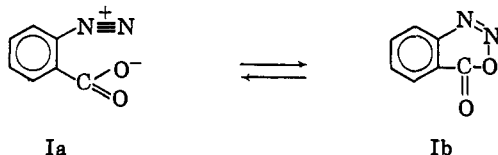


BENZYNES via APROTIC DIAZOTIZATION OF ANTHRANILIC ACIDS: A CONVENIENT SYNTHESIS OF TRIPTYCENE AND DERIVATIVES

Sir:

Benzynes have been generated under aprotic conditions by fragmentation of suitably *ortho* disubstituted benzenes.¹ Most of these methods suffer from either limited availability of "benzynes" precursor, cumbersome experimental techniques and/or low yields of desired product. As a result "benzynes" has not found widespread use as a synthetic intermediate.

It has been found that *anthranilic acids* are readily diazotized by alkyl nitrites² in aprotic media^{3a,b} to give presumably I (a and b) which undergoes fragmentation to benzyne, nitrogen and carbon dioxide.



The intermediacy of benzyne was demonstrated by entrapping with anthracene to form triptycene in *isolated yields* of 50–75%.

Reaction can be effected by slow addition of a solution of the anthranilic acid to a refluxing stirred solution of alkyl nitrite and benzyne acceptor. Gas evolution occurs immediately and ceases within a few minutes after the addition is complete. If the reactants are mixed at once a vigorous reaction ensues and the yields of desired product are greatly diminished, *e.g.*, triptycene 9–16% *via* g.l.c. This probably is a result in part of the reaction of benzyne with unreacted anthranilic acid.^{1d} When higher boiling solvents are used (acetonitrile, dioxane, benzene) it is somewhat advantageous to add alkyl nitrite concurrently with the solution of anthranilic acid to minimize the thermally induced decomposition of the nitrite.⁴

1,4-Epoxy-1,4-dihydronaphthalene,^{5a} 1-methyl- and 1,4-dimethyl-1,4-epoxy-1,4-dihydronaphthalenes^{5b} were prepared from anthranilic acid, amyl nitrite and a one molar excess of the corresponding furan in yields of 75–88%.

Aprotic diazotization of 5-bromoanthranilic acid⁶ (22 mmoles) in acetonitrile containing anthracene (51 millimoles) gave 2-bromotriptycene, m.p. 168.5–169° in 75% yield.^{7a,b}

(1) (a) E. LeGoff, *J. Am. Chem. Soc.*, **84**, 3786 (1962); (b) L. Horner and H. Bruggeman, *Ann.*, **635**, 22 (1960); (c) J. A. Kampmeier and E. Hoffmeister, *J. Am. Chem. Soc.*, **84**, 3787 (1962); (d) M. Stiles and R. G. Miller, *ibid.*, **82**, 3802 (1960); (e) R. S. Berry, G. N. Spokes and M. Stiles, *ibid.*, **82**, 5240 (1960); **84**, 3750 (1962); (f) M. Stiles, U. Burckhardt and A. Haag, *J. Org. Chem.*, **27**, 4715 (1962); (g) G. Wittig and H. F. Ebel, *Angew. Chem.*, **72**, 564 (1960); *Ann.*, **650**, 20 (1961); (h) G. Wittig and R. W. Hoffmann, *Angew. Chem.*, **73**, 435 (1961).

(2) Anthranilic acid reacts with isoamyl nitrite in methanol (trace of sodium methoxide) at –10° to give a mixture of orange and yellow crystals (~50% yield) which reacts with anthracene in aprotic media to give triptycene in low yield. Private communication: D. F. Farnum, *cf. ref. 1d*.

(3) (a) Refluxing dichloromethane, acetone, tetrahydrofuran, 2-butanone, acetonitrile, etc.; (b) preliminary experiments with 3-amino-2-naphthoic acid, 5-nitroanthranilic acid and 3-aminoisocotinic acid indicate that the corresponding arynes are generated in high yield.

(4) Anthracene (1.0 g.) and amyl nitrite (1.5 ml.) in refluxing acetonitrile (50 ml.) evolved brown fumes (nitrogen dioxide, presumably from nitric oxide and air) and gave an unidentified base-soluble product (0.15 g.).

(5) (a) G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1349 (1956); (b) E. Wolthuis, *J. Org. Chem.*, **26**, 2215 (1961).

(6) A. S. Wheeler and W. M. Oates, *J. Am. Chem. Soc.*, **32**, 77 (1910).

(7) (a) Analytic values for all the compounds described in this paper were consistent with the indicated structures; (b) the presence of about 10% 1-bromotriptycene was indicated by g.l.c. Products (1- and 2-bromotriptycenes) and proportions were identical (infrared, g.l.c. retention volumes, etc.) with material prepared from 2-(phenyliodonium)-5-bromophenyl-carboxylate (*cf. LeGoff, ref. 1a.*) which was prepared from the same 5-bromoanthranilic acid. The presence of 3-bromo isomer (~10%) was demonstrated by decarboxylation of the acid which gave a mixture of *ortho*- (~10%) and *para*- (~90%) bromoanilines (g.l.c.)

2-Methyltriptycene (m.p. 173.5–174°)⁸ was prepared in 50% yield from 5-methylanthranilic acid (30 mmoles), anthracene (56 millimoles) and amyl nitrite (55 mmoles) in acetonitrile.

9-Carbomethoxytriptycene⁹ and 9-triptaldehyde⁹ were prepared in moderate yields (~50%) in a one-step synthesis from the respective 9-carbomethoxy- and 9-formylanthracenes and anthranilic acid–amyl nitrite. The desired products were easily separated from unreacted anthracenes by treating the reaction mixture with N-ethylmaleimide, followed by column chromatography over alumina.

Preparation of Triptycene.—A solution of anthranilic acid (20 g., 0.146 mole) in acetone or tetrahydrofuran (110 ml.) was added during 4 hr. to a refluxing mixture of anthracene (>98%, 25 g., 0.140 mole) and amyl nitrite (18.5 g., 0.158 mole) in dichloromethane (400 ml.). The dichloromethane and other volatile products (amyl alcohol) were removed by distillation and replaced by xylene (~200 ml.). Maleic anhydride (10 g.) was added and the xylene solution refluxed 15 min., allowed to cool somewhat, added to cold water (600 ml.) and diluted with dichloromethane. The lower organic layer was extracted several times with 15% aqueous potassium hydroxide, evaporated to dryness, and the brown crystalline residue washed with cold methanol and pentane to give pale yellow to light brown triptycene 22 g. (59%). Recrystallization from methylcyclohexane (charcoal) afforded pure (g.l.c.) white material, m.p. 253–254° (19.1 g. first crop).

F. M. L. is now engaged in utilizing this technique for the synthesis of mono- and disubstituted triptycenes in conjunction with the study of electrophilic substitution on triptycenes.

(8) Identical with authentic material: R. L. Litle and F. M. Logullo, unpublished data.

(9) Previously prepared in a six-step synthesis: P. D. Bartlett and F. D. Greene, *J. Am. Chem. Soc.*, **76**, 1088 (1954).

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THE ISOMERIZATION OF ALLYL ALCOHOLS WITH COBALT HYDROCARBONYL

Sir:

The recent report¹ mentioning, without experimental detail, the isomerization of allyl alcohol to propionaldehyde by iron pentacarbonyl prompts us to describe a similar isomerization with cobalt hydrocarbonyl, which we have been studying for the last several years.

Previous work in this Laboratory² showed that olefins are rapidly isomerized by cobalt hydrocarbonyl at room temperature under one atmosphere of carbon monoxide. The isomerization is a catalytic reaction but the hydrocarbonyl is consumed by the competitive hydroformylation of the olefin. By small changes in relative concentrations it is possible to vary the rate of either reaction. Allyl alcohol (and its derivatives) is a particularly attractive substrate for isomerization–hydroformylation competition studies because, should isomerization occur, the isomerized product would tautomerize rapidly to propionaldehyde and thus equilibrium reactions are unlikely.

The results of reactions between allyl (and substituted allyl) alcohol and cobalt hydrocarbonyl are shown in Table I.

When the experiment with allyl alcohol was duplicated except that DCo(CO)₄ was used in place of HCo(CO)₄, the propanol was found by n.m.r. spectroscopy to be

(1) G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, **84**, 4591 (1962).

(2) G. I. Karapinka and M. Orchin, *J. Org. Chem.*, **26**, 4187 (1961).