accord with the supposition that here, as with other pseudo bases, ethers are formed.

When solutions in methyl alcohol of the ethyl or *n*-butyl ethers of I are heated, the methyl ether is produced. Likewise the methyl ether is converted to the ethyl ether in hot ethyl alcohol. Interconversion of other pseudo base ethers has been reported.[3–5,20]

The ethers are readily cleaved by acid, giving the alcohol and 1,2,3-triphenylquinoxalinium salt. For example, when the *n*-butyl ether is dampened with aqueous ethanol containing hydrochloric acid (*ca.* 4*N*), the odor of *n*-butyl alcohol is noticeable after only fifteen seconds. If the ethyl or *n*-butyl ether is dissolved in aqueous ethanol about 2*N* in hydrochloric acid, the solution, after standing at room temperature for five minutes, yields a precipitate of the pseudo base, I, when diluted with water and made alkaline. The methyl ether is cleaved less rapidly under these conditions, requiring about thirty minutes.

Pseudo base I was first made by Kehrmann and Messinger,[16] who crystallized the crude product twice from boiling ethyl alcohol. The color and melting point reported for the crystallized product suggest that it could have consisted partly of the pseudo base ethyl ether. Indeed, crystallization must be carried out quickly if ether formation is to be avoided. If the ethyl alcohol solution of I is boiled more than three minutes, the product which crystallizes consists of the ether. It is possible that other workers also overlooked an unsuspected reaction of quinoxaline pseudo bases with alcohol. For example, the analytical data given by Jacobson[13–15] for his pseudo bases, all of which were crystallized from ethyl alcohol, do not exclude the possibility that some of his products were actually the ethyl ethers.

Although pseudo bases are generally written as carbinols, many of them conceivably could exist in an alternative, open form having a carbonyl group rather than hydroxyl.[21] The absence of a carbonyl band and presence of a hydroxyl band in the infrared spectrum of I rules out the open structure *N*-phenyl-*N'*-α-phenylphenacylidine-*o*-phenylenediamine.

EXPERIMENTAL

Melting points of the pseudo base, I, and its ethers depend on the rate of heating and therefore are of limited use for characterization. The data given first were obtained using the Fisher-Johns apparatus. The sample was heated in 5 min. to within 5° of initial melting. Rate of heating was then 1° per min. until melting started. The rate was then reduced to 0.5° per min. The data in parentheses were obtained using a hot stage with temperature gradient (Kofler-Heizbank, made by Reichert Co., Austria). The sample was dropped on the preheated stage. The approximate minimum temperature at which rapid melting occurred was recorded. Below this temperature, melting was slow and due, presumably, to decomposition. Above this temperature, melting occurred at about the same rate as for pure, stable compounds above their melting points. The temperatures determined in this way should be much closer to the true melting points than those found by slow heating.

1,2-Dihydro-1,2,3-triphenyl-2-quinoxalinol (I) was made as described previously[16] except that the pseudo base was precipitated using potassium hydroxide solution rather than ammonia, and the crude product was crystallized three times from 1:1 cyclohexane-benzene rather than from ethyl alcohol. The brilliant yellow crystals are not fluorescent; m.p. 143–147° (195°).

Anal. Calcd. for $C_{26}H_{20}ON_2$: C, 82.95; H, 5.36; N, 7.44. Found: C, 82.9; H, 5.5; N, 7.2.

1,2-Dihydro-2-methoxy-1,2,3-triphenylquinoxaline. Three grams of I was dissolved in 100 ml. of boiling methyl alcohol. After 4 min., crystals of the product formed. Boiling was continued for another minute. The product (2.88 g.) was separated from the cooled mixture and recrystallized from methyl alcohol. The very pale yellow crystals fluoresce brilliant blue; m.p. 143–147° (175°).

Anal. Calcd. for $C_{27}H_{22}ON_2$: C, 83.05; H, 5.68; N, 7.18. Found: C, 83.4; H, 5.4; N, 7.4.

1,2-Dihydro-2-ethoxy-1,2,3-triphenylquinoxaline. A solution of 3 g. of I in 60 ml. of absolute ethyl alcohol was boiled for 7 min The product (1.38 g.) which crystallized from the cooled solution was recrystallized from ethyl alcohol. The pale yellow crystals fluoresce brilliant blue; m.p. 126–129° (145°).

Anal. Calcd. for $C_{28}H_{24}ON_2$: C, 83.14; H, 5.98; N, 6.93. Found: C, 83.2; H, 5.6; N, 6.9.

2-n-Butoxy-1,2-dihydro-1,2,3-triphenylquinoxaline. A solution of 3 g. of I in 18 ml. of *n*-butyl alcohol was boiled for 10 min. The product (3.15 g.) which crystallized from the cooled solution was recrystallized from *n*-butyl alcohol. The light yellow crystals fluoresce brilliant blue-green; m.p. 118–121° (140°).

Anal. Calcd. for $C_{30}H_{25}ON_2$: C, 83.30; H, 6.52; N, 6.48. Found: C, 83.6; H, 6.6; N, 6.5.

Interconversion of the ethers of I. Solutions of the ethyl and *n*-butyl ethers in methyl alcohol were heated at 70° for 2 and 5 hr., respectively. Crystals of the methyl ether formed during the heating. The product was identified by its infrared spectrum. A solution of the methyl ether in absolute ethyl alcohol was heated 6 hr. at 70°. The cooled solution gave crystals of the ethyl ether, identified by their infrared spectrum.

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[20] A. Werner, *Ber.*, **34**, 3300 (1901).

[21] R. C. Elderfield, *Heterocyclic Compounds*, Vol. 4, R. C. Elderfield, ed., Wiley, New York, 1952, Chap. 1, p. 232.

An Attempted Reductive Rearrangement of Norcamphor

W. M. JONES

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A recent examination[1] of the stereochemistry of the reduction of 4-*t*-butylcyclohexanone with trimethylamine borane in the presence of boron fluoride led to the conclusion that the reduction proceeds by an initial attack of the boron fluoride on

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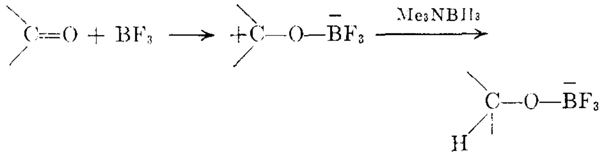
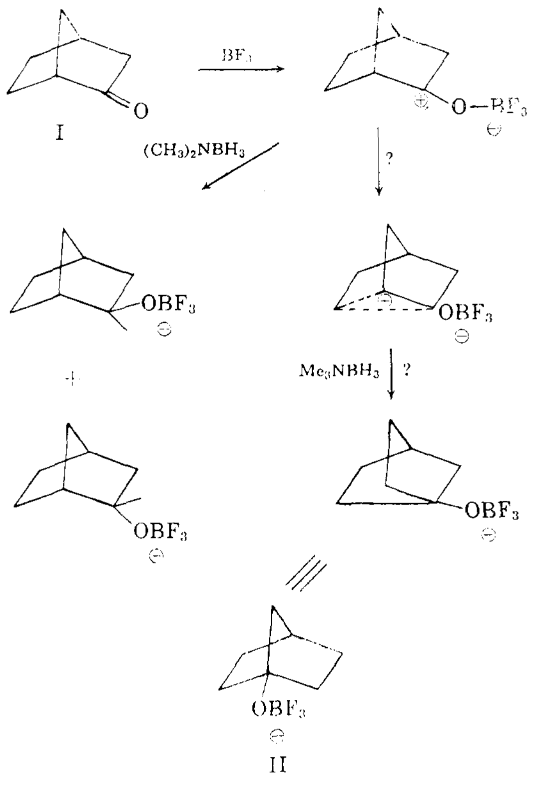
[1] W. M. Jones, *J. Am. Chem. Soc.*, **82**, 2528 (1960).

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



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

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).



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)-