## 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 "benzyne" precursor, cumbersome experimental techniques and/or low yields of desired product. As a result "benzyne" has not found widespread use as a synthetic intermediate.

It has been found that *anthranilic acids* are readily diazotized by alkyl nitrites[2] in aprotic media[3a,b] to give presumably I (a and b) which undergoes fragmentation to benzyne, nitrogen and carbon dioxide.



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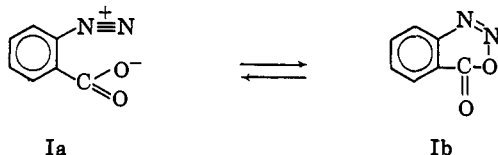
The intermediacy of benzyne was demonstrated by entrapping with anthracene to form triptycene in *isolated yields* of 50–75%.

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 acid[6] (22 mmoles) in acetonitrile containing anthracene (51 millimoles) gave 2-bromotriptycene, m.p. 168.5–169° in 75% yield.[7a,b]

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-Carbomethoxytriptycene[9] and 9-triptaldehyde[9] 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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(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-aminoisonicotinic 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-bromophenylcarboxylate (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.)

## THE ISOMERIZATION OF ALLYL ALCOHOLS WITH COBALT HYDROCARBONYL

Sir:

The recent report[1] 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 Laboratory[2] 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. L. Karapinka and M. Orchin, J. Org. Chem., 26, 4187 (1961).

TABLE I
THE REACTION OF ALKYL ALCOHOLS WITH COBALT HYDROCARBONYL (1 ATM. CO, 25°)

| Alcohol Structure | mmoles | HCo(CO)₄, mmoles | Gas absorbed, mmoles | Products Compound | mmoles | Yield, % |
|---|---|---|---|---|---|---|
| $CH_2=CHCH_2OH$ | 9.0 | 4.65 | 0.7 | $CH_3CH_2CHO$ | 1.9 | 21[a] |
| | | | | $CH_2=CH(CH_2)_2CH=CH_2$ | Trace | |
| | | | | Hydroxyaldehyde[b] | 0.7[c] | 30[c,d] |
| $CH_3CH=CHCH_2OH$ | 16.5 | 3.3 | −1.1[e] | $CH_3CH_2CH_2CHO$ | 0.5 | 3.0[a] |
| $CH_2=CHCHOHCH_3$ | 30 | 6.2 | 2.0 | $CH_3CH_2COCH_3$ | 1.1 | 3.7[a] |
| | | | | Hydroxyaldehyde[b] | 2.9[f] | 94[d] |
| $CH_2=CHCOH(CH_3)_2$ | 23 | 4.6 | 1.6 | Hydroxyaldehyde[b] | 1.1[f] | 48[d] |

[a] Based on starting alcohol. [b] Not identified. [c] Estimated from gas absorption. [d] Based on starting HCo(CO)₄ and the following stoichiometry: 2HCo(CO)₄ + alcohol + CO → products. [e] This gas was evolved. Approximately 3 mmoles of starting material was unaccounted for which may have gone to products or complexes with accompanying CO evolution. [f] By Fritz analysis.[3]

exclusively $CH_2DCH_2CHO$. This fact and the data of Table I may be rationalized on the basis of the 1,3-hydrogen shift previously proposed[2] for the olefin isomerization, which when applied to the allyl alcohols may be written

$$CH_2=CHCH_2OH \ + \ DCo(CO)_4 \ \longrightarrow$$





$$\longrightarrow HCo(CO)_4$$
$$+$$
$$CH_2DCH=CHOH \rightarrow CH_2DCH_2CHO$$
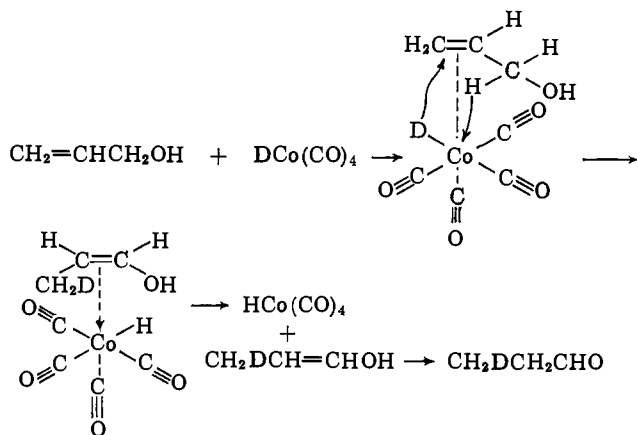
The failure to secure any isomerization with $CH_2=CHCOH(CH_3)_2$ (Table I) may be ascribed to the absence of an allylic hydrogen.

Although the products (hydroxyaldehydes, hemiacetal, dihydrofuran or its polymers) which would result from hydroformylation were not isolated or identified, hydroformylation requires CO absorption and the formation of $Co_2(CO)_8$, both of which were observed.

When $CH_2=CHCH_2OD$ was treated with HCo(CO)₄ and the propanol isolated and examined, the n.m.r. spectrum definitely indicated the absence of $CH_3CHD-CHO$ which might have been expected on the basis of the above mechanism. However, rapid exchange of the enolic form, either with HCo(CO)₄ or possibly with the α-methylene of the deuterated allyl alcohol may have occurred. The n.m.r. spectrum did not completely exclude the possibility of trace amounts of $CH_2DCH_2CHO$ nor was a deuterium balance attempted.

The allyl alcohol was injected into a 50-ml. flask containing an octane solution of HCo(CO)₄ under CO. The solution was stirred rapidly at room temperature until all the HCo(CO)₄ disappeared,[4] usually about 10 min. Triphenylphosphine was added to remove the cobalt complexes from solution and the supernatant solution was removed and analyzed by vapor phase chromatography (v.p.c.). DCo(CO)₄ was prepared by exchange of HCo(CO)₄ in octane solution with pure D₂O.[5] After treatment of the allyl alcohol with DCo-(CO)₄, the propanol was removed by vacuum distillation and purified by v.p.c. The n.m.r. spectrum was obtained with a CCl₄ solution, using the Varian A-60 instrument. The methylene produced a complex

triplet centered at 138 c.p.s. from the Si(CH₃)₄ band. The n.m.r. spectrum of the propanal from treatment of $CH_2=CHCH_2OD$ with HCo(CO)₄ showed a triplet centered at 578 c.p.s. due to the carbonyl hydrogen.

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## DIHYDROFULVALENE

*Sir:*

Small amounts of a deep red hydrocarbon, not further characterized, have been reported to accompany dehydroisodicyclopentadiene (II) when the latter is prepared by gas-phase dehydration of 1-dicyclopentadienol (I) over alumina at 260°.[1] We have found that a deep red hydrocarbon (III), presumably the same substance, may be obtained in about 30% yield and a good state of purity by steam-distilling a mixture of I and dilute aqueous acid, and have shown III to be 1,2-dihydrofulvalene.



I      II[2]      III
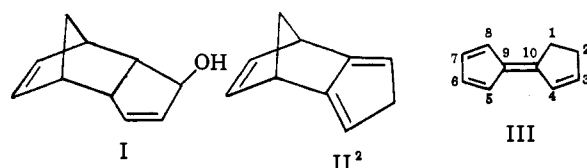
When a solution of I[3] in a minimum of carbon tetrachloride is added dropwise to boiling 0.2% aqueous tartaric acid, and the distillate, after rectification through a 36-cm. vacuum-jacketed Vigreux column, is passed continuously through carbon tetrachloride, III accumulates in the organic phase. The use of a less acidic aqueous solution leads to significant distillation of starting alcohol while a more acidic solution causes excessive formation of a tan, insoluble polymer. The fulvene is very oxygen-sensitive,[4] and the entire operation must be conducted in an atmosphere of prepurified nitrogen. The solution of III was dried over anhydrous magnesium sulfate, and polar impurities were removed by passing it through a short (ca. 5 cm.) column of silica gel. Removal of the solvent at 10–15 mm. pressure and room temperature left a deep red oil, the infrared spectrum of which showed no detectable impurities. The hydrocarbon could be evaporatively distilled, with some loss, under high vacuum at room

(3) J. S. Fritz, S. S. Yamamura and E. C. Bradford, *Anal. Chem.*, **31**, 260 (1959).
(4) R. W. Goetz and M. Orchin, *J. Org. Chem.*, **27**, 3698 (1962).
(5) G. L. Karapinka, Ph.D. Dissertation, University of Cincinnati, 1962.

(1) K. Alder, F. H. Flock and P. Janssen, *Ber.*, **89**, 2689 (1956).
(2) The conclusions of Alder, Flock and Janssen regarding the location of the double bonds in II and in isodicyclopentadiene are sustained by an n.m.r. study of the latter by T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, **84**, 865 (1962).
(3) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).
(4) J. H. Day, *Chem. Rev.*, **53**, 167 (1953), and references cited therein.