

## Aryne Formation in the Triptycene Series

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We have studied the reactions of halo-triptycenes under conditions which lead to aryne formation in other aromatic systems.<sup>1</sup>

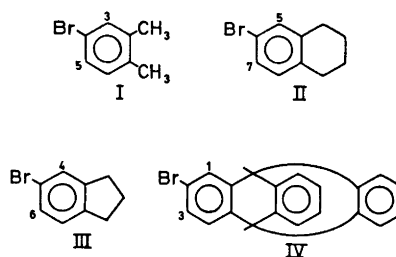
When 2-bromotriptycene (IV) is treated with potassium amide in liquid ammonia at  $-33^{\circ}\text{C}$ , a mixture of 1- and 2-amino-triptycene results. A mixture of 1- and 2-piperidinotriptycene is similarly formed from 2-bromotriptycene and lithium piperide in boiling ether. In both reactions the isomer ratio (1-amine:2-amine), as determined by column chromatography or NMR spectrometry, was between 26:74 and 21:79. The nearly constant isomer ratio indicates that 1,2-triptycene may have formed as a common intermediate. But formation of some 2,3-triptycene could not be excluded, since a constant ratio between the two triptycenes might lead to the same result. That the latter aryne hardly can be an important intermediate is, however, evidenced by the fact that 1-chlorotriptycene, from which 2,3-triptycene cannot be formed, when reacted with lithium piperide in boiling ether gave the two piperidinotriptycenes in nearly the same ratio (27:73) as above.

2-Fluoro-, 2-chloro-, and 2-bromotriptycene were reacted with phenyllithium in ether. The bromo compound reacted exclusively *via* halogen-metal interconversion to give, upon hydrolysis, triptycene, whereas fluoro- and chlorotriptycene both yielded a mixture of phenyltriptycenes. The mixture has not yet been completely separated, although we have succeeded in isolating some 1-phenyltriptycene from the reaction of 2-chlorotriptycene. This indicates that this reaction, too, goes *via* 1,2-triptycene.

There are relatively large amounts of unreacted starting materials besides some insoluble products in the described aryne reactions, but optimal conditions have not yet been aimed at.

2-Fluorotriptycene as well as the four amines and 1-phenyltriptycene have not been described before. 2-Fluorotriptycene was made by a Schiemann reaction from 2-aminotriptycene. 1-Amino- and 2-amino-triptycene were also obtained by reduction of the corresponding nitrotriptycenes with hydrazine and Raney-nickel.

The fact that 2-bromotriptycene (IV) is exclusively metallated in the more hindered 1-position by lithium piperide in ether may be compared with the results reported for some other compounds having similar structural features.



4-Bromo-1,2-xylene (I), 6-bromotetraline (II), and 5-bromoindane (III) undergo metallation in positions 5-, 7-, and 6-, respectively, with increasing difficulty relative to the other *ortho*-position to bromine.<sup>1</sup> These three compounds are, in the order given, characterized by an increasing rigidity of the alkyl substituent system connected with the aromatic ring, and an increasing double bond character of one of the aromatic bonds in question (the 3,4-, 5,6-, and 4,5-bond, resp.).<sup>1</sup>

The exclusive formation of 1,2-triptycene from IV is, therefore, understandable in terms of structural strain and would suggest a higher bond order and a shorter bond length for the 1,2-bond relative to the 2,3-bond in IV. This conclusion seems, however, to be contradicted by recent examinations<sup>2,3</sup> of the crystal and molecular structure of triptycene, showing these two bonds to be almost equal in length.

The isomer ratio found for the addition of lithium piperide to 1,2-triptycene, once this bond has formed, agrees well with those reported for other arynes with an alkyl substituent adjacent to the aryne bond.<sup>1</sup>

*Experimental.* 1-Chloro-, 2-bromo-, 1-nitro-, and 2-nitrotriptycene were prepared by the method described by Friedman and Logullo.<sup>4,5</sup>

*2-Fluorotriptycene.* 2.15 g (8 mmol) of 2-aminotriptycene dissolved in hot acetone were added dropwise to 120 ml of 6 N hydrochloric acid. The cooled suspension of the amine hydrochloride was diazotized with an aqueous solution of 552 mg (8 mmol) of sodium nitrite during 30 min. An eventual excess of nitrite was destroyed with urea and a twofold excess of sodium tetrafluoroborate added. The diazonium tetrafluoroborate was filtered off, dried *in vacuo*, and decomposed when slowly added to 50 ml of refluxing xylene. The xylene was removed by steam distillation and the residue extracted with ether yielding 1.84 g of crude 2-fluorotriptycene, m.p. 178–180°C. Repeated sublimation at 170°C/1.5 mmHg gave m.p. 232–234°C. (Found: C 88.53; H 5.08; F 6.38. Calc. for C<sub>20</sub>H<sub>13</sub>F: C 88.21; H 4.81; F 6.98.)

*Reduction of 1- and 2-nitrotriptycene to 1- and 2-aminotriptycene.* A solution of 5.25 g (17.6 mmol) of 2-nitrotriptycene in 150 ml of toluene and 50 ml of ethanol was heated on the steambath in a 1 liter flask fitted with stirrer and reflux condenser. 6 ml of hydrazine hydrate (100 %) and approximately 100 mg of Raney-nickel were rapidly added, causing instantaneous ebullition. (*Caution.* The volume of the flask should not be less than 1 liter in order to prevent the solution from boiling over). After 30 min at reflux a little amount of hydrazine hydrate and Raney-nickel was added and reflux continued for another 30 min. In the presence of a little fresh Raney-nickel the solvent was stripped off until alkaline vapours no longer appeared. The solution was filtered and evaporated to dryness yielding 4.60 g (97 %) of crude 2-aminotriptycene, m.p. 237–238°C. An analytical sample was obtained by removal of some contaminating anthraquinone by sublimation at 110°C/0.1 mmHg. M.p. 248–249°C. (Found: C 88.98; H 5.45; N 5.55. Calc. for C<sub>20</sub>H<sub>13</sub>N: C 89.19; H 5.61; N 5.20.)

By the same procedure 1-nitrotriptycene gave 90 % of 1-aminotriptycene, m.p. 227–229°C. Two recrystallizations from benzene gave m.p. 231–232°C. (Found: C 88.79; H 5.43; N 5.20.)

*Metallation experiments.* (a) 1-Amino- and 2-aminotriptycene. 2-Bromotriptycene (666 mg, 2 mmol) was rapidly added to a stirred suspension of potassium amide (from 0.4 g of

potassium in 30 ml of liquid ammonia). After 20 h at –33°C unchanged potassium amide was destroyed by ammonium chloride, 10 ml of ether added, and the ammonia allowed to evaporate. After further addition of 30 ml of ether and reflux for 15 min, work up as in (b) yielded 88 mg of crude amines. From the ethereal layer 480 mg of crude 2-bromotriptycene were isolated, the yield of amines thus being 59 % based on unrecovered starting material. The amines were separated on alumina (Merck I–II, 30×1.5 cm, light petroleum with increasing amounts of benzene) to give 23 mg 1-aminotriptycene, m.p. 227–229°C and 65 mg 2-aminotriptycene, m.p. 237–238°C. Isomer ratio 26:74.

(b) 1-(Piperidino)- and 2-(piperidino)triptycene. To a solution of 1.0 g (3 mmol) of 2-bromotriptycene and 0.38 g (4.5 mmol) of piperidine in 50 ml of ether was added, during 30 min, a solution of 4.5 mmol of phenyllithium and 0.38 g of piperidine in 10 ml of ether. A nitrogen atmosphere was used. The colour of the reaction mixture being at first cloudy white slowly changed over yellow to brown. After reflux for 20 h the mixture was hydrolyzed. After washing with water the ethereal layer was dried and then saturated with dry hydrogen chloride. The precipitated amine hydrochlorides were decomposed with sodium carbonate. Separation on alumina (Merck I–II, light petroleum/benzene) gave 100 mg 1-(piperidino)triptycene, m.p. 216–217°C (Found: C 89.42; H 6.83; N 4.06. Calc. for C<sub>26</sub>H<sub>23</sub>N: C 88.98; H 6.87; N 4.15), and 280 mg 2-(piperidino)triptycene, m.p. 175–176°C (from benzene). (Found: C 88.23; H 6.96; N 4.40.) Isomer ratio 26:74.

In another run with a twofold excess of piperidine the mixture of the piperidino-triptycenes was analyzed by NMR giving an isomer ratio of 21:79. The total yield of amines was 57 %.

In the reaction with 1-chlorotriptycene the isomer ratio was determined by NMR to 27:73.

*1-Phenyltriptycene.* A solution of 576 mg (2 mmol) of 2-chlorotriptycene and 9 mmol of phenyllithium in 30 ml of ether was refluxed for 24 h under a nitrogen atmosphere. Hydrolysis followed by usual work up gave 160 mg of crude product. Purification on alumina (Merck I–II, 35×2 cm, light petroleum/benzene) followed by recrystallization from benzene gave 52 mg (7.9 %) of 1-phenyltriptycene, m.p. 272–273°C. (Found: C 93.89; H 5.42. Calc. for C<sub>26</sub>H<sub>18</sub>: C 94.51; H 5.49.)

1. Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*, Verlag Chemie, Weinheim/Bergstr.—Academic, New York, London 1967.
2. Anzenhofer, K. and de Boer, J. J. *Z. Krist.* **131** (1970) 103.
3. Hazell, R. G., Pawley, G. S. and Lund Petersen, C. E. *Submitted to J. Cryst. and Mol. Structure.*
4. Friedman, L. and Logullo, F. M. *J. Org. Chem.* **34** (1969) 3089.
5. Logullo, F. M. Dissertation, *Univ. Microfilms, Ann Arbor*, 65—13, 774.

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