Communications TO THE EDITOR

Structure of Amphenone B and Related Amphenones

Sir:

Due to increased interest in Amphenone B[1] after its initial synthesis by Allen and Corwin,[2] further chemical studies seemed to be in order. One of the main purposes was to find new potential routes to the synthesis of amphenone-like compounds.

Originally the symmetrical glycol (I) was submitted to a pinacol-pinacolone rearrangement. The pinacolone formula (II) was assigned to Amphenone B by Allen and Corwin based on the results of a rather drastic alkali fission of its *N,N'*-tetramethyl derivative and an apparent negative iodoform test.[2] The course of the rearrangement in favor of this pinacolone (II) seemed to be in agreement with the findings of previous investigators[3] who demonstrated that generally in a symmetrical pinacol it is the strongest electron donating moiety which will migrate. Thus, in this particular instance, the methyl group being the only electron donator in the glycol (I) would migrate in preference to the benzene ring if its substituent existed as a *p*-ammonium ion.

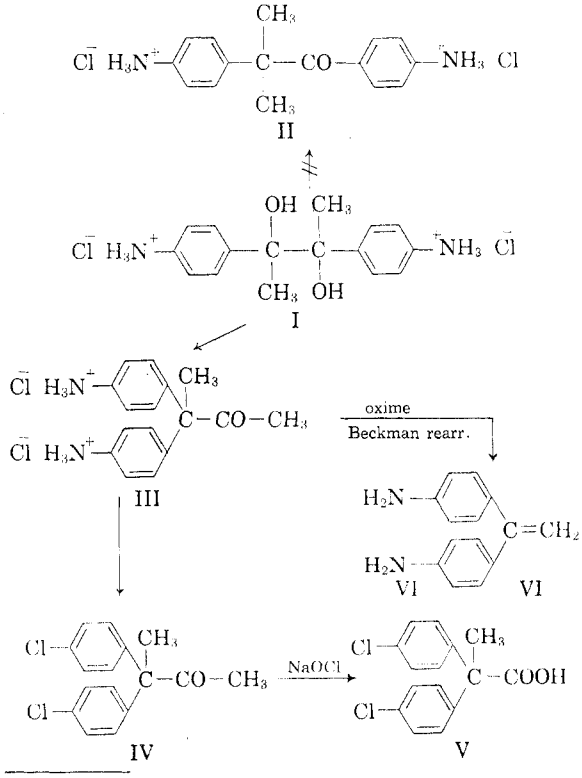
In a recent review[4] it has been stated that the pinacol-pinacolone rearrangement of symmetrical glycols seems to be far more complicated than anticipated previously and in view of these facts the question arose whether Amphenone B was to be formulated as (II) or could possibly have structure (III). The correctness of the latter formulation was proved by the following experiments.

Replacement of the amino groups of Amphenone B (III) by chlorine resulted in the ketone (IV) (73%, m.p. 58–60°) which was found to be identical to 3,3-bis(*p*-chlorophenyl)butanone-2[5] as indicated by mixed melting point and infrared spectra. Oxidation of ketone (IV) also yielded α,α-bis(*p*-chlorophenyl)propionic acid (m.p. 160–161°).[5]

The oxime of Amphenone B (90%, m.p. 220–222°, calcd. for $C_{16}H_{19}N_3O$: C, 71.35; H, 7.12; N, 15.62. Found: C, 71.07; H, 7.11; N, 15.47). was subjected to a Beckmann rearrangement by heating it in polyphosphoric acid to 120° for 15 minutes. The product isolated was identified as 1,1-bis(*p*-aminophenyl)ethylene (VI) (70%, m.p. 170–172°, calcd. for $C_{14}H_{14}N_2$: C, 79.96; H, 6.71; N, 13.32. Found: C, 80.03; H, 6.69; N, 13.61).

A similar course of the Beckmann rearrangement followed by deamination was observed by Price and Mueller[6] who obtained 1,1-dianisylethylene from the oxime of 3,3-dianisyl-2-butanone. The structure of compound VI is also supported by the infrared absorption bands: 890 cm.$^{-1}$ (>C=CH$_2$), 1620 cm.$^{-1}$ (C=C) and 833 cm.$^{-1}$ (*p*-disubstituted benzene).

The amino groups of VI were exchanged for chlorine via diazotation. The resulting 1,1-bis(*p*-chlorophenyl)ethylene showed a melting point of 84–85° (reported 84.6–85.8)[7] and the same ultraviolet absorption spectrum as found by Grummitt, Marsh, and Stearns.[8]



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The structure of Amphenone B as being (III) was also indicated by the fact that an iodoform reaction yielded 20–25% iodoform as determined spectrophotometrically.[9] The ultraviolet spectrum of Amphenone B showed the absence of a benzoyl-type carbonyl group.

A comparison of the ultraviolet spectra of the pinacolones obtained by rearrangement of 3,4-bis-(*p*-aminophenyl)-3,4-hexanediol[2] and 2,3-bis-*p*-dimethylaminophenyl)-2,3-butanediol[10] indicate these pinacolones to be 4,4-bis(*p*-aminophenyl)-hexanone-3 and 3,3-bis(*p*-dimethylaminophenyl)-butanone-2.

We are grateful to Mr. L. Dorfman and his staff for the microanalyses and the spectral data.

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Received February 18, 1957

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(−)-Menthoxyacetic Esters of the *Cis* and *Trans* Forms of *Meso*-3,4-diphenylcyclopentanol

Sir:

We wish to report the synthesis of the (−)-menthoxyacetic esters of the *cis* and *trans* forms of *meso*-3,4-diphenylcyclopentanol. The *cis* form was prepared by the reaction of the *cis* form of *meso*-3,4-diphenylcyclopentanol[1] with (−)-menthoxyacetyl chloride in pyridine. After purification by chromatographic adsorption and repeated crystallization from 95% ethanol and from *n*-pentane, it melted at 66.5–67.0°; $[\alpha]_D^{25}$ − 49.3° ± 0.2°, c = 0.035 g. per cc. in methyl ethyl ketone.

Anal. Calcd. for $C_{29}H_{38}O_3$: C, 80.14; H, 8.81. Found: C, 80.10, 80.29; H, 8.80, 8.85.

The *trans* form was prepared by the reaction of the *p*-toluenesulfonyl ester of the *cis* alcohol with the sodium salt of (−)-menthoxyacetic acid. After exhaustive purification it melted at 76.5–77.0°; $[\alpha]_D^{25}$ − 55.1° ± 0.2°, c = 0.035 g. per cc. in methyl ethyl ketone.

Anal. Calcd. for $C_{29}H_{38}O_3$: C, 80.14; H, 8.81. Found: C, 80.14, 80.19; H, 8.86, 8.75.

The difference of 5.8° in the rotation of the *cis* and *trans* forms of the menthyl esters confirms the view that diastereoisomers of this type may be expected to differ in optical rotation.[2]

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Received March 8, 1957

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