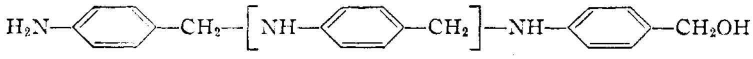
***p*-Carbethoxybenzyl Alcohol.**[28]—Treatment of 0.35 mole of this alcohol with synthesis gas gave 15.6 g. (27%) of ethyl (*p*-methyl)-benzoate, b.p. 85° at 4 mm. to 106° at 8 mm. Hydrolysis of this ester gave *p*-methylbenzoic acid, m.p. 175.5–180.5°[29] (mostly 179.5–180.5°), from which was prepared *p*-toluamide, m.p. 159.0–160.4°,[29] recrystallized from water. The remainder of the product was a high-boiling, unidentified residue.

To show that the ester group was inert under reaction conditions, 0.7 mole of ethyl benzoate was treated with 3000 p.s.i. of 1:1 gas at 190° in the presence of a cobalt catalyst. No gas was absorbed, and the only product obtained on distillation was starting material (73%), identified as benzoic acid, m.p. 121.7–122.6°.

***p*-Nitrobenzyl Alcohol.**—Ten grams of cobalt(II) acetate tetrahydrate in 50 ml. of benzene was converted to cobalt carbonyl by treatment with 170 atm. of 1:1 synthesis gas for 1 hour at 180°. To this solution was added 62.6 g. (0.41 mole) of *p*-nitrobenzyl alcohol,[30] m.p. 92.6–94.4°; 9.8 mole per cent. of cobalt as cobalt carbonyl was present. The mixture was then treated with synthesis gas for 5 hours at 185–190° in the usual manner. The products were poured from the reaction vessel and filtered; a brown solid (I) and an orange filtrate (II) were obtained. A large amount of a brown brittle solid (III) was left in the autoclave.

The filtered solid (I) was extracted with 200 ml. of methanol, leaving a residue which weighed 19 g. and contained 2.76% cobalt. This residue is probably polymeric *p*-aminobenzyl alcohol with residual cobalt. The methanol solution was concentrated to about 100 ml. and then poured into 400 ml. of water. The resulting yellow precipitate was filtered, dissolved in benzene and reprecipitated with petroleum ether to give 21 g. of unreacted *p*-nitrobenzyl alcohol, m.p. 92.8–94.0°, no depression when mixed with an authentic sample. Concentration of the orange filtrate (II) to about 50 ml. and cooling the solution gave 4 g. more of starting alcohol, m.p. 91.4–93.0°. The filtrate was taken to dryness and the residue recrystallized from ethanol-water to yield 3 g. of *p*-nitrobenzyl acetate, m.p. 75.4–76.8°, no depression when mixed with an authentic sample. A total of 25 g. (40%) of *p*-nitrobenzyl alcohol was recovered; an additional 3.7% of the alcohol was recovered as the acetate.

An ultimate analysis of the brown solid left in the reaction vessel revealed that it contained a much higher percentage of carbon (76.6%) than the starting material (54.9%), indicating reduction of the nitro group of *p*-nitrobenzyl alcohol. *p*-Aminobenzyl alcohol easily polymerizes in the presence of traces of acids[3] to a polymer of the structure



The ultimate analysis of III was consistent with a polymer of *p*-aminobenzyl alcohol of the above structure with *x* equal to 2.

Anal. Calcd. for $C_{28}H_{30}O_4N$: C, 76.68; H, 6.90. Found: C, 76.56; H, 6.56.

Reduction of Nitrobenzene.—Ten grams of cobalt(II) acetate tetrahydrate in 50 ml. of benzene was converted to cobalt carbonyl by treatment with 204 atm. of 1:1 synthesis gas for 2 hours at 180°. The autoclave was opened and 71.8 g. (0.58 mole) of nitrobenzene in 20 ml. of benzene was added to the solution of cobalt carbonyl (6.9% cobalt based on nitrobenzene). This mixture was then heated with 218 atm. of 2:1 synthesis gas for 4 hours at 185°.

Steam distillation of the acidified reaction mixture gave 32 g. (44%) of nitrobenzene, b.p. 80–101° at 22 mm. The pot residue was made alkaline with 10% sodium hydroxide and the steam distillation continued. The distillate was extracted with ether, and the extract on treatment with hydrogen chloride gave 5.5 g. of aniline hydrochloride, m.p. 196.8–198.2°, no depression when mixed with an authentic sample.

The non-steam-distillable portion of the reaction product was extracted with ether. Evaporation of the ether gave 2.6 g. of acetanilide, m.p. 113.6–114.4°, no depression when mixed with an authentic sample. The acetylation was obviously achieved by the acetic acid from cobaltous acetate. No attempt was made to improve the yield of aniline.

BRUCETON, PENNA.

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[28] F. H. Case, THIS JOURNAL, **47**, 1145, 3003 (1925).

[29] H. Fischli, *Ber.*, **12**, 615 (1879).

[30] *Org. Syntheses*, **24**, 81 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

The Reaction of *p*-Nitrostyrene Oxide with Sodiomalonic Ester

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p-Nitrostyrene oxide has been shown to react with sodiomalonic ester to give diethyl (β-*p*-nitrophenyl-β-hydroxyethyl) malonate. This result has been interpreted to indicate the superiority of steric over electronic factors in this displacement reaction involving the ring opening of an epoxide ring by an anionoid reagent.

Styrene oxide has been shown to react with anions or anionoid reagents (in the absence of acid catalysts) *via* attack of the reagent at the β-carbon atom of the oxide[1-5] rather than *via* attack at the α-carbon atom.[6] For example, sodiomalonic ester gave the β-substituted α-phenylethyl alcohol,[1] rather than the isomeric primary alcohol.

It has been suggested, on the one hand, that the predominance of attack at the β-carbon atom over that at the α-atom is due to an anomalous electron-releasing effect of the phenyl group, causing the α-carbon atom to assume a negative charge relative to the β-atom, thus hindering attack by an anion at the α-atom,[1] or, on the other hand, that the lower reactivity of the α-position is due to the steric effect of the bulky phenyl group.[2,7,8]

It seemed worthwhile to us to study the direction of ring opening of the analogous *p*-nitrostyrene oxide with sodiomalonic ester, in order to obtain evidence as to whether the results might best be attributed to electronic or to steric factors. While

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[1] R. R. Russell and C. A. VanderWerf, THIS JOURNAL, **69**, 11 (1947).

[2] R. M. Adams and C. A. VanderWerf, *ibid.*, **72**, 4368 (1950).

[3] M. Tiffeneau and E. Fourneau, *Compt. rend.*, **146**, 697 (1908).

[4] L. L. Kitchen and C. B. Pollard, *J. Org. Chem.*, **8**, 342 (1943).

[5] L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949).

[6] S. Winstein and R. B. Henderson in R. C. Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 34, report that Winstein and Ingraham have found some of the isomeric primary alcohol in the methoxide-catalyzed addition of methyl alcohol to the epoxide ring.

[7] E. E. van Tamelen, G. Van Zyl and G. D. Zuidema, THIS JOURNAL, **72**, 488 (1950).

[8] C. O. Guss and H. G. Mautner, *J. Org. Chem.*, **16**, 887 (1951).

there may be some question in regard to classifying the phenyl group as an electron source or as an electron sink[1,9] relative to hydrogen, the addition of the powerful electron-attracting[9] *p*-nitro group should enhance markedly the reactivity of the α-position toward nucleophilic attack, assuming a dominant electronic factor.[10] On the other hand, if the steric factor is predominant, then attack at the β-carbon atom should obtain, as with styrene oxide.

The latter possibility was realized. *p*-Nitrostyrene oxide reacted with sodiomalonic ester in absolute ethyl alcohol to give diethyl (β-*p*-nitrophenyl-β-hydroxyethyl)-malonate in 46% yield. The identity of this compound was shown by its conversion to γ-*p*-nitrophenyl-γ-butyrolactone which was identical with the product obtained by nitration of γ-phenyl-γ-butyrolactone.[1]

This result suggests that the principal factor responsible for the preferential attack of the nucleophilic agent at the primary carbon, rather than the secondary carbon atom, in styrene oxide is steric rather than electronic.

Experimental

***p*-Nitrostyrene** was prepared according to the method of Strassburg, Gregg and Walling,[11] and **α-*p*-nitrophenyl-β-bromoethanol** was prepared from it by the procedure of Read and Reid.[12]

***p*-Nitrostyrene Oxide.**—To an ice-cold slurry of 112 g. (0.46 mole) of α-(*p*-nitrophenyl)-β-bromoethanol in 200 ml. of ethanol was added rapidly a cold solution of 20 g. (0.5 mole) of sodium hydroxide in 200 ml. of ethanol. The cold solution was allowed to come to room temperature, filtered to remove sodium bromide and evaporated to one-third its volume. Water was added to dissolve the residual sodium bromide. The solid product, recrystallized from small quantities of methanol–water, about 4:1, yielded 45 g. (61%), m.p. 84–86° (cor.). Sublimation under vacuum resulted in flat, glassy needles, m.p. 85–87° (cor.).[13]

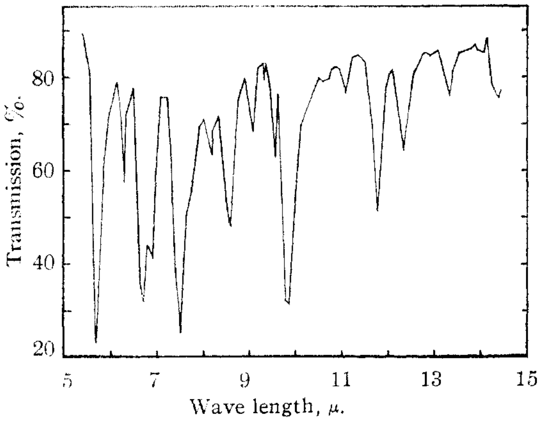

Fig. 1.—Infrared absorption spectrum of γ-*p*-nitrophenyl-γ-butyrolactone.

γ-Phenyl-γ-butyrolactone[1] (3.7 g., 23 mmoles) was nitrated according to the procedure described by Forman and McElvain for the nitration of β-phenylethyl bromide.[14] The precipitate of **γ-*p*-nitrophenyl-γ-butyrolactone** was recrystallized from a 1:2 mixture of chloroform and carbon tetrachloride. The yield of purified material, m.p. 112–113° (cor.), was 800 mg. (17%).

Anal.[15] Calcd. for $C_{10}H_9O_4N$: C, 57.97; H, 4.38; N, 6.76. Found: C, 58.00; H, 4.32; N, 6.88.

The position of the nitro group was proved by oxidation of the lactone with potassium permanganate to *p*-nitrobenzoic acid, m.p. 235–237°, mixed m.p. with an authentic sample 235–237°.

α-Carbethoxy-γ-*p*-nitrophenyl-γ-butyrolactone.—This lactone was prepared by the condensation of 500 mg. (3.1 mmoles) of *p*-nitrostyrene oxide with sodiomalonic ester (prepared from 200 mg. (8.7 mmoles) of sodium and 1.1 g. (7.0 mmoles) of ethyl malonate) in 30 ml. of absolute ethanol, substantially as described for styrene oxide by Russell and VanderWerf.[1] The reaction mixture was not hydrolyzed directly, as these authors described, but instead the mixture was poured onto ice, and the cold suspension was extracted with ether. The ether was removed by distillation, and the resulting yellow oil crystallized slowly. After crystallization was complete, the product was washed free of oily contaminant with cold ether and then recrystallized from a mixture of ether and petroleum ether (b.p. 30–60°). The yield was 390 mg. (46%) of the lactone, which apparently formed spontaneously in the alkaline solution from the initially formed (β-*p*-nitrophenyl-β-hydroxyethyl)-malonic ester. The melting point was 108–109.5° (cor.).

Anal. Calcd. for $C_{13}H_{13}O_6N$: N, 5.02; sapn. equiv., 279. Found: N, 5.06; sapn. equiv., 278 and 277.

γ-*p*-Nitrophenyl-γ-butyrolactone by Hydrolysis and Decarboxylation.—A suspension of 97 mg. of α-carbethoxy-γ-*p*-nitrophenyl-γ-butyrolactone in 50 ml. of 0.1 *N* 10% aqueous ethanolic sodium hydroxide was heated at 80° for one hour. The solution was acidified and the solvents were evaporated. The organic residue was extracted with hot chloroform and the chloroform was then removed by evaporation. The residue was warmed at 125–135° until the evolution of gas had ceased (about 15 minutes). The cooled, solid lactone was recrystallized from a chloroform-carbon tetrachloride mixture, giving 50 mg. (70%) of the pure material, melting at 112.5–113.5° (cor.). Mixtures with nitrated γ-phenyl-γ-butyrolactone in varying ratios showed no melting point depression. The two substances showed identical infrared absorption spectra in both mineral oil suspension and chloroform solution. The absorption spectrum for the nitrated γ-phenyl-γ-butyrolactone in mineral oil suspension is shown in Fig. 1.

Acknowledgment.—The authors wish to thank Messrs. W. B. Evans and C. H. Tieman for preparations of *p*-nitrostyrene and of *p*-nitrostyrene oxide and Mrs. Patricia Ramey for performing the nitrogen analyses and determining the infrared spectra.

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[10] G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1815 (1935).

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[12] J. Read and W. G. Reid, *J. Chem. Soc.*, 1487 (1928).

[13] C. O. Guss and H. G. Mautner[8] report a melting point of 85–86°.

[14] E. L. Forman and S. M. McElvain, THIS JOURNAL, **62**, 1436 (1940).

[15] The analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.