Reaction of Thiodiglycol with n-Butyl Alcohol in Equimolecular Proportions.—A mixture consisting of thiodiglycol (122.2 g., 1 mole), n-butyl alcohol (74.1 g., 1 mole) and p-toluenesulfonic acid monohydrate (5.7 g., 0.03 mole) was held at 145–150° for three hours in a stainless steel tube. The reaction mixture was dissolved in 500 cc. of ether, the aqueous layer discarded and the ether solution washed with 2% sodium carbonate and finally with water until neutral. After removal of the ether and unreacted alcohol the residue was distilled and the following fractions were collected: p-oxathiane,[4] 10 g. (9.6% based on the thiodiglycol), b.p. 147–149° (760 mm.).

(4) H. T. Clarke, J. Chem. Soc., **101**, 1805 (1912), reported 147° 755 mm.) for the boiling point of 1,4-thioxane.

2-Hydroxyethyl 2-n-butoxyethyl sulfide, 23 g. (12.9% based on the thiodiglycol), b.p. 152–154° (20 mm.).

Anal. Calcd. for $C_8H_{18}O_2S$: S, 17.98; MR_D, 50.29. Found: S, 18.0; $n^{20}D$ 1.4744; $d^{20}_{15.5}$ 0.9919; MR_D, 50.59.

Bis-(2-n-butoxyethyl) sulfide, 33 g. (14.1% based on the thiodiglycol), b.p. 162–164° (20 mm.).

Anal. Calcd. for $C_{12}H_{26}O_2S$: S, 13.68; MR_D, 68.89. Found: S, 14.08; $n^{20}D$ 1.4560; $d^{20}_{15.5}$ 0.9308; MR_D, 68.46.

Residue, 64 g., consisting of polymeric ethers (61.4% calculated as $(OCH_2CH_2SCH_2CH_2)_n$ and based on the thiodiglycol).

PAULSBORO, NEW JERSEY

Chemistry of the Oxo and Related Reactions. VI. Experiments with Meta- and Para-Substituted Benzyl Alcohols

BY IRVING WENDER, HAROLD GREENFIELD, SOL METLIN AND MILTON ORCHIN
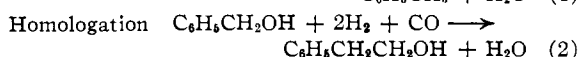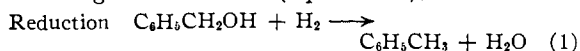
RECEIVED FEBRUARY 25, 1952

Nuclear-substituted benzyl alcohols react with synthesis gas ($2H_2$:1CO) in the presence of a cobalt catalyst to give a mixture containing a substituted toluene derived from the hydrogenolysis of the hydroxyl group (reduction) in addition to a substituted 2-phenylethanol (homologation). The effect of the substituent on the over-all rate of the reaction and on the product distribution was studied in a series of semi-quantitative experiments. The rate of reaction decreased in the following order: p-OCH₃ ≫ p-CH₃ > m-CH₃, p-t-butyl > H > p-Cl > m-OCH₃ ≫ m-CF₃. The proportion of homologation product as compared to reduction product also increased in the order in which the substituent is capable of releasing electrons but this effect was not nearly as pronounced as the effect on the reaction rate.

Treatment of benzyl alcohol with synthesis gas ($2H_2$:1CO) and a cobalt catalyst gives a mixture consisting of the hydrocarbon, toluene and the homologous alcohol, 2-phenylethanol, in a ratio of about 2:1.[1,2] When substituted benzyl alcohols of the type $C_6H_5CR'R''OH$ (where R' and R'' are alkyl and/or aryl groups) are similarly treated, the corresponding hydrocarbons are formed almost exclusively.[2] The study has now been extended to nuclear-substituted benzyl alcohols to determine (a) the relative proportions of the hydrogenated and homologated products, and (b) the effect of different substituent groups on the speed of the two reactions. All reactions were conducted at 185–190° with an initial pressure of 238 atm. of 2:1 synthesis gas ($2H_2$:1CO).

The alcohols, solvent benzene and dicobalt octacarbonyl catalyst were placed in an autoclave which was heated from room temperature to 190° in 110 minutes. The rates with which the various substituted alcohols reacted with synthesis gas were followed by observing the drop in pressure recorded on a Bourdon gage (680 atm.) attached to the autoclave. The results are shown in Tables I and II.

Although the stoichiometry of the reduction reaction (equation 1) is quite different from that of the homologation reaction (equation 2), both reactions

Reduction $C_6H_5CH_2OH + H_2 \longrightarrow$
$$C_6H_5CH_3 + H_2O \quad (1)$$
Homologation $C_6H_5CH_2OH + 2H_2 + CO \longrightarrow$
$$C_6H_5CH_2CH_2OH + H_2O \quad (2)$$
usually proceed simultaneously, and the rate of gas absorption can be used as a rough measure of the speed of the over-all reaction.

(1) I. Wender, R. Levine and M. Orchin, THIS JOURNAL, **71**, 4160 (1949).
(2) I. Wender, H. Greenfield and M. Orchin, ibid., **73**, 2656 (1951).

The time interval required to absorb one mole of gas per mole of starting alcohol was used qualitatively to compare reaction rates. The temperatures at which this absorption occurred varied; Table II gives time and temperature data. Thus, p-methoxybenzyl alcohol had absorbed one mole-equivalent of gas six minutes after the temperature reached 80°; the temperature at the end of this time interval was only 92°. p-Methylbenzyl alcohol absorbed this amount of gas between 80 and 166° in 44 minutes. Table II also shows that the rates of uptake of gas were in the following order: p-OCH₃ ≫ p-CH₃ > m-CH₃, p-t-butyl > H > p-Cl > m-OCH₃ ≫ m-CF₃. This sequence of substituents is in the order of their ability to release electrons. All the benzyl alcohols having electron-releasing substituents started to react between 80 and 166°. Benzyl alcohol started to absorb gas at 180°. The alcohols having electron-attracting substituents reacted so slowly at 190° that starting alcohol was recovered after 5 hours; some dehydrogenation of the starting alcohol occurred, and significant quantities of the corresponding aldehydes were identified in the reaction products from these experiments.

Table I shows that, in general, as the relative speed of the reaction decreased, the quantity of product derived from homologation decreased as compared to that from hydrogenolysis. For example, after 5 hours at 190° more than half the original m-methoxybenzyl alcohol was recovered unchanged, and nearly all of the reacted portion was reduced. However, p-methoxybenzyl alcohol reacted more than 10^4 times as fast as m-methoxybenzyl alcohol; and the major part of the p-methoxy compound reacted by homologation, although considerable p-methoxytoluene (hydrogenation) was secured.

TABLE I

REACTION OF SUBSTITUTED BENZYL ALCOHOLS WITH SYNTHESIS GAS $(2H_2:1CO)^a$

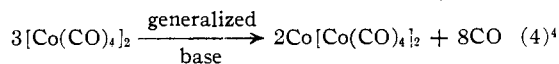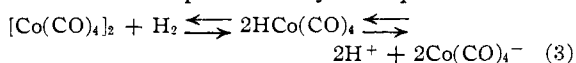| Substituent	Hydro-carbon, %	Homologated alcohol, %	% Homolo-gated / % Hydro-carbon	Recovered starting alcohol, %	Other products
p-Methoxy	16	44	4.9	0	Approximately 34% high-boiling polymer, probably aldol of p-methoxyphenylacetaldehyde[b]
p-Hydroxymethyl	27	39 12[c]	1.9	0	
p-Methyl	58	24	0.6	0	8% of high-boiling polymer, probably aldol[b]
m-Methyl	52	36	.7	0	1–2% m-methylbenzaldehyde
p-t-Butyl	54	28	.5	0	<1% p-t-Butylbenzaldehyde
Benzyl	63	31	.5	0	
2,4,6-Trimethyl	58	18	.3	0	
p-Chloro	41	16	.4	31	4% p-chlorobenzaldehyde
m-Methoxy	23	ca. 2	0.1	56	4% m-methoxybenzaldehyde
m-Trifluoromethyl	5			78	4% m-trifluoromethylbenzaldehyde
p-Carbethoxy	27				High-boiling products
p-Nitro				44	Polymer of p-aminobenzyl alcohol

^{a} Initial total pressure of 2:1 synthesis gas was 238 atm. Maximum time allowed for reaction was 5 hours at 185–190°. ^{b} This product added to yield of homologated product in column 4. ^{c} This yield refers to the dihomologated alcohol, p-phenylene-β,β'-diethanol.

2,4,6-Trimethylbenzyl alcohol reacted rapidly with synthesis gas to yield 58% of hydrocarbon and 18% of homologated alcohol. Evidently the o-methyl groups did not impose any serious steric restriction on either hydrogenolysis or homologation.

The reaction of p-nitrobenzyl alcohol illustrates the retarding effect of an electron-attracting group in the para position upon both the reduction and homologation reactions. Almost half of the starting alcohol (40%) was recovered unchanged. After removal of the liquid products from the autoclave, a brown solid was left, the ultimate analysis of which was consistent with polymeric p-aminobenzyl alcohol. Reduction of the nitro group was evidently the fastest reaction; the aminobenzyl alcohol formed is known to polymerize very rapidly in the presence of traces of acids.[3] The possibility of reducing nitro groups with synthesis gas and a cobalt catalyst suggested by this experiment was realized by the reduction of nitrobenzene to aniline.

Discussion of Mechanism

Although most of the catalyst is added to the reaction mixture as dicobalt octacarbonyl, after completion of the reaction some of the carbonyl appears in the water of reaction as the cobalt carbonyl anion, $[Co(CO)_4]^-$. The transformation of dicobalt octacarbonyl to the anion may take place by either of two routes represented by the equations

$$[Co(CO)_4]_2 + H_2 \rightleftharpoons 2HCo(CO)_4 \rightleftharpoons$$
$$2H^+ + 2Co(CO)_4^- \quad (3)$$

$$3[Co(CO)_4]_2 \xrightarrow[\text{base}]{\text{generalized}} 2Co[Co(CO)_4]_2 + 8CO \quad (4)^4$$

It is probable that both reactions occur and that the mixture contains $[Co(CO)_4]_2$, Co^{++}, $Co(CO)_4^-$ and the acid, $HCo(CO)_4$.

The rate measurements listed in Table II were semi-quantitative, and determination of product distribution (Table I) was frequently difficult. Nevertheless, the data indicate: (a) Electron-re-

(3) A. P. Phillips and A. Maggiolo, J. Org. Chem., 15, 659 (1950).
(4) I. Wender, H. Sternberg and M. Orchin, THIS JOURNAL, 74, 1216 (1952).

TABLE II

RELATIVE RATES OF REACTION OF SUBSTITUTED BENZYL ALCOHOLS

Substituent	Time,[a] minutes	Temperature,[b] °C.	Relative reaction rate[c]
p-Methoxy	6	92	1×10^4
p-Methyl	44	166	2×10^2
m-Methyl	67	188	5×10^1
p-t-Butyl	67	188	5×10^1
Hydrogen	82	190	1
p-Chloro	109	190	0.8
p-Carbethoxy[d]	231	190	.4
m-Methoxy[d]	254	190	.3
m-Trifluoromethyl	10,000[e]	190	.01

^{a} Time required to absorb one mole of gas per mole of starting alcohol after the temperature reached 80°. ^{b} Temperature reached at the end of time interval in column 2. The last four alcohols started to react at 190°; benzyl alcohol started to absorb gas slowly at 180°. ^{c} On the assumption that the reaction rate doubles for each 10° rise, this column indicates the ratio of time necessary for one mole of gas to be absorbed per mole of benzyl alcohol at 190°, to the time required for the substituted benzyl alcohol at 190°. The average of the temperature recorded in column 3 and 80° is taken as the temperature at which the reaction started. ^{d} The rate data for p-carbethoxy and for m-methoxybenzyl alcohols are for 0.35-mole runs and are therefore not strictly comparable with the other data which is for 0.6-mole runs. ^{e} Only 5% of the alcohol reacted in 5 hours, and several days would probably be required to absorb one mole equivalent of gas.

leasing substituents in the meta and para positions markedly increase the rate of both the reduction (equation 1) and homologation (equation 2) reactions; and (b) the proportion of homologation product as compared to reduction product also increases in the order in which the substituent is capable of releasing electrons; however, this effect is not nearly as pronounced as the effect on the reaction rates. These facts suggest that reactions (1) and (2) may both proceed via a common carbonium ion intermediate formed by reaction of the alcohol with the acid, $HCo(CO)_4$,[5] and further that this intermediate is transformed to the various final products at different rates. The homologated

(5) I. Wender, S. Metlin and M. Orchin, ibid., 73, 5704 (1951).

product can result from the carbonium ion by attack of nucleophilic carbon monoxide[6] followed by hydrogenation. The reduced product can result from reduction of the intermediate ion to a radical[7] which may then abstract a hydrogen atom from cobalt hydrocarbonyl.[2]

Alternate mechanisms may be written but further discussion at the present time appears unwarranted. If the reduction reaction does proceed by way of a radical intermediate, a study of the rate of hydrogenation may yield clues to the effect of nuclear substituents on the ease of formation and stability of the intermediate benzyl radicals. Such a kinetic study is now under way in this Laboratory using benzhydrol (Ph_2CHOH) and nuclear-substituted benzhydrols.

Experimental[8]

All experiments were run in an American Instrument Co., 500-ml. stainless-steel autoclave. Unless otherwise specified, the reactions were conducted with 0.6 mole of the substituted benzyl alcohol at 185–190° and with 6.6 mole per cent. of cobalt as dicobalt octacarbonyl[2] in 50 ml. of benzene. The starting pressure in all cases was 238 atm. (measured at 25°) of 2:1 synthesis gas ($2H_2$:$1CO$) which had been manufactured and compressed at the Bureau of Mines. The maximum time allowed for reaction to occur was 5 hours. The amount of substituted benzaldehyde present in starting benzyl alcohol and in the reaction products was determined by titration with hydroxylamine hydrochloride.[9] The reaction of p-methylbenzyl alcohol will be described in some detail as an example.

p-**Methylbenzyl** Alcohol.—This alcohol, m.p. 57.8–58.7°, was prepared in 64% yield by the reduction of p-toluic acid with lithium aluminum hydride. Fifty ml. of benzene, 5.3 g. of dicobalt octacarbonyl, 1 g. of cobalt(II) carbonate and 73.2 g. (0.6 mole) of p-methylbenzyl alcohol were placed in the autoclave. Synthesis gas ($2H_2$:$1CO$) was added until the pressure reached 238 atm. at 25°; this corresponded to approximately 3.8 moles of gas. The autoclave was heated to 190° within 110 minutes. Because the high-pressure lines leading from the compressor to the autoclave and from the autoclave to the gage are easily plugged by solid matter in the reaction vessel, the bomb was not rocked until the temperature reached 70° (40 minutes). Gas absorption started at approximately 128–136°; the maximum pressure obtained was 306 atm. at 136–147°. The temperature of the autoclave was held at 185–190° for two hours, during which time the pressure dropped to 252 atm. The reaction vessel was allowed to cool overnight to room temperature (28°); the pressure at this temperature was 163 atm. The gases were then vented to the atmosphere.

Distillation of the reaction mixture yielded 37 g. (58%) of p-xylene, b.p. 137–138°, n^{25}D 1.4932, identified by its infrared absorption spectrum; 20 g. (24%) of 2-(p-methylphenyl)-ethanol, boiling range 114–125° at 12–9 mm., identified as its phenylurethan, m.p. 115.2–115.8°[10]; and 7 g. of an unidentified yellow liquid, boiling range 118–203° at 10 mm.

p-**Methoxybenzyl** Alcohol.—With p-methoxybenzyl alcohol (b.p. 109–110° at 2–3 mm.) gas absorption started at about 70° and was essentially complete 35 minutes later when the temperature was 130°. Two products were isolated from the reaction mixture by distillation. The first fraction consisted of 11.5 g. (16%) of p-methoxytoluene, b.p. 45–49° at 2–3 mm. Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.73; H, 8.43.

The second fraction consisted of 40.1 g. (44%) of 2-(p-

methoxyphenyl)-ethanol, b.p. 125–126° at 4 mm. Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.00; H, 7.99.

The phenylurethan of this alcohol was recrystallized from 90–100° petroleum ether and melted at 127.0–128.6°. Anal. Calcd. for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32. Found: C, 71.17; H, 6.44.

A black residue of 30 g. remained in the pot. At a pot temperature of 300° and a pressure of 4 mm., this residue started to decompose but did not distil. A duplicate experiment was performed with almost exactly the same results. It was suspected that this high molecular weight reaction product was formed by aldolization of p-methoxyphenylacetaldehyde. In an effort to enhance aldehyde formation and aldolization, the reaction of p-methoxybenzyl alcohol with synthesis gas and a cobalt catalyst was conducted at 80°; both hydrogen and carbon monoxide were rapidly absorbed at this temperature. The reaction products contained small amounts of p-methoxytoluene and 2-(p-methoxyphenyl)-ethanol, but the chief product was an undistillable, sweet-smelling residue. An ultimate analysis of the residue was consistent with the formula

$$(p\text{-}CH_3OC_6H_4)CH_2CH_2CH(p\text{-}CH_3OC_6H_4)CHOHCH\text{-}$$
$$(p\text{-}CH_3OC_6H_4)CH_2OH$$
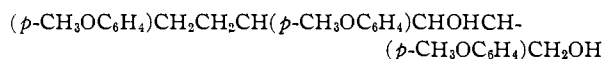
Anal. Calcd. for $C_{27}H_{32}O_5$: C, 74.28; H, 7.39; mol. wt., 436. Found: C, 73.97; H, 7.28; mol. wt., 368.

This could be formed by aldolization of p-methoxyphenylacetaldehyde, followed by dehydration and hydrogenation, then aldolization of the new aldehyde with another mole of p-methoxyphenylacetaldehyde followed by hydrogenation.

p-t-**Butylbenzyl** Alcohol.—This alcohol was prepared in 88% yield by the lithium aluminum hydride reduction of p-t-butylbenzoic acid.[11] The alcohol contained about 1% of p-t-butylbenzaldehyde. Two derivatives of p-t-butylbenzyl alcohol were prepared. The phenylurethan, m.p. 62.7–63.4°, was recrystallized from 35–60° petroleum ether.

Anal. Calcd. for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47. Found: C, 76.41; H, 7.26.

The α-naphthylurethan, m.p. 159.4–160.1°, was recrystallized from 90–100° petroleum ether. Anal. Calcd. for $C_{22}H_{23}NO_2$: C, 79.25; H, 6.95. Found: C, 79.11; H, 6.63.

Three fractions were obtained by distillation of the reaction products. The first fraction consisted of 47.8 g. (54%) of p-t-butyltoluene, b.p. 93–95° at 28 mm., n^{25}D 1.4906.

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.89. Found: C, 88.90; H, 10.89.

The second fraction consisted of 30.1 g. (28%) of 2-(p-t-butylphenyl)-ethanol, b.p. 122–123° at 6 mm. This alcohol was identified as its phenylurethan, m.p. 78.2–79.0°,[12] recrystallized from 35–60° petroleum ether. Hydroxylamine hydrochloride titration of this fraction indicated that 0.7 g. (< 1%) of p-t-butylbenzaldehyde was present. This aldehyde was identified as its p-nitrophenylhydrazone, m.p. 214.9–215.9°,[13] recrystallized from ethanol-water, and as its 2,4-dinitrophenylhydrazone, m.p. 249–251°, recrystallized from ethanol-ethyl acetate.

Anal. Calcd. for $C_{17}H_{18}N_4O_4$: C, 59.64; H, 5.30. Found: C, 59.45; H, 5.12.

A third fraction, weighing 3.7 g. and distilling from 128° at 5 mm. to 156° at 7 mm., was not identified.

p-**Hydroxymethylbenzyl** Alcohol.—This alcohol was prepared in 83% yield by the hydrolysis of α,α'-dibromo-p-xylene with aqueous sodium carbonate[14]; it melted at 118.0–119.4°. Fifty grams (0.36 mole) of p-hydroxymethylbenzyl alcohol, 50 ml. of benzene, 2 g. of dicobalt octacarbonyl and 1 g. of cobalt(II) carbonate (5.6 mole per cent. cobalt) were treated with synthesis gas as outlined above. Three compounds were isolated and identified in the reaction products. Distillation yielded 10.4 g. (27%) of p-xylene, b.p. 136.5–137.0°, identified by its infrared absorption spectrum. The second fraction consisted of 18.9 g.

(6) H. Pines and V. Ipatieff. THIS JOURNAL, **69**, 1337 (1947).

(7) J. B. Conant and B. F. Chow, ibid., **55**, 3752 (1933).

(8) All melting points are corrected. Macroanalyses were performed by the Bureau of Mines and are reported to two decimal places; microanalyses are by G. L. Stragand, University of Pittsburgh, and are reported to one decimal place. Infrared absorption spectra were run under the direction of Dr. R. A. Friedel.

(9) W. M. Bryant and D. M. Smith, THIS JOURNAL, **57**, 57 (1935).

(10) I. G. Farbenindustrie A.-G., French Patent 752,478 (1933); C. A., **28**, P 1047⁹ (1934).

(11) We are indebted to the Shell Chemical Corp. for a sample of this acid.

(12) P. Cagniant and Ng. Ph. Buu-Hoi, Bull. soc. chim., **9**, 111 (1942).

(13) J. W. Baker, W. S. Nathan and C. W. Shoppe, J. Chem. Soc., 1847 (1935).

(14) E. Bourquelot and A. Ludwig, Compt. rend., **159**, 213 (1914).

(39%) of 2-(p-methylphenyl)-ethanol, b.p. 140–145°, at 23 mm., identified as the phenylurethan,[16] m.p. 114.3–115.3°, recrystallized from 60–68° petroleum ether. A third fraction consisted of 7.1 g. (12%) of p-phenylene-β,β'-diethanol, b.p. 180–185° at 2 mm., m.p. 85.3–86.5,[16] recrystallized from 60–68° petroleum ether–benzene.

m-**Methoxybenzyl Alcohol.**—This alcohol was prepared in 75% yield by the lithium aluminum hydride reduction of m-methoxybenzoic acid. Forty-eight grams (0.35 mole) of m-methoxybenzoic alcohol was treated with synthesis gas using 5.7 mole per cent. cobalt (2 g. of dicobalt octacarbonyl and 1 g. of cobalt(II) carbonate) and 50 ml. of benzene. Three fractions were obtained by distilling the reaction product. The lowest-boiling component was m-methoxytoluene, 10 g. (23%), micro b.p. 176°, n^{25}D 1.5111. Nitration of this fraction yielded 2,4,6-trinitro-3-methoxytoluene, m.p. 91.4–92.2°,[17] recrystallized from ethanol–water. The second fraction weighed 29 g. and distilled from 144° at 20 mm. to 138° at 6 mm. with decomposition in the distillation flask, which made it difficult to maintain a low pressure. This fraction contained 2 g. (4%) of m-methoxybenzaldehyde, identified as its 2,4-dinitrophenylhydrazone, m.p. 219.7–220.4°,[18] recrystallized from ethanol–ethyl acetate. The semicarbazone of m-methoxybenzaldehyde was also prepared from this fraction and melted at 201.5–202.5°, recrystallized from ethanol–water.

Anal. Calcd. for $C_9H_{10}N_4O_5$: C, 56.0; H, 5.7. Found: C, 56.2; H, 5.6.

Dehydration[19] of a portion of this fraction with potassium hydroxide yielded a very small amount of product which absorbed bromine in glacial acetic acid. It was concluded that very little 2-(m-methoxyphenyl)-ethanol was present and most of this fraction was undoubtedly m-methoxybenzyl alcohol (56%) which was identified as its α-naphthylurethan, m.p. 100.6–102.2 (recrystallized from 60–68° petroleum ether), no depression on mixed melting point with an authentic sample.

Anal. Calcd. for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58. Found: C, 74.09; H, 5.67.

The residue of 5.4 g. was soluble in ether and on distillation gave about 3 g. of an unidentified viscous yellow liquid, b.p. 206–224° at 5 mm., n^{25}D 1.5588.

2,4,6-**Trimethylbenzyl Alcohol.**—This alcohol was prepared in 41% yield by the lithium aluminum hydride reduction of 2,4,6-trimethylbenzoic acid, and in 62% yield by the lithium aluminum hydride reduction of 2,4,6-trimethylbenzyl chloride. One hundred ml. of benzene, 47.9 g. (0.32 mole) of 2,4,6-trimethylbenzyl alcohol, 2.0 g. of dicobalt octacarbonyl and 1 g. of cobalt(II) carbonate (6.2 mole per cent. cobalt) were treated with synthesis gas as above. A yield of 24.9 g. (58%) of 1,2,3,5-tetramethylbenzene, b.p. 90–91° at 22 mm., n^{25}D 1.5111, was secured.

Anal. Calcd. for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.46; H, 10.63.

There was also obtained 9.3 g. (18%) of 2-(2,4,6-trimethylphenyl)-ethanol, b.p. 141° at 14 mm., m.p. 79.0–81.4°.[20] Its α-naphthylurethan melted at 175.2–176.4°, recrystallized from 90–100° petroleum ether.

Anal. Calcd. for $C_{22}H_{23}NO_2$: C, 79.25; H, 6.95. Found: C, 79.53; H, 6.87.

p-**Chlorobenzyl Alcohol.**—This alcohol was prepared by refluxing a mixture of 260 g. (1.6 moles) of p-chlorobenzyl chloride, 230 g. of sodium carbonate and 2300 ml. of water for four days. Distillation yielded 182 g. (80%) of p-chlorobenzyl alcohol which, after recrystallization from 60–68° petroleum ether, melted at 70.6–71.6°. Four compounds were identified in the products from the reaction of this alcohol with synthesis gas under the conditions described earlier. The lowest-boiling fraction consisted of 31 g. (41%) of p-chlorotoluene, b.p. 162–163°, n^{25}D 1.5197.

Anal. Calcd. for C_7H_7Cl: C, 66.41; H, 5.57. Found: C, 66.23; H, 5.60.

The second fraction distilled at 132–134° (16 mm.); 12 g. (14%) of unreacted p-chlorobenzyl alcohol was isolated from this distillate by fractional crystallization. This alcohol melted at 70.3–71.2° (recrystallized from 60–68° petroleum ether), no depression on mixed melting point with an authentic sample. The remainder of this fraction (29 g.) consisted of a mixture of p-chlorobenzyl alcohol, p-chlorobenzaldehyde and 2-(p-chlorophenyl)-ethanol. Dehydration of a portion of this mixture with molten potassium hydroxide yielded p-chlorostyrene, isolated and identified as its dibromide, m.p. 42.6–43.8°,[21] recrystallized from 35–60° petroleum ether at the temperature of an acetone–Dry Ice-bath.

Anal. Calcd. for $C_8H_7ClBr_2$: C, 32.2; H, 2.4. Found: C, 32.3; H, 2.4.

The amount of p-chlorobenzaldehyde in the mixture was 3.5 g. (4%), identified as its 2,4-dinitrophenylhydrazone, m.p. 266–267°,[22] recrystallized from ethyl acetate.

Anal. Calcd. for $C_{13}H_9N_4O_4Cl$: C, 48.7; H, 2.8. Found: C, 49.2; H, 3.0.

m-**Trifluoromethylbenzyl Alcohol.**—This alcohol was prepared by hydrolysis of m-trifluoromethylbenzyl chloride.[23] A solution of 115 g. (50% in excess of theory) of sodium carbonate in 850 g. of water in a 3-liter flask was heated to reflux and 273 g. of m-trifluoromethylbenzyl chloride was added during 1 hour. The mixture was allowed to reflux with stirring for 69 hours. After cooling, the organic layer was washed with water until the washings were neutral to litmus and then the alcohol was dried over anhydrous sodium sulfate. Distillation of the dried, crude alcohol yielded 164 g. (73%) of m-trifluoromethylbenzyl alcohol, b.p. 119° at 30 mm., n^{25}D 1.4577. The α-naphthylurethan of this alcohol melted at 124.4–125.4°, recrystallized from 60–68° petroleum ether.

Anal. Calcd. for $C_{19}H_{14}NO_2F_3$: C, 66.1; H, 4.1. Found: C, 66.3; H, 4.2.

This alcohol reacted very slowly with synthesis gas to yield 5 g. (5%) of m-methylbenzotrifluoride, b.p. 127°,[24] n^{25}D 1.4254, and 84 g. of a mixture of unreacted alcohol and m-trifluoromethylbenzaldehyde, b.p. 107–108° at 20 mm. The yield of m-trifluoromethylbenzaldehyde was 2.3 g. (2%), identified as its 2,4-dinitrophenylhydrazone, m.p. 254–257°,[25] recrystallized from ethanol.

Anal. Calcd. for $C_{14}H_9N_4O_4F_3$: C, 47.5; H, 2.6. Found: C, 47.1; H, 2.6.

The remainder of this fraction was presumably unreacted m-trifluoromethylbenzyl alcohol, 81.7 g. (78%), n^{25}D 1.4580, identified as its α-naphthylurethan, m.p. 124.2–125.4°; no depression on mixed melting point with an authentic sample.

Benzyl Alcohol.—The reaction of this alcohol has been reported previously.[2] The products were toluene (63%) and 2-phenylethanol (32%).

m-**Methylbenzyl Alcohol.**—This alcohol was prepared in 87% yield by the lithium aluminum hydride reduction of m-toluic acid. After reaction with synthesis gas, distillation of the mixture yielded: (a) 33 g. (52%) of m-xylene, b.p. 138–140°, identified by its infrared absorption spectrum; (b) a fraction distilling at 98–100° at 7 mm. and consisting of 29 g. (36%) of 2-(m-methylphenyl)-ethanol, identified as its phenylurethan, m.p. 65.1–65.4°,[26] recrystallized from 60–68° petroleum ether, and about 1 g. of m-methylbenzaldehyde (1–2%), identified as its p-nitrophenylhydrazone, m.p. 151–157°,[27] recrystallized from ethanol–water.

(15) I. G. Farbenindustrie A.-G., German Patent 752,478 (1933); C. A., **28**, P1047³ (1934).

(16) P. Ruggli and H. Theilheimer, *Helv. Chim. Acta*, **24**, 899 (1941).

(17) J. J. Blanksma, *Rec. trav. chim.*, **21**, 331 (1902).

(18) V. Deulofeu, R. Labriola and B. Berinzaghi, *J. Org. Chem.*, **12**, 217 (1947).

(19) R. L. Frank, C. W. Adams, R. E. Allen, R. Gander and P. V. Smith, THIS JOURNAL, **68**, 1366 (1946).

(20) J. Sordes, *Compt. rend.*, **195**, 247 (1932).

(21) Reported melting point, 53.5–54°, D. Sontag, *Ann. chim.*, [11] **1**, 359 (1934).

(22) J. Graymore and D. R. Davies, *J. Chem. Soc.*, 294 (1945).

(23) We are indebted to the Hooker Electrochemical Company for a sample of m-trifluoromethylbenzyl chloride and for the directions for its hydrolysis.

(24) J. H. Simons and E. O. Ramler, THIS JOURNAL, **65**, 391 (1943).

(25) H. Gilman, L. Tolman, F. Yeoman, L. A. Woods, D. A. Shirley and S. Avakian, *ibid.*, **68**, 427 (1946).

(26) Reported melting point, 59–60°, M. T. Bogert and P. M. Apfelbaum, *ibid.*, **60**, 930 (1938).

(27) C. W. Shoppee, *J. Chem. Soc.*, 700 (1932).

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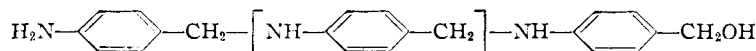
To show that the ester group was inert under reaction conditions, 0.7 mole of ethyl benzoate was treated with 3000 p.s.i. of 1:1 gas at 190° in the presence of a cobalt catalyst. No gas was absorbed, and the only product obtained on distillation was starting material (73%), identified as benzoic acid,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

p-Nitrobenzyl Alcohol.—Ten grams of cobalt(II) acetate tetrahydrate in 30 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-

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

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

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

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

$$\text{H}_2\text{N}-\langle\!\!\!\bigcirc\!\!\!\rangle-\text{CH}_2-\Big[\text{NH}-\langle\!\!\!\bigcirc\!\!\!\rangle-\text{CH}_2\Big]-\text{NH}-\langle\!\!\!\bigcirc\!\!\!\rangle-\text{CH}_2\text{OH}$$

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.

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

BY STANLEY J. CRISTOL AND ROBERT F. HELMREICH

RECEIVED MARCH 17, 1952

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.

(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.

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

(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).