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THE REACTION OF INDIGO WITH HYDRAZINE

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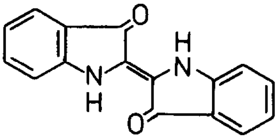
In 1921 Borsche and Meyer reported[1] that indigo (1) on treatment with $N_2H_4 \cdot H_2O$ and NaOH in $EtOH/H_2O$ readily could be converted to a sparingly soluble compound, "desoxyindigo", assigned structure 2. This formulation was accepted by later workers[2,3] and reviewers[4-6]. In addition to "desoxyindigo" Seidel[3] later coined the name "dehydrodesoxyindigo" (assigned structure 3) to a purported secondary product of "desoxyindigo".

We wished to prepare 2, as a precursor to 4 or 5, which we needed in connection with a structure elucidation.[7] Furthermore we wanted to compare the reactivity of 2 with that of the corresponding benzofuran derivatives (*cf.* the preceding paper).

The procedure given by Borsche and Meyer finished as follows. "Dann liessen wir abkühlen und oxydierten[8] durch Durchsaugen eines langsamen Luftstromes, so lange noch etwas ausfiel". Under strongly alkaline conditions 2 (if present) should be expected to appear in the anionic form, *i.e.* 6, which should be readily susceptive to oxidative coupling.[9] Consequently, we had doubts in advance about the correctness of the structures given to "desoxyindigo", and "dehydrodesoxyindigo". This was confirmed by high resolution MS which showed the composition to be $C_{32}H_{20}N_4O_2$ (M^+=492.1599).[10] From these data we suggested[11] structure 7a, which was corroborated by an independent synthesis (addition of 9, *cf.* ref. 12, to 8,[13] followed by alkaline hydrolysis of 7b to 7a).



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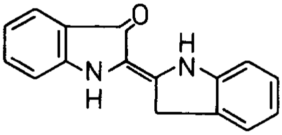

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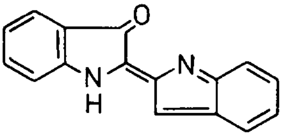

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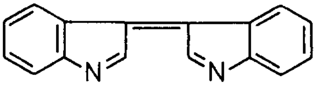

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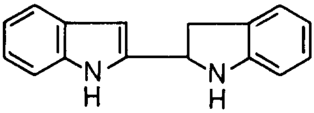

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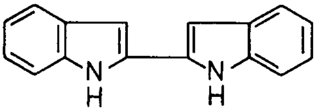

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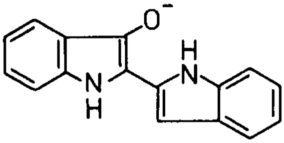

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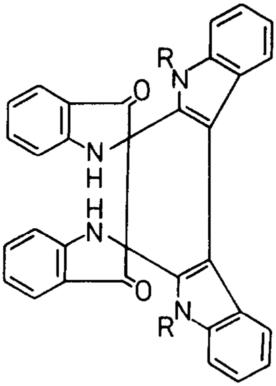
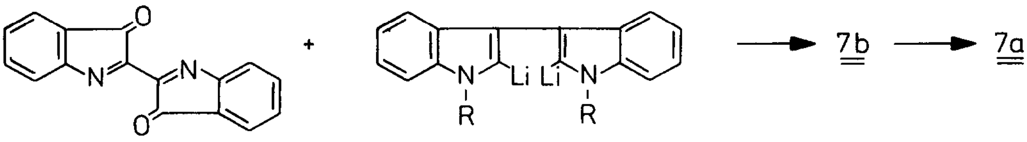


7 a $R=H$

b $R=SO_2C_6H_5$



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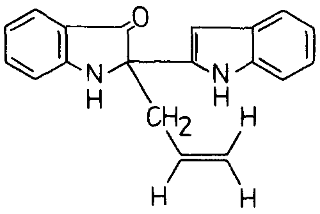
9 $R=SO_2C_6H_5$

A more "direct" synthesis, namely interaction of 8 with 3,3′-biindolyl in hot toluene resulted in hydrogen transfer (giving 1 and 10) rather than the desired addition.

The monoacetate (11) of the desired compound 2 could be prepared by introduction of Ac_2O (rather than air) to Borsche′s reaction mixture. Addition of allyl chloride similarly gave beautiful crystals[14] of 12. Interestingly Saxton[15] has obtained the isomer 13 by addition of allyl bromide to an alkaline solution assumed to contain the anion 14.



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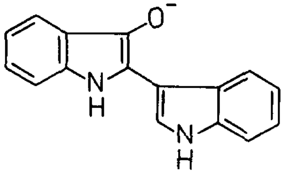

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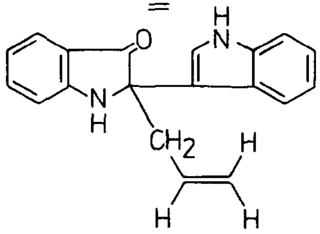

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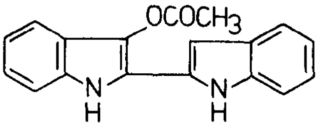

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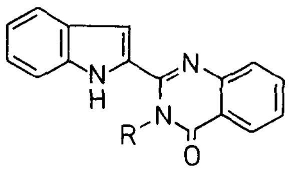
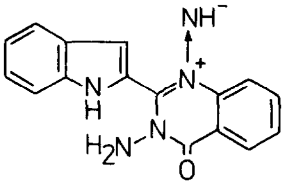


15 a R=NH2
b R=H



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We have also studied the interaction of anhydrous N_2H_4 with indigo (1). At low (35 °C) temperatures a product, A,[16] with the composition $C_{16}H_{13}N_5O$ was obtained, whereas the same reagents at higher (100 °C) temperatures furnished, in good yield, a closely related product, B,[17] with the composition $C_{16}H_{12}N_4O$. The structure of compound B can, through X-ray diffraction analysis, be assigned the structure 15a. Treatment of 15a or compound A (tentatively assigned structure 16) with Raney nickel gave 15b, which also could be independently synthesized by treating indole-2-carboxylic acid in pyridine with $(CF_3CO)_2O$ followed by anthranilic amide.

REFERENCES AND NOTES

1. W. Borsche and R. Meyer, *Berichte* 54, 2854 (1921), R. Meyer, Diss. Göttingen, (1920).

2. W. Madelung and P. Siegert, *Berichte* 57, 222 (1924).

3. (a) P. Seidel, *Berichte* 77, 788 (1944), *cf.* also ref. 3b.
   (b) P. Seidel, *Berichte* 83, 20 (1950).

4. W.C. Sumpter and F.M. Miller, "Heterocyclic Compounds with Indole and Carbazole Systems", A. Weissberger, Ed., Interscience Publishers, Inc., New York, N.Y., (1954) p. 184.

5. B. Robinson, *Chem. Rev.* 69, 785 (1969).

6. M. Sainsbury in "Rodd's Chemistry of Carbon Compounds" 2nd ed. S. Coffey, Ed., Vol. 4. Heterocyclic Compounds Part B, Elsevier, Amsterdam (1977) p. 349.

7. (a) 2,2'-Biindolyl is a notoriously elusive[7b] compound and we and other workers[7c] have encountered considerable difficulties in attempts to reproduce the literature procedures.
   (b) S.A. Faseeh and J. Harley-Mason, *J. Chem. Soc.*, 4141 (1957).
   (c) K.-H. Steinmetzer, Diss. Würzburg (1973) p. 41.

8. Borsche and Meyer did not suggest any structure for the implied primary reduction product.

9. W.I. Taylor and A.R. Battersby, Eds. , "Oxidative Coupling of Phenols", Marcel Dekker Inc. New York, N.Y., (1967).

10. Crude samples showed a peak at m/e 494 indicating the presence of a precursor of 7a. Attempts to isolate this compound failed.

11. This reassignment means that several structures and conclusions in references 2 and 3 are in need of revision.

12. R.J. Sundberg and H.F. Russell, *J. Org. Chem.* 38, 3324 (1973).

13. L. Kalb, *Berichte* 42, 3642 (1909).

14. M.p. 171-173 °C. IR(KBr) 3390, 3270 (NH); 1690 (C=0), 1620 cm^{-1}.
    MS: 289 (M+1, 5), 288 (M, 22), 287 (4), 259 (12), 248 (24), 247 (100), 246 (7), 219 (9), 218 (13), 167 (4). Only peaks higher than 3% above m/e 150 are listed.

15. E. Houghton and J.E. Saxton, *J. Chem. Soc.* (C), 595 (1969).

16. M.p. 225-227 °C, MS: 292 (M+1, 20), 291 (M, 100), 276 (18), 275 (62), 262 (7), 261 (5), 247 (4), 233 (2), 232 (2), 219 (2). Only peaks higher than 2% above m/e 200 are listed.

17. M.p. 214-216 °C, MS: 277 (M+1, 20), 276 (M, 100), 248 (16), 247 (90), 219 (7), 218 (7). Only peaks higher than 2% above m/e 200 are listed.

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