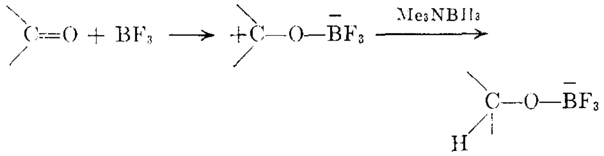
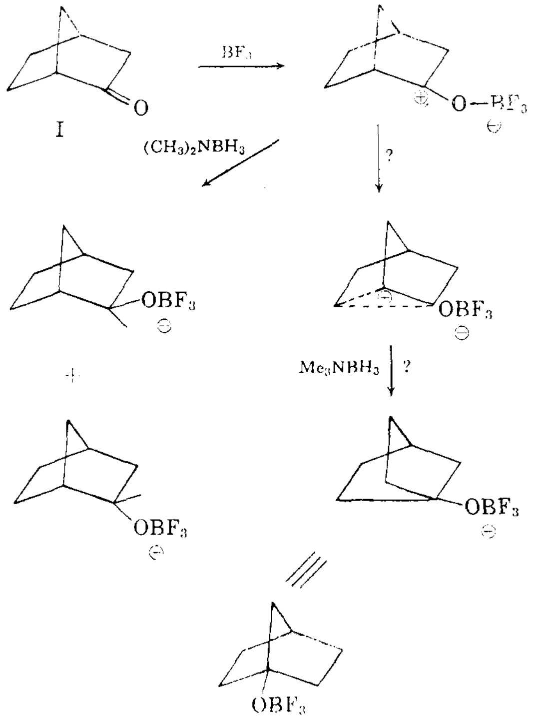
the carbonyl oxygen followed by intermolecular hydride transfer from the amine borane moiety to the electron deficient carbonyl carbon.



$$>C{=}O + BF_3 \longrightarrow {+}C{-}O{-}\overset{-}{B}F_3 \xrightarrow{Me_3NBH_3} \underset{H}{>}C{-}O{-}\overset{-}{B}F_3$$

In view of the apparent mechanism of this reaction and the known facile rearrangements of bicyclo-[2.2.1]heptanes with electron deficiencies at the number two position,[2] we felt that it would be interesting to examine the products resulting from the reduction of norcamphor (I) with this system. Thus, although predominant attack of the amine borane at the number two position was anticipated, it was felt that a real possibility existed for attack at the number one carbon with concomitant rearrangement. This, of course, would lead to the isomeric 1-norcamphanol (II).



II

1-Norcamphanol was therefore synthesized for comparison and the reduction of norcamphor with trimethylamine borane and boron fluoride effected. Gas chromatographic analysis of the resulting products showed no detectable 1-norcamphanol. Thus, despite the fact that an appreciable positive charge is apparently generated at C-2 and despite the fact that the hydride is predominately transferred from an *exo* conformation (approximately 90% by g.l.p.c.), there apparently does not exist enough positive charge at C-1 to lead to any appreciable hydride transfer to this position.

EXPERIMENTAL

exo- and endo-norborneol. The *exo*-isomer was synthesized for comparison purposes by the method of Komppa and Beckmann[3]; m.p. 127–128.5°; reported m.p. 127–128°.

endo-norborneol was synthesized by the method of Alder and Rickert[4]; m.p. 149–150°; reported m.p. 149–150°.

1-Norcamphanol (m.p. 154.5–155.5°; reported[5] m.p. 155–156.5°) was prepared according to the method of Whelan[5] from the corresponding carboxylic acid. The crude acid used in the reaction was obtained by dissolving the corresponding carboxamide (prepared by the method of Boehme,[6] m.p. 231–233°; reported[6] m.p. 234–236°) in glacial acetic acid, adding a few drops of concentrated hydrochloric acid and a five-fold excess of sodium nitrite in water. The mixture was warmed on a steam bath until nitrogen evolution ceased. The mixture was then poured into water and extracted with ether. The ether was washed several times with water and then dried over sodium sulfate. The ether was removed by distillation through a Vigreux column. The crude acid was then used directly in the Curtius reaction as described by Whelan.[5]

Method of reduction. Reductions were effected with trimethylamine borane in the presence of boron fluoride etherate in dry diglyme solvent according to the method previously reported.[1] The reductions were studied in both hot (steam bath) and cold (to 0°) solution. In no case was there detected any trace of 1-norcamphanol.

Analyses of the reduction mixtures. Reaction mixtures from the reductions were worked up in the normal manner.[1] The products were examined by g.l.p.c. using an eighteen foot column of F. and M. prepared Tide in a Perkin-Elmer 154-B vapor fractometer at 159° and an internal pressure 12 p.s.i. Before using the packed column, it was baked at 190° for 24 hr. in a slow stream of Helium. Under the conditions specified the following retention times (from the air peak) were observed: norcamphor—10.0 min.; 1-norcamphanol—12.4 min.; *endo*-norborneol—13.4 min.; *exo*-norborneol—14.2 min.

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[2] *E.g.*, see E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Henry Holt, New York, 1959, p. 594.

[3] G. Komppa and S. Beckmann, *Ann.*, **512**, 172 (1934).

[4] K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1940).

[5] W. P. Whelan, Jr., dissertation, Columbia University, 1952.

[6] W. R. Boehme, *J. Am. Chem. Soc.*, **80**, 4740 (1958).

Cyanoethylation of Bisphenols

J. R. HOLSTEN

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Two previously unreported dinitriles, bis[*p*-(2-cyanoethoxy)phenyl]methane and 2,2-bis[*p*-(2-cyanoethoxy)phenyl]propane, have been prepared by dicyanoethylation of the corresponding bisphenols, bis(4 - hydroxyphenyl)methane and 2,2 - bis(4-hydroxyphenyl)propane (Bisphenol A). The corresponding new diamines, bis[*p*-(3-aminopropoxy)-

phenyl]methane and 2,2-bis[*p*-(3-aminopropoxy)phenyl]propane, were prepared by hydrogenation of the dinitriles.

The general procedure adopted for these preparations is a modification of that of Cook, and Reed[1] They described the cyanoethylation of phenol and the dicyanoethylation of such compounds as 4,4′-dihydroxybiphenyl and the various dihydroxybenzenes and naphthalenes. "Undue" polymerization of acrylonitrile was encountered during cyanoethylation of phenolic compounds at 120–140° using either sodium metal or trimethylbenzylammonium hydroxide as the basic cyanoethylation catalyst. However, with sodium methoxide as catalyst, polymerization of the acrylonitrile was only slight.

In the present cyanoethylation procedure, sodium *t*-butoxide was used as the basic catalyst. It was thought that this catalyst, because of its greater basicity, might be more effective than the sodium methoxide. A large excess of acrylonitrile was used to insure dicyanoethylation of the bisphenol and also to serve as the solvent. Cuprous chloride was added as a stabilizer[2] for the acrylonitrile, although the necessity of this addition was not demonstrated.

Catalytic hydrogenations of the two dinitriles to the corresponding diamines were carried out in 1,2-dimethoxyethane over Raney cobalt. When hydrogenation was complete, the diamines had remarkable thermal stability, showing no signs of decomposition during distillation at pot temperatures up to 250°. Some decomposition was encountered, however, during distillation of diamine samples obtained from hydrogenations in which less than the theoretical amount of hydrogen had been absorbed. Both distilled diamines solidified slowly on standing at room temperature.

The purity of the bis [*p*-(3-aminopropoxy)-phenyl] methane obtained is somewhat dubious as indicated by a very low nitrogen analysis. However, a sample of this material did undergo condensation polymerizations typical of diamines.

EXPERIMENTAL[3]

2,2-Bis[p-(2-cyanoethoxy)phenyl] propane. The autoclave for the cyanoethylations consisted of two 1-l. glass resin pots clamped together at their flanges so that one served as a lid. The bottoms of the pots were rounded for improved structural strength. A neoprene gasket was clamped between the two ground glass surfaces. The bottom pot was adapted with a thermowell extending from its upper side wall to a point near the middle bottom of the pot. The reactor top held a side U-arm attached to a pressure gauge. The U-arm was filled with mineral oil. Another side arm on the reactor top was attached to a safety valve set at 50 p.s.i.g. Stirring was provided by a Teflon-coated magnetic stirring bar.

Bisphenol A (m.p. 160.5–162°), 91.2 g. (0.40 mole), 0.8 g. of sodium *t*-butoxide, and 4.0 g. of cuprous chloride were added to the autoclave. Cautious addition of 400 ml. (6 moles) of cold, distilled, unstabilized acrylonitrile to the solid mixture caused an extremely vigorous reaction. However, the reaction subsided quickly. After the autoclave was closed, the reaction mixture was stirred and heated to 100° during 1 hr. and then heated under autogenous pressure (13.5–20 p.s.i.g.) at 104 ± 4° for 17.5 hr. before being cooled to room temperature. It is believed that improved yields of the dinitrile might be obtained by operating at a higher temperature. This possibility was not investigated because of leaks around the gasket in the autoclave at higher pressures.

The reaction mixture was stripped of unchanged acrylonitrile and the residue taken up in 500 ml. of chloroform. The mixture was filtered, and the filtrate was washed successively with five 100-ml. portions of 5% aqueous sodium hydroxide, two 125-ml. portions of 5% hydrochloric acid, and 250-ml. portions of water until the last washing was neutral to *p*Hydrion paper. The washed organic solution was dried over anhydrous sodium sulfate, filtered, and stripped of solvent, leaving 98.6 g. of a buff-colored solid. This residue was recrystallized from 500 ml. of absolute ethanol after treatment with decolorizing carbon (Nuchar 190-C). The yield of slightly buff-colored 2,2-bis[*p*-(2-cyanoethoxy)phenyl] propane, m.p. 78–79°, was 80.3 g. After two recrystallizations from 300-ml. portions of a 5:2 by volume mixture of carbon tetrachloride and absolute ethanol, the pure product, 74.6 g., melted at 80.0–80.5°.

Anal. Calcd. for $C_{21}H_{22}N_2O_2$: C, 75.42; H, 6.63; N, 8.38. *Found*: C, 75.72; H, 6.41; N, 8.28.

Recovery of the unreacted phenols by acidification of the basic washings was not investigated.

2,2-Bis[p-(3-aminopropoxy)phenyl]propane. One hundred and sixty-four grams (0.49 mole) of the above purified dinitrile, 250 ml. of 1,2-dimethoxyethane, 25 g. of Raney cobalt, and 97 g. (5.7 moles) of ammonia were charged to a 1410-ml. Aminco hydrogenation bomb. The hydrogenation proceeded smoothly between 48–118° while at 2900–3200 p.s.i.g. The catalyst was removed by filtration under a nitrogen blanket, and the solvent was removed under reduced pressure. There remained 163 g. of a very viscous, caramel-colored liquid. Distillation of this liquid through a simple Claisen-type distilling head gave 138 g. of clear, colorless, viscous 2,2-bis[*p*-(3-aminopropoxy)phenyl]propane, b.p. 216–217.5°/0.4 mm.

Anal. Calcd. for $C_{21}H_{30}N_2O_2$: C, 73.65; H, 8.83; N, 8.18. Found: C, 73.79; H, 8.22; N, 8.12.

Bis[p-(2-cyanoethoxy)phenyl]methane. The cyanoethylation of bis(4-hydroxyphenyl)methane[4] was carried out under essentially the same conditions as described above. A mixture of 60 g. (0.3 mole) of bis(4-hydroxyphenyl)methane (m.p. 159–160°), 0.6 g. of sodium *t*-butoxide, 3.0 g. of cuprous chloride, and 300 ml. (4.5 + moles) of acrylonitrile was stirred at 104 ± 4° (20–23 p.s.i.g.) for 17.5 hr. After the unchanged acrylonitrile was removed, the residue was taken up in 425 ml. of chloroform, filtered, and the filtrate washed as before. The residue, after removal of the chloroform, was recrystallized successively from 125 ml. of 4:1 dioxane-water, 110 ml. of dioxane, and 50 ml. of dioxane. The yield of colorless bis [*p*-(2-cyanoethoxy)phenyl]methane, m.p. 115.5–116.0°, was 30.3 g. An additional 11.0 g. of pure product was obtained by evaporation of the mother liquors and recrystallization of the residue. An analytical sample of bis-[*p*-(2-cyanoethoxy)phenyl]methane, m.p. 117.0–117.2°, was obtained by further recrystallizations, first from ethyl acetate and then from a 5:5:2 dioxane-ethanol-water solution.

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(1) A. H. Cook and K. J. Reed, *J. Chem. Soc.*, 920 (1945).

(2) I. G. Farbenindustrie A.-G., Brit. Patent **457,621** (December 2, 1936); *Chem. Abstr.*, **31**, 3068 (1937).

(3) All melting points and boiling points are uncorrected. Elemental analyses were by the Chemstrand Research Center Analytical Laboratories.

(4) This bisphenol was prepared by the procedure of W. Staedel, E. Haase, and E. Moyat, *Ann.*, **283**, 163 (1894).

Anal. Calcd. for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.15. Found: C, 74.60; H, 5.69; N, 8.99.

Bis[p-(3-aminopropoxy)phenyl]methane. The above purified dinitrile, 30.3 g., was dissolved in 500 ml. of 1,2-dimethoxyethane and hydrogenated as in the preceding hydrogenation. Ten grams of freshly prepared Raney cobalt catalyst and 115 g. (7 moles) of ammonia were used. The hydrogenation proceeded smoothly between 84–116° while at 3280–3460 p.s.i.g. The crude diamine was flash-distilled at 0.5 mm. All distillate, boiling up to 240° was collected. This clear, colorless distillate was redistilled through a 4″-Vigreux column (Mini-Lab) at 0.5 mm. pressure. Nineteen and one-half grams of distillate boiling at 219–222° was collected.

Anal. Calcd. for $C_{19}H_{26}N_2O_2$: N, 8.91. Found: N, 7.70.

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Acid Constants of Heteroannular Substituted Ferrocenoic Acids

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Since we reported the use of *N,N*-diphenylcarbamyl chloride as a useful reagent for preparation of ferrocenoic acid and its heteroannular substituted derivatives,[2] several additional ferrocenoic acids have been prepared and their pK_a values determined in 50% ethanol.

Although 1-benzoyl-1′-diphenylcarbamylferrocene was not reduced by hydrogen at 45 p.s.i. in ethyl acetate over palladium on charcoal for ten hours, it was readily reduced with sodium borohydride to 1-(α-hydroxybenzyl)-1′-diphenylcarbamylferrocene (II). Hydrolysis of II yielded 1-(α-hydroxybenzyl)-1′-ferrocenoic acid (III), and catalytic reduction of III gave 1-benzyl-1′-ferrocenoic acid (IV).

The pK_a values of III and IV, along with values determined for other previously prepared acids[2] are listed in Table I. Nesmeyanov[3,4] had previously reported pK_a values for some of these and other acids in 68% methanol. Table I lists the values from Nesmeyanov for comparison.

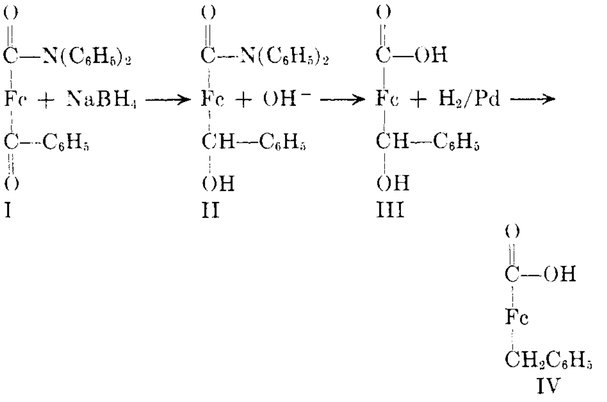
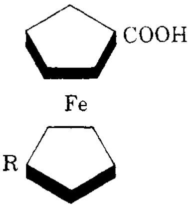


TABLE I

pK_a VALUES OF SUBSTITUTED FERROCENOIC ACIDS IN 50% ETHANOL AT 24°



R	pK_a, 50% Ethanol	pK_a 68% Methanol[3,4]
$-C_2H_5$	6.34 ± 0.01	6.43
$-CH_2C_6H_5$	6.25 ± 0.01	—
—H	6.11 ± 0.01	6.29
$-COC_6H_5$	5.90 ± 0.04	—
$-CH(OH)C_6H_5$	5.84 ± 0.01	—
$-COCH_3$	5.76 ± 0.02	5.90

pK_a for benzoic acid in 50% ethanol at 25°, 5.68[5]

It can be seen that the acid strengths of the substituted ferrocenoic acids vary in the expected manner according to the electron donating or withdrawing properties of the substituent. Further, a plot of our pK_a values against Hammett *para* sigma constants[5,6a] yielded a satisfactory straight line of slope 0.74. Nesmeyanov's values for 68% methanol similarly treated gave a slope of 0.81.

Although sigma constants are not known for the α-hydroxybenzyl group,[6b] it does appear that the α-hydroxybenzylferrocenoic acid is out of line with

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(1) Taken in part from a Ph.D. dissertation of Robert Eisenthal submitted to the University of North Carolina, January 1961.

(2) W. F. Little and R. Eisenthal, *J. Am. Chem. Soc.*, **82**, 1577 (1960).

(3) A. N. Nesmeyanov and O. A. Reutov, *Doklady Akad. Nauk., S.S.S.R.*, **115**, 518 (1957).

(4) A. N. Nesmeyanov and O. A. Reutov, *Izvest. Akad. Nauk., S.S.S.R.*, 926 (1959); *Chem. Abstr.*, **54**, 469 (1960).

(5) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(6)(a) Sigma constants are available for but four of the substituent groups used; acid constants are not reported for benzylbenzoic acid or α-hydroxybenzylbenzoic acid. (b) A reasonable estimate for the Hammett *para* sigma constant is +0.012. T. Kuwana, D. E. Bublitz, and G. Hoh, *J. Am. Chem. Soc.*, **82**, 5811 (1960), have reported chronopotentiometric quarter wave potentials, $E_{\frac{1}{4}}$, for a number of substituted ferrocenes, including α-hydroxybenzylferrocene. While these workers reported correlation of the quarter wave potentials with Taft polar sigma constants, we have found that the data are correlated much better with Hammett *para* sigma constants, and from such a plot the *para* sigma for the α-hydroxybenzyl group can be obtained as approximately +0.012. Using this value, our acid constant for α-hydroxybenzylferrocenoic acid does not fit on the line; it is a much stronger acid than predicted.