Anal. Calcd. for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 7.99. Found: C, 68.66; H, 4.99; N, 7.85.

4-Azanaphthoquinone-1,2 (IVa).—To a solution of 0.10 g. (0.62 mmole) of 3,4-dihydroxyquinoline in 10 ml. of glacial acetic acid at 20°, a suspension of 0.5 g. of chromium trioxide in 10 ml. of glacial acetic acid was added slowly. The mixture was warmed on a steam bath to 40° and allowed to stand at room temperature overnight. The dark green mixture was diluted with 50 ml. of water and the pale yellow microcrystals of 4-azanaphthoquinone-1,2 that separated were collected and recrystallized from methanol or dioxane, 45 mg. (45%), dec. > 285°.[4]

Anal. Calcd. for $C_9H_5NO_2$: C, 67.92; H, 3.17; N, 8.80. Found: C, 67.98; H, 3.25; N, 8.62.

A phenazine derivative of IVa was prepared from *o*-phenylenediamine dihydrochloride and sodium acetate in glacial acetic acid and recrystallized from xylene as a red powder, dec. > 300°.

Anal. Calcd. for $C_{15}H_9N_3$: C, 77.90; H, 3.92; N, 18.17. Found: C, 77.98; H, 4.17; N, 17.90.

3-Methyl-4-azanaphthoquinone-1,2 (IVb).—A solution of 0.11 g. (0.0062 mole) of 3,4-dihydroxyquinaldine in 50 ml. of anhydrous methanol was shaken with 4 g. of dry silver oxide and 15 g. of anhydrous sodium sulfate for 10 min. and filtered. The yellow filtrate was evaporated to dryness under reduced pressure at room temperature and the yellow residue collected. Four recrystallizations from 95% ethanol afforded yellow plates of 3-methyl-4-azanaphthoquinone-1,2, 46 mg. (42%), m.p. 261–265° dec. Elemental analysis was not obtained due to unstability.

3-Methyl-4-azanaphthoquinone-1,2 upon treatment with *o*-phenylenediamine dihydrochloride and sodium acetate in glacial acetic acid afforded the corresponding phenazine, which recrystallized from benzene as red plates, m.p. 321–322.5° dec.

Anal. Calcd. for $C_{16}H_{11}N_3$: C, 78.35; H, 4.52; N, 17.13. Found: C, 78.42; H, 4.39; N, 17.41.

Dakin Oxidation of 2-Phenyl-3-formyl-4-hydroxyquinoline (IIIc).—To a solution of 0.42 g. (0.0017 mole) of 2-phenyl-3-formyl-4-hydroxyquinoline in 1.7 ml. of 1 *N* sodium hydroxide, 2.31 g. of 3% hydrogen peroxide was added in one portion. A color change from deep orange to pale yellow was accompanied by an exothermic reaction. Upon cooling to room temperature the disodium salt of the anthranil of phenylglyoxylic acid (V) precipitated which recrystallized from 95% ethanol as yellow microcrystals, dec. > 350°, 380 mg. (72%).

Anal. Calcd. for $C_{15}H_9NO_4Na_2$: C, 57.51; H, 2.90; N, 4.47. Found: C, 57.28; H, 3.11; N, 4.77.

Refluxing V with an excess of 2,4-dinitrophenylhydrazine in ethanol (10% hydrochloric acid) afforded the 2,4-dinitrophenylhydrazone of phenylglyoxylic acid, m.p. and mixture m.p. 196–197°.

Acknowledgment.—We are indebted to the National Institutes of Health, U. S. Public Health Service (Grant CA-06566), for partial financial support of this work.

Hydroboration of Diphenylacetylene

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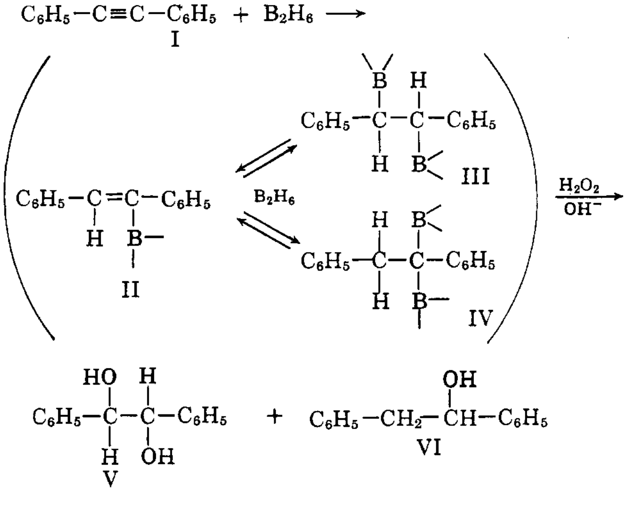
Addition of diborane to olefins (hydroboration) followed by oxidative workup has been shown to be a reaction of general utility in the synthesis of alcohols.[1] The reaction is stereospecific—*i.e.*, *cis* addition of the elements of water, and the least substituted alcohol is generally formed.[1a,b]

We were interested in applying this hydration scheme to the formation of *d,l* or *erythro* diols from acetylenes. Terminal acetylenes have been reported to yield aldehydes on hydroboration.[2,3] When we applied the reaction to diphenylacetylene (I) we found that in addition to the expected *d,l*-dihydrobenzoin (V) (37%), a large amount (40%) of 1,2-diphenylethanol (VI) was also formed. Small amounts of *trans*-stilbene and of desoxybenzoin were also found. No *meso*-dihydrobenzoin nor any rearranged 1,1-diphenyl-1,2-ethanediol was detected. The starting diphenylacetylene was virtually free of any stilbene as shown by infrared studies.



It is apparent that 1,2-diphenylethanol (VI) cannot result by a normal path from either of the expected intermediates II, III, or IV. Desoxybenzoin could be formed in the reaction on oxidation of intermediate II or IV and hydrolysis. To ensure that, at the time of formation of desoxybenzoin, diborane or any B—H compound needed to effect reduction to VI will have been destroyed, acetone was added prior to oxidative work-up; this did not affect the product distribution. Brown and Zweifel[3] also observed predominant formation of monoalcohols in the hydroboration of acetylenes and attributed these results to hydrolytic cleavage of an intermediate of type IV.[4] Alternatively, borane-induced elimination of the elements of >B—B< from intermediate III, followed by hydroboration of the resulting stilbene, could lead to alcohol VI and at the same time explain the isolation of a small amount of *trans*-stilbene. Abnormal products of a different nature were reported in the hydroboration of di-*tert.*-butyl-

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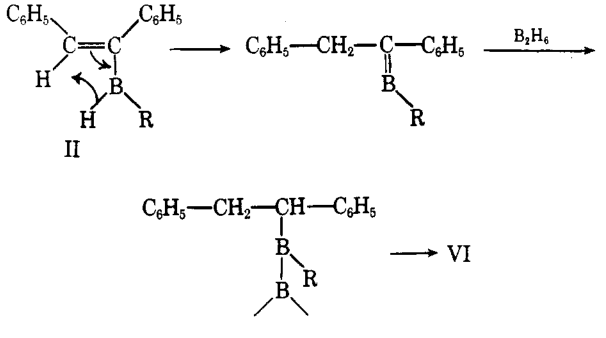
[1] (a) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 247 (1959) and subsequent papers; for a review see H. C. Brown, *Tetrahedron*, **12**, 117 (1961). (b) A. Hassner and C. Pillar, *J. Org. Chem.*, **27**, 2914 (1962).

[2] H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 1512 (1959).

[3] H. C. Brown and G. Zweifel, *ibid.*, **83**, 3834 (1961).

[4] One also could envisage a process of internal hydride transfer in intermediate II, as pictured:



acetylene.[5] It appears that hydroboration of acetylenes is not a cleanly predictable reaction but leads to a mixture of products

Experimental

All melting points are uncorrected. Infrared spectra were run in potassium bromide on a Beckman I R 5 instrument.

Reaction of Diphenylacetylene (I) with Diborane.—Diphenylacetylene (I), m.p. 60–61°, was prepared from stilbene *via* the dibromide.[6] Its infrared spectrum, by comparison with spectra of mixtures of diphenylacetylene and stilbene, indicated the presence of less than 2% of stilbene if any. Into a solution of 1.0 g. of diphenylacetylene (I) in dry tetrahydrofuran at 0° was passed diborane, generated from 3 g. of sodium borohydride and excess boron trifluoride etherate in diglyme. The solution was kept at 4° for 14 hr. Excess diborane was destroyed by addition of ice and the mixture was stirred with 25 ml. of 3 *N* sodium hydroxide and 15 ml. of 25% hydrogen peroxide for 40 min. The mixture was extracted with ether. The organic layer was washed with ferrous sulfate solution, then five times with water, dried, and evaporated. The residue (1.05 g.) was taken up in benzene and chromatographed over 30 g. of Merck aluminum oxide. The eluted fractions were evaporated and the residues identified by infrared, melting point, and mixed melting point comparison with authentic samples. The following results were obtained: Fraction 1 (35 mg.) melted at 125°. Upon crystallization from aqueous alcohol and then from petroleum ether (b.p. 40–60°) it gave material melting at 124–126°; mixed with *trans*-stilbene, m.p. 127°, it melted at 124–126°.

Fractions 2–4 (34 mg. of an oil that slowly crystallized) were identified by infrared and through its 2,4-dinitrophenylhydrazone, m.p. 203–205°, as desoxybenzoin.

Fraction 5 (453 mg.) melted at 46–56° and upon crystallization from petroleum ether (b.p. 60–90°) at 59–62°. Mixed melting point and infrared comparison with authentic material, m.p. 65°, prepared by hydroboration of *trans*-stilbene, identified it as 1,2-diphenylethanol (VI).

Fraction 6 (78 mg.) was a mixture difficult to separate.

Fractions 7–9 (372 mg.) were essentially *d,l*-dihydrobenzoin (V). Crystallization from water followed by drying and recrystallization from petroleum ether (b.p. 60–90°) gave material. m.p. 120–120.5°, identical in all respects with authentic *d,l*-dihydrobenzoin, prepared from benzil.

Fractions 10–11 (17 mg.) were likewise slightly impure *d,l*-dihydrobenzoin.

Acknowledgment.—We gratefully acknowledge financial support (Grant CY-4474) by the National Institutes of Health.

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[5] T. J. Logan and T. J. Flautt, *J. Am. Chem. Soc.*, **82**, 3446 (1960).

[6] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., 1957, p. 181.

Some Studies on Tropenylazulenes[1,2]

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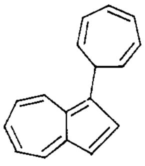
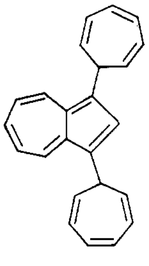
The recent publication of the reaction of azulene with tropenium perchlorate and of an attempt to obtain the interesting (1-azulyl)tropenium ion[5] prompt us to report the results of similar, independent studies. Our objectives were, first, the preparation of tropenylazulenes[6] and, second, the removal of a hyride ion to form a (1-azulyl)tropenium ion structure.

Treatment of azulene with tropenium fluoroborate afforded two crystalline products, 1-tropenylazulene (I) and 1,3-dinitropenylazulene (II). The latter was the principal product even when an excess of azulene was used.[7] With a 50% excess of azulene, for example, 19% of I and 51% of II were obtained, and if one equivalent of pyridine was present the yield of II was 62%.

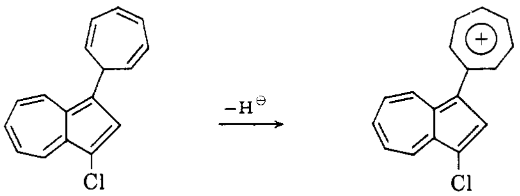


I



II

As the formation of a (1-azulyl)tropenium ion would involve reaction with a positive species, a 1-tropenylazulene having a simple, inert substituent in the nucleophilic 3-position was desired and 1-tropenyl-3-chloroazulene (III) was chosen. The reaction of 1-chloroazulene with tropenium fluoroborate gave a blue oil which exhibited an absorption maximum in the visible spectrum corresponding to that expected for III,[8] but was unaccountably difficult to purify and gave only fair analytical values. The n.m.r. spectrum was consistent with the assigned structure. There were three sets of multiplets centered at *ca.* 3.3, 3.8, and 4.57 p.p.m., each of relative intensity two, for the three types of vinyl protons, and a triplet at 6.67 p.p.m. of intensity one for the saturated hydrogen. The remainder of the spectrum corresponded to that of a 1,3-disubstituted azulene.[9] The further fact that this same substance was formed by the reaction of I with N-chlorosuccinimide established its identity sufficiently to permit its use in the hydride exchange experiments.



III IV

The addition of a slight excess of triphenylmethyl fluoroborate to a solution of III in dry acetonitrile caused a rapid color change from blue to green. From the reaction mixture were isolated a small amount of a colorless solid identified as tropenium fluoroborate by its ultraviolet spectrum, a low yield of triphenylmeth-

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[1] From the Ph.D. thesis of Lanny L. Replogle, University of Washington, July, 1960.

[2] Supported in part by a grant (G 7397) from the National Science Foundation.

[3] National Science Foundation Senior Postdoctoral Fellow, 1960–1961.

[4] National Science Foundation Coöperative Fellow, 1959–1960. Present address: Department of Chemistry, San Jose State College, San Jose, Calif.

[5] K. Hafner, A. Stephan, and C. Bernhard, *Ann.*, **650**, 42 (1961).

[6] Tropenyl will be used as the name for the 7-cycloheptatrienyl group.

[7] K. Hafner, *et al.* (ref. 5), reported II to be the sole product of their analogous reaction.

[8] λ_{max} (obsd.) 628 mμ, λ_{max} (calcd.) 630 mμ based on $\Delta\lambda_{max}$ for the chloro group as +30 mμ [*cf.* E. J. Cowles, *J. Am. Chem. Soc.*, **79**, 1093 (1957)], and $\Delta\lambda_{max}$ for the tropenyl group as +20 mμ (see Experimental).

[9] A. G. Anderson and L. L. Replogle, unpublished results.