

ATTEMPTED SYNTHESIS OF A SUBSTITUTED [2.2.2]PROPELLANE DERIVATIVE FROM TRIPTYCENE DERIVATIVES

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(Received in the UK 5 September 1973; Accepted for publication 14 September 1973)

Abstract—Bromotriptycene derivatives substituted at the bridgehead were subjected to varying reaction conditions in the attempt to obtain a substituted [2.2.2]propellane. The desired cyclization was not effected. The bromine atoms were replaced by hydrogens.

In view of the conclusion made by Stohrer and Hoffmann regarding the stability of strained small-ring propellanes towards base¹ and in view of their conclusions regarding [2.2.2]propellane **1** in particular *vis-a-vis* the bridgehead biradical **2** on the one hand and 1,4-dimethylenecyclohexane **3** on the other hand¹ we decided to choose a substrate which could not reasonably be expected to seek a route to **6** the formal analog of **3**, but rather, might perhaps afford the substituted [2.2.2]propellane **5**. Such a substrate would of course be a substituted triptycene **4**, e.g. **4a** or **4c**.

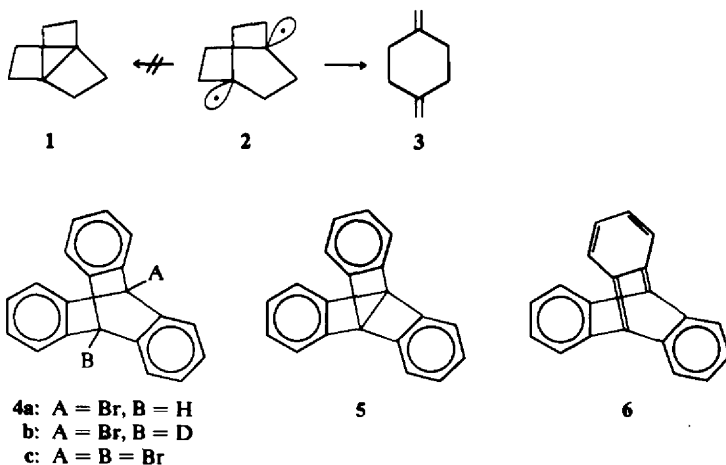
There would appear *a priori* to be little point to study compounds of type **4** in view of the classical work of Bartlett² in this field but for our now having solvents of higher dielectric constant which might give results different from the viewpoint of rate from those earlier obtained.³ Further, others appear to have had the same idea using bicyclic substrates, *inter alia* bridgehead dihalides in the bicyclo[3.2.1]octane bicyclo[2.2.2]octane and bicyclo[2.2.1]heptane series.⁴ Their work prompts us to report our results with compounds of type **4**.

9-Bromotriptycene **4a** was prepared from 9-bromoanthracene⁵ and 9,10-dibromotriptycene **4c** was similarly prepared from 9,10-dibromoanthracene⁵ by reaction with benzene.^{7,8}

Reactions of **4a** and **4c** were carried out in which both free radical and ionic intermediates might exist. Thus reactions were carried out with **4c** and metals capable of effecting a Wurtz reaction, sodium and potassium, analogous to those reported for the bicyclo[2.2.2]octane series.⁴ The Wurtz reaction was not accomplished successfully and **4a** was obtained.

Irradiation of **4c** in acetone also failed to give the desired ring closure; **4a** was again obtained.

In addition **4a** was subjected to the action of lithio cyclohexylisopropylamine in HMPA, to sodamide in liquid ammonia and to sodium hydride in DMSO, in each case to no avail. However it was reduced to triptycene by using sodiumhydride in HMPA. Use of **4b** showed that the last reactions did not effect loss of deuterium from 9-deuterio-10-bromotriptycene and triptycene-d, was obtained. Thus, it is not reasonable to assume that the



propellane **5** might have been formed in the reaction as a fleeting intermediate, then undergoing hydrogenolysis. If the latter were the case more hydrogen by far should be found at the bridgehead positions in the triptycene isolated and very little triptycene-d, could have been isolated. So in the end even the newer solvents have in this case not changed the picture developed several decades ago.

Scheme 1 summarizes the reactions carried out and the interconversions which were effected.

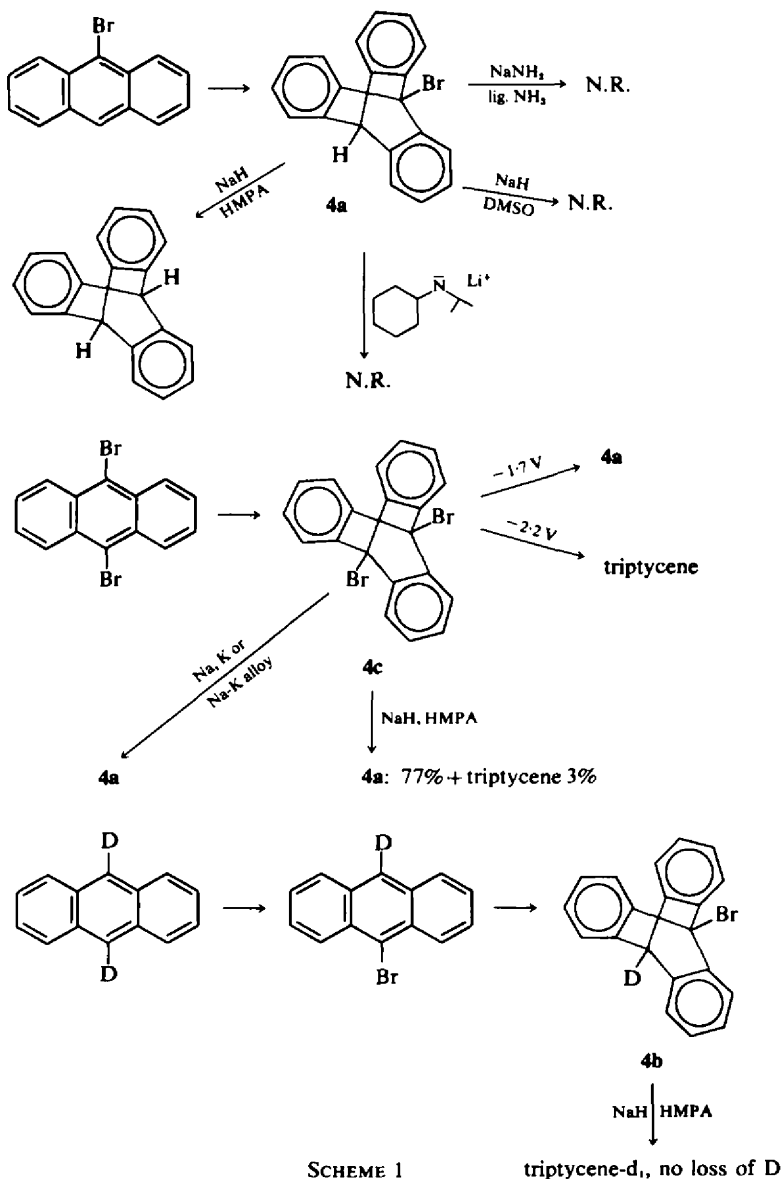
The electrochemical approach, successful in the case of [3.2.1]propellane¹⁰ failed in this case and **4c** afforded **4a** or triptycene itself at -1.7v and -2.2v , respectively.

EXPERIMENTAL

9-Bromoanthracene was prepared according to the published procedure,² in 95% yield, m.p. $96\text{--}96.5^\circ$ (Lit.³ m.p. $98\text{--}99^\circ$) 9-Bromotriptycene, **4a** was prepared according to the literature^{7,8} and purified by gas chromatography (SE-30, 0.5 m, 250°), m.p. $250\text{--}252^\circ$ (Lit.⁷ m.p. $246\text{--}247^\circ$).

Reaction of **4a** with bases

(a) Solid **4a** (200 mg) was added to a soln of Na (50 mg) in liq NH_3 (100 ml). A vigorous reaction continued for 10 min. Stirring was continued for 10 min more. Ether was added (100 ml) and the mixture was allowed to reach room temp during 3 hr. The whole was washed with water (3×100 ml), the ether layer was dried. Removal of solvent afforded pure **4a** (180 mg). No other product was isolated.



SCHEME 1

triptycene-d, no loss of D

(b) To a soln of **4a** (250 mg) in HMPA (20 ml) was added lithio-cyclohexylisopropyl amine (0.95 ml ; 9.75×10^{-4} mole) and the mixture was stirred in an inert atmosphere at room temp for 24 h. Analysis by GLC and TLC showed that no new product was formed. The mixture was heated at 80° for 24 h with no reaction occurring.

(c) To a soln of **4a** (250 mg) in DMSO (25 ml) was added NaH (40 mg). No reaction was observed but a pink color, later turning to deep orange, appeared upon heating to 80° . The mixture was kept at 80° for 24 h. Monitoring again showed that no reaction had taken place. The usual workup afforded pure **4a** (235 mg) but no additional product was isolated.

(d) A soln of **4a** (0.84 g) in HMPA (20 ml) and NaH (0.24 g) was heated under reflux with stirring for 24 h. After workup, triptycene, **5** (0.58 g ; 92%) was isolated, m.p. $249\text{--}250^\circ$, identical to authentic triptycene.

9,10-Dideuterioanthracene. A mixture of zinc couple prepared from zinc (2.5 g) and copper sulfate (19 mg) was stirred under reflux in a mixture of benzene (50 ml) containing anthrone (1 g) and NaOD (2N; 45 ml) during 18 h. To the cooled mixture was added benzene (100 ml). The organic layer was separated, concentrated (to 20 ml) and cooled. The *dideuterioanthracene* separated as colorless plates (0.9 g ; quant), m.p. 217.5° . M^+ , m/e 136, indicated >90% D content. NMR spectrum indicated absence of H-9 and H-10 of normal anthracene.

9-Deuterio-10-bromoanthracene was prepared as above for the undeuterated analog. The dideuterio compound (0.9 g) afforded the bromo-compound (1.2 g), m.p. $96\text{--}96.5^\circ$. M^+ , m/e 211 showed >90% D content.

9-Deuterio-10-bromotriptycene 4b was prepared as above for normal analog. M^+ , m/e 335 (>95% D). NMR spectrum showed no bridgehead H atom.

Treatment of 4b with NaH in HMPA was carried out as above. No loss of D was observed in the NMR or mass spectra of the deuteriotriptycene thus obtained (M^+ , m/e 255).

9,10-Dibromoanthracene was prepared in 63% yield by the published procedure,⁶ m.p. $221\text{--}222^\circ$ (Lit.⁶ m.p. $221\text{--}222^\circ$).

9,10-Dibromotriptycene, 4c. **9,10-Dibromoanthracene** (3.3 g) was added to a soln of *i*-amyl nitrite (6.3 ml) in glyme (500 ml). To this soln was added a soln of anthranilic acid (5.0 g) in glyme (100 ml) during 3 h. The whole was heated under reflux overnight, cooled and EtOH (25 ml) was added followed by aq KOH (10%; 25 ml). The ppt which formed slowly was removed (0.5 g ; 1.9%), m.p. $315\text{--}316^\circ$ light petroleum $60\text{--}70^\circ$).

Treatment of 4c with metals. (a) Reaction of **4c** with Na in refluxing glyme for 5 h as well as in lower boiling solvents afforded only recovered starting material. (b) A soln of **4c** (120 mg) in *n*-octane (10 ml) was heated under reflux with Na-K alloy under N_2 for 5 h. Excess metal was dis-

solved by adding MeOH and the solvent was removed in a vacuum. The residue was dissolved in ether, the whole was washed with water and the ether soln dried ($MgSO_4$). The crude product was chromatographed on basic alumina (20 g). First to be eluted with was recovered starting material (33 mg), next was **4a** (40 mg), m.p. $250\text{--}251^\circ$ identical by mixed m.p. and spectroscopically to an authentic specimen.

Photolysis of 4c. A soln of **4c** (100 mg) in acetone (20 ml) containing triethylamine (0.2 ml) was irradiated for 35 min with an Osram 200 watt high pressure mercury lamp. Removal of solvent and TLC on alumina using *n*-hexane afforded **4a** (25 mg) as the *only* isolable product, m.p. $248\text{--}249^\circ$, identical to an authentic specimen.

Electrolysis of 4c. Electrolysis was carried out in a triple electrode system at controlled potential. The working electrode was Hg, the counterelectrode Pt and the reference electrode was calomel.

(a) Electrolysis of a solution of **4c** (100 mg) in DMF (100 ml; 0.1 M in tetrabutylammonium perchlorate) was carried out at a potential of -2.2 v . When the current decayed, the soln was diluted with water (100 ml) and the whole was extracted several times with *n*-hexane. The combined extracts were washed with water and dried ($MgSO_4$). Evaporation afforded a crude solid (68 mg) which was purified on a column of basic alumina (15 g) using *n*-hexane as eluent. Triptycene (57 mg), m.p. $249\text{--}250^\circ$ (methylcyclohexane) was obtained. It was identical by mixed m.p. and spectroscopically with an authentic sample. (b) Repetition as in (a) except for the potential which was maintained at -1.7 v , gave **4a** (60 mg), m.p. $254\text{--}255^\circ$, identical to an authentic specimen.

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