of the epoxide to α-phenylpropionaldehyde. Heating the epoxide in carbon tetrachloride with pyridine (0.1 *M*) at 180° for 20 hr afforded a complex mixture derived, in part, from reaction of the pyridine with the solvent.

B. Decomposition of the Peroxylactone in the Presence of α-Methylstyrene Oxide.—A solution of peroxylactone (0.05 *M*), epoxide (0.0496 *M*), and pyridine (0.1 *M*) in carbon tetrachloride was heated at 134° for 14 hr. Analysis by vpc on column A showed peaks (relative to *p*-bromotoluene = 1.00) at 1.43 (small, unknown), 1.54 (acetophenone, 8%), 1.73 (α-methylstyrene oxide, 84%), 2.24 (benzyl methyl ketone, 15%), 2.38 (small, unknown), and 2.48 (propiophenone, 69%).

C. α-Methoxystyrene. Thermal Stability.—A solution of α-methoxystyrene (0.05 *M*) and pyridine (0.01 *M*) in carbon tetrachloride was degassed, sealed, and heated at 134° for 14 hr. Analysis by vpc on column A showed two unresolved peaks at 1.55 and 1.6 (relative to *p*-bromotoluene = 1.00); no peak or shoulder was observed at 1.63, the relative retention time for α-methoxystyrene.

D. Decomposition of the Peroxylactone in the Presence of α-Methoxystyrene.—A solution of peroxylactone (0.058 *M*), α-methoxystyrene (0.05 *M*), and pyridine (0.1 *M*) in carbon tetrachloride was degassed, sealed, and heated at 134° for 14 hr. The reaction mixture (extensive tar formation) was analyzed by vpc on column A; peaks (relative to *p*-bromotoluene = 1.00) were observed at 0.47, 1.54 (large), 1.70 (large), 2.20 (small), 2.42 (small); these peaks do not correspond to those from decomposition of peroxylactone alone or of the enol ether alone.

Ring Expansion of 2-Substituted 1-Indanones to 2-Hydroxyisocarbostyril Derivatives. Scope and Mechanism of Reaction. A Spectral Study of the Lactam–Lactim Tautomerism in Isocarbostyrils[1]

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The addition of *n*-butyl nitrite to a 1:1 molar equivalent of 2-alkyl-1-indanone [R = CH_3 (**1b**), C_2H_5 (**1c**), C_3H_7 (**1d**), *iso*-C_3H_7 (**1e**), *n*-C_4H_9 (**1f**), and *t*-C_4H_9 (**1g**)]–hydrochloric acid, and to a 2-phenyl- (**1h**) and 2-cyano-1-indanone (**1k**)–sodium alkoxide mixture, produced 2-hydroxy-3-alkyl- or -arylisocarbostyrils (**3b–3h** and **3k**, respectively) in decreasing yields (69–14%). Reverse addition of acid to an indanone–nitrite mixture led to the isolation of the stable dimeric 2-alkyl-2-nitroso-1-indanones [**2b–2g** and **2i** (R = Ac)] in decreasing yields (90–20%). Since **2b–2g** were isomerized to **3b–3g**, respectively, in both acid (92–96%) and base (90–96%), the nitrosation step (**1** → **2**) clearly determines product yield in the conversion **1** → **3**. Reduction of **3b–3f** and **3h** with iodine and red phosphorus in glacial acetic acid led to the known 3-alkyl- or -arylisocarbostyrils (**4b–4f** and **4h**). Both hydrochloric acid and methanolic sodium methoxide converted **2i** to 2-oximino-1-indanone (**2a**), as did nitrosation of 1-indanone (**1a**). 2-Carboxy-1-indanone (**1j**) underwent nitrosative decarboxylation to **2a**. Ring-opened intermediates in the isomerization **2b** → **3b** are suggested by the conversion of *o*-carboxy- (**19**) and *o*-carbomethoxybenzyl methyl ketoxime (**24**) to **3b**, in acid and base, respectively. 2,3,3-Trimethyl-1-indanone (**1m**), 2-methyl- (**32a**), and 2-ethyl-1-tetralone (**32b**) were converted to their respective nitroso dimers, **2m**, **33a**, and **33b**. Acid treatment of **2m** and base treatment of **33a** and **33b** led to ring-opened hydrolysis products, 3-methyl-3-(*o*-carboxyphenyl)-2-butanone oxime (**29**), 4-(*o*-carboxyphenyl)-2-butanone (**34a**), and 1-(*o*-carboxyphenyl)-3-pentanone (**34b**), respectively. A similarity of ultraviolet spectra, the presence of a C-4 vinyl proton signal in the nmr of **3b**, **4b**, and 2,3-dimethylisocarbostyril (**35**), and the lack of N→O absorption in **3b**, is consistent with the existence of 2-hydroxy-3-methylisocarbostyril and 3-methylisocarbostyril predominantly in their respective lactam forms, **3b** and **4b**. Infrared, ultraviolet, and nmr data are reported for compounds in the series **1–4**, inclusive.

In the first description of this novel ring expansion,[2] we reported that addition of *n*-butyl nitrite to a 1:1 molar equiv of 2-methyl- (**1b**) and 2-ethyl-1-indanone (**1c**)–hydrochloric acid mixture produced 2-hydroxy-3-alkylisocarbostyrils (**3b** and **3c**, respectively). With lower acid concentrations and reversal of the mode of addition (acid to indanone–nitrite mixture), the stable dimeric precursors, 2-methyl- (**2b**) and 2-ethyl-2-nitroso-1-indanone (**2c**) were isolated. Compounds **2b** and **2c** isomerized to **3b** and **3c**, respectively, rapidly in refluxing methanolic sodium methoxide solution and more slowly in concentrated hydrochloric acid. Reduction of **3b** and **3c** in glacial acetic acid with iodine and red phosphorus led to isocarbostyrils **4b** and **4c**, respectively.

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[2] E. J. Moriconi, F. J. Creegan, C. K. Donovan, and F. A. Spano, *J. Org. Chem.*, **28**, 2215 (1963).