initial concentration of III was varied from 0.1 to 0.44*M*. In each case the kinetic experiments were followed to at least 75% completion and then allowed to proceed for infinite time. Final values of conversion always corresponded to from 95 to 100% isomerization to IV. Graphical treatment of the rate data afforded very clean first-order plots. Table I records the first-order rate constants which were obtained.

TABLE I

First-Order Rate Constants for the Thermal Isomerization of 2-*tert.*-Butyl-3-Phenyloxazirane to *N*-*tert.*-Butyl Benzaldoxime

Temp., °C. ± 0.05°	Initial Oxazirane Concentration, (mole/l.)	k_1,[a] (sec.$^{-1}$) × 10^7
100.0	0.437	545
	0.252	537
85.0	0.116	530
	0.241	119
	0.229	113
	0.120	113
	0.115	117
	0.233	5.40
60.0	0.127	5.40

[a] Average k_1 values are 5.37×10^{-5} at 100.0°, 1.16×10^{-5} at 85.0° and 5.40×10^{-7} (sec.$^{-1}$) at 60.0°.

A plot of reciprocal temperature *versus* log k_1 produced a good straight line from which $\Delta H\ddagger$ was found to be 28 kcal. per mole between 60 and 100°. The entropy of activation, $\Delta S\ddagger$ was found to be -3 ± 1 entropy units, a value which indicates that the structures of oxazirane reactant and nitrone product are equally rigid. The slight negative value may indicate increased solvation of the transition state due to the development of a strong N → O dipole.

EXPERIMENTAL

Materials. Acetonitrile was Eastman Spectrograde. Diethyl carbitol was technical grade which had been rigorously purified according to the procedure given by Brown, Meade, and Subba Rao[2] for the purification of diglyme. The material so obtained boiled at 94–96° at 33 mm., n^{20}_D 1.4115. 2-*tert.*-Butyl-3-phenyloxazirane (III) was generously supplied by W. D. Emmons (ref. 1) and was further purified by chromatography on silica gel using methylene chloride solvent followed by vacuum distillation. The pure material boiled at 63° at 0.8 mm., $n^{24}D$ 1.5081. The ultraviolet spectrum of the compound in acetonitrile solvent showed only end absorption.

Pure *N*-*tert.*-butylbenzaldoxime (IV) was obtained from the same source, m.p. 75–77°. The ultraviolet spectrum of this compound in acetonitrile solvent gave λ_{max} 289 mμ with an extinction coefficient of 1.68×10^4.

Kinetic procedure. Solutions of 2-*tert.*-butyl-3-phenyloxazirane (0.1 to 0.44*M*) in pure diethyl carbitol were prepared in 10-ml. volumetric flasks. The flasks were placed in the appropriate thermostat at zero time. At intervals small aliquots were removed and delivered to a volume of acetonitrile which was subsequently made up to 10 ml. with the same solvent. Optical density readings were made at 298 mμ with a Model DK-1 Beckman spectrophotometer and the concentration of nitrone (IV) was computed. Points were taken until the reaction had progressed to 75% completion. After several days (or weeks at lower temperatures) the rearrangement of III to IV was found to be essentially complete as determined by the ultraviolet absorption spectrum of the reaction mixture.

First-order plots were prepared by plotting log (oxazirane) *vs.* time. The first-order constants obtained are shown in Table I.

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[2] H. C. Brown, E. J. Meade, and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

Cyanoethylation of Phenol; Isolation of an *ortho*- Addition Product[1]

H. W. Johnston[2] and F. J. Gross[3]

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The carbon-carbon cyanoethylation of the more active phenols, such as resorcinol, to give *beta*-substituted propionitriles in the presence of anhydrous zinc chloride and anhydrous hydrogen chloride is well known.[4] Phenol itself does not react under these conditions, but if a more active catalyst, anhydrous aluminum chloride, is used, a good yield of β-(*p*-hydroxyphenyl)propionitrile is obtained.[5] Recently Westfahl and Gresham reported the addition of vinylidene cyanide to phenol in the presence of anhydrous aluminum chloride at 30–35° to give β-(*p*-hydroxyphenyl)α-cyanopropionitrile in 45% yield.[6] A trace of the δ-lactone of β-(*o*-hydroxyphenyl)propionic acid (melilotol), I, was tentatively identified by means of its infrared spectrum. This compound was formed, presumably, by hydrolysis and decarboxylation of the parent cyano compound during isolation of the products of the Friedel-Crafts reaction.

The authors have noted a result similar to that of Westfahl and Gresham. Phenol was cyanoethylated in the presence of anhydrous aluminum chloride and dry hydrogen chloride. (It was noted that the use of hydrogen chloride considerably lowered the viscosity of the reaction mixture, presumably by minimizing the formation of the insoluble salt, $C_6H_5OAlCl_2$.) The expected β-(*p*-

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[1] In part, an undergraduate senior research project by F. J. Gross.

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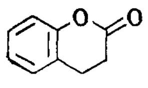
[3] Present address: Swift and Co., Newark, N. J.

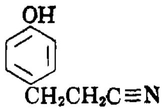
[4] W. D. Langley and R. Adams, *J. Am. Chem. Soc.*, **44**, 2326 (1922); L. C. Behr, J. E. Kirby, R. N. MacDonald, and C. W. Todd, *J. Am. Chem. Soc.*, **68**, 1296 (1946).

[5] R. Schnabel, German Patent **870,273**, March 12, 1953.

[6] J. C. Westfahl and T. L. Gresham, *J. Am. Chem. Soc.*, **76**, 1076 (1954).

hydroxyphenyl)propionitrile, II, was obtained in 72% yield. In addition, a careful fractional distillation of the products of the reaction gave the δ-lactone of β-(o-hydroxyphenyl)propionic acid, I, in 3% yield.


I


II

Although several experiments were made, at no time under the reaction conditions used, was any trace of the *ortho*-cyanoethylphenol observed. It is reasonable to expect that this compound or its tautomeric imine was attacked by the neighboring *ortho*-phenolate ion in the aluminum chloride complex or during the subsequent hydrolysis of the complex ions. The relatively low yield of this *ortho* addition compound suggests steric hindrance.

EXPERIMENTAL

Four hundred grams (3 moles) of anhydrous c.p. aluminum chloride was added slowly with rapid mechanical stirring at 15° to 564 g. (6 moles) of freshly distilled phenol and 387 g. (6 moles) of freshly distilled acrylonitrile. Dry hydrogen chloride was passed into the rose-colored viscous slurry over a period of about 1.5 hr. during which time there was a pronounced decrease in viscosity of the mixture.

The slurry was heated to 80° whereupon it dissolved to a dark red fluid solution. Although further external heating was discontinued the reaction was strongly exothermic and refluxed at 105°. Addition of dry gas was continued over a period of 1.5 hr. after which the mixture was allowed to cool.

The contents of the reaction vessel were poured over 2 kg. of cracked ice and stirred until the precipitated salts redissolved. The dark red phenolic layer was removed by means of a separatory funnel and the aqueous portion was extracted with two 250-ml. portions of toluene which were combined with the phenolic material. The organic mixture was washed several times with 10% potassium chloride solution and stripped of solvent at reduced pressure.

Vacuum distillation of the residue through a 24-in. helix-packed column connected to a distillation head equipped for partial take-off gave 374 g. of phenol, b.p. 69° at 7 mm.; 15 g. of melilotol (containing phenol as a contaminant), b.p. 84–109° at 1 mm.; and 317 g. of β-(p-hydroxyphenyl)-propionitrile, b.p. 157–163° at 1 mm., m.p. 58–59°, which is in agreement with that recorded in the literature.[7] Alkaline hydrolysis of this nitrile gave phloretinic acid, m.p. 127–129°.[8]

Redistillation of the second fraction gave melitolol, b.p. 111–112° at 2.5 mm., identified by comparison of its infrared spectrum with that of an authentic sample prepared by an independent method.[9,10]

Strong bands in the infrared spectrum of the lactone were noted at 1775, 1242, 1227, 1140, and 760 cm.$^{-1}$ Hydrolysis of the lactone with aqueous KOH followed by acidification gave melilotic acid, m.p. 81–83°. A mixed melting point with an authentic sample[9] showed no depression.

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α-Phenylcycloalkylideneacetic Acids

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α-Phenyl-3-methylcyclohexylidenaecetic, α-phenyl-4-methylcyclohexylideneacetic and α-phenylcycloöctylideneacetic acids have been prepared by dehydration of the required α-phenyl-α-(1-hydroxycycloalkyl)acetic acids[1] with acetic anhydride according to the procedure described for α-phenylcyclohexylideneacetic acid.[2] The ultraviolet absorption spectra of the new acids were compared with those of α-phenylcyclohexylideneacetic acid[2,3] and α-phenyl-1-cyclohexenylacetic acid.[3] The spectrum of each new acid was essentially coincident with that of α-phenylcyclohexylideneacetic acid,[4] which indicated that each possessed the α-phenylcycloalkylideneacetic acid structure rather than that of the corresponding α-phenyl-1-cycloalkenylacetic acid. The much lower adsorption above 220 mμ shown by α-phenyl-1-cyclohexenylacetic acid was expected, since the ethylenic bond in this compound is not in conjugation with the benzene nucleus.

EXPERIMENTAL

α-Phenyl-3-methylcyclohexylideneacetic acid. This acid, obtained in 22% yield after recrystallization from petroleum ether (90–100°), melted at 142–148°; it was undoubtedly a mixture of geometric isomers.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.24; H, 7.86: neut. equiv., 230.3. Found: C, 78.20; H, 8.10; neut. equiv., 230.1.

α-Phenyl-4-methylcyclohexylideneacetic acid. This acid melted at 122–124° after recrystallization from absolute ethanol; yield 36%.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.24; H, 7.86; neut. equiv., 230.3. Found: C, 78.28; H, 8.19; neut. equiv., 229.3.

α-Phenylcycloöctylideneacetic acid. This acid, obtained in 11% yield, melted at 139–141° after recrystallization from absolute ethanol.

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(4) The ultraviolet absorption spectrum determined by us for α-phenylcyclohexylideneacetic acid was in agreement with that reported by K. Scholz, M. Spillman, E. Tagmann, and K. Hoffman [*Helv. Chim. Acta*, **35**, 2016 (1952)] for a basic ester of this acid.