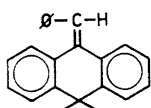


Preparation and Dehydration of 9-Benzyl-9-hydroxy- 10-dihydroanthracene

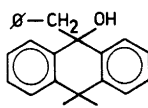
KENNETH G. FLYNN and
GÖRAN BERGSON

*Chemical Institute, University of Uppsala,
Uppsala, Sweden*

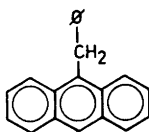
In connection with our studies of transannular tautomerism in 9,10-substituted dihydroanthracenes, it became of interest to prepare 9-benzylidene-9,10-dihydroanthracene (I).



(I)



(II)



(III)

We report, in this note, some preliminary findings related to the synthesis of (I).

Barnett and co-workers¹ had reported in 1923 that the reaction of anthrone with benzylmagnesium chloride, in most cases, gave 9-benzyl anthracene (III) directly instead of the expected anthranol (II). In only one instance did Barnett isolate a material that might be assigned the structure of (II). In that one case, a low-melting solid (50°) was obtained, but it was reported to form (III) spontaneously on standing overnight in a vacuum desiccator.

We have found, on repeating the experiments of Barnett *et al.*, that careful neutralization of the Grignard reaction mixture gives (II) in good yield. The structure of (II) was proven spectrally (IR, UV, and NMR) and by elemental analysis. No evidence for its "spontaneous" dehydration to (III) could be found. However, dehydration to (III) was smoothly effected at ambient temperatures by means of P₂O₅ in benzene.

A most interesting observation was made that not only do (II) and (III) appear to have the same melting point but a mixed melting point shows little or no depression. This suggested that (II) was dehydrating during the melting point determination. Accordingly, dehydration on a larger scale using "melting-point conditions" gave a quantitative yield of (III). The ease of dehydration suggests that transannular elimination of H₂O occurs directly and that (I) is probably not an intermediate. Further experiments leading to (I) are in progress.

Experimental. 9-Benzyl-9-hydroxy-9,10-dihydroanthracene (II). Solid, pulverized anthrone (12.0 g, 0.062 mole) was added in portions to a stirred, ice-cold, ethereal solution (500 ml) of benzylmagnesium chloride which had been prepared from benzyl chloride (0.21 mole) and magnesium turnings (0.21 mole). Stirring was continued for 2 h at 0° and neutralization was then carried out using a saturated solution of NH₄Cl.² Vacuum evaporation of the ether solvent gave the product directly, in 60 % yield. Recrystallization from ligroin gave a white solid, m.p., 129–131°. (Found: C 88.04; H 6.39; Calc. for C₂₁H₁₈O (286.35): C 88.08; H 6.33).

The infrared spectrum showed a well-defined doublet in the OH stretching region, at 3510 and 3390 cm⁻¹, respectively. The ultraviolet spectrum had pronounced maxima at 266 mμ and 273 mμ. The spectrum was typical of a dihydroanthracene, as determined by comparison with other published spectra.³ The NMR spectrum in chloroform had a 1-proton peak at 2.37 ppm (hydroxyl proton determined by deuterium labelling) a two-proton peak at 3.0 ppm (benzylic protons) and a 2-proton quartet centered at 3.22 ppm. (All δ values relative to TMS.) The appearance of the quartet was consistent with two non-equivalent protons bound to the same carbon atom⁴ and was therefore assigned to the C-10 protons. The coupling constant for the C-10 protons, J_{AB}, was 19 cps.

The dehydration product of (II), 9-benzyl anthracene was characterized by comparison of its melting point,¹ infrared spectrum⁵ and ultraviolet spectrum⁶ with those published previously.

We wish to thank Professor Arne Fredga for all the facilities placed at our disposal. A grant from the *American-Scandinavian Foundation* is gratefully acknowledged. The elemental analyses were carried out at the Analytical Department of the Chemical Institute.

1. Barnett, E. de B., Cook, J. W. and Wiltshire J. L. *J. Chem. Soc.* **1927** 1724.
2. Fieser, L. F. *Experiments in Organic Chemistry* D. C. Heath and Co., Boston, U.S.A., 3rd Ed., p. 270.
3. Tardieu, P. *Ann Chim.* **6** (1961) 1445.
4. Roberts, John D. *Nuclear Magnetic Resonance* McGraw-Hill, New York 1959, p. 56.
5. Cannon, C. G. and Sutherland, G. B. B. M. *Spectrochim Acta* **4** (1951) 373.
6. Barnett, E. de B., Cook, J. W. and Ellison, T. E. *J. Chem. Soc.* **1928** 855.

Received October 1, 1964.

Tautomerism in Isotopically Substituted Indenes*

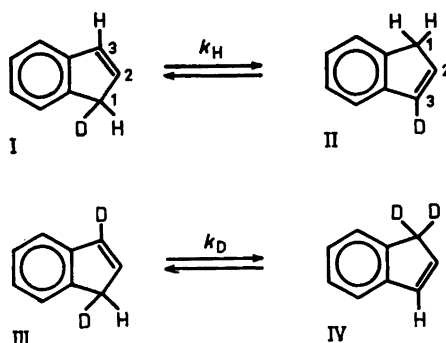
GÖRAN BERGSON

Chemical Institute, University of Uppsala, Uppsala, Sweden

Some time ago, the author showed¹ that intramolecular proton-transfer takes place in indene under certain conditions, and preliminary results were reported of a study of this tautomeric rearrangement using 1-D-indene in pyridine solution with triethylamine as a catalyst at 30°C. We have also shown in a study of dialkylindenes that the reaction is completely stereospecific under the above mentioned conditions.²

Quite recently, Roth³ reported evidence for intramolecular proton-migration in 1-deutero-indene and 1,1,3-trideutero-indene in the gas phase at about 200°C, and McLean and Haynes⁴ found similar rearrangements in substituted cyclopentadienes. Roth's results indicate the intermediate formation of isoindene, implying a deuterium shift to the 2-position. Under the conditions used by the present author, however, only shifts between positions 1 and 3 have been observed. Since reaction conditions as well as the results are quite different in our investigations, it is evident that different mechanisms for the rearrangements are operative.

In this paper, the results of kinetic measurements of the rates of the tautomeric rearrangements $I \rightleftharpoons II$ and $III \rightleftharpoons IV$ are



reported. The former reaction involves protium-migration (deuterium-migration is non-observable) and the latter, deuterium-migration. Thus, the kinetic isotope effect can be studied if I and III (or II and IV) are prepared and subjected to tautomerizing conditions.

I was prepared by deuteration of indenyl sodium and III by protonation of 1,3-dideuteroindenyl sodium. The latter was made from trideuteroindene which was obtained from hydrogen exchange between indene and D_2O . The structures of I and III were confirmed by their NMR-spectra. Thus, I shows signals at 6.76 and 6.27 ppm (δ , relative to TMS, neat) due to the protons at the 3- and 2-position, respectively. Each of these signals is split into two doublets with the coupling constants $J_{23} = 5.5 \pm 0.1$, $J_{12} = 1.9 \pm 0.1$ and $J_{13} = 1.8 \pm 0.1$ cps which are in good agreement with those found for indene.⁵ The signal at 3.02 ppm, due to the proton in position 1, is split into seven peaks in accordance with the coupling scheme shown in Fig. 1. The geminal H-D coupling constant, J_{HD} , is 3.2 ± 0.2 cps, corresponding to $J_{HH} = 20.8$ cps since $\gamma_D/\gamma_H = 0.1535$.⁶

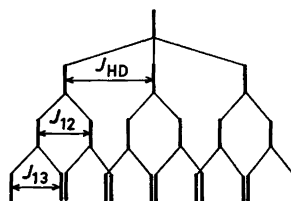


Fig. 1. Spin-spin coupling scheme for the proton in position 1 of compound I.

* Part VIII in the series "Proton-Mobility in the Indene Ring-System". Part VII. *Acta Chem Scand.* **18** (1964) 1498.