Tetrahedron Vol. 36, pp. 1439 to 1443
Pergamon Press Ltd., 1980. Printed in Great Britain

SYNTHESIS OF 2,2'-BIINDOLYLS BY COUPLING REACTIONS

JAN BERGMAN and NILS EKLUND
Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

(*Received in UK 20 August 1979*)

Abstract—Coupling reactions of indoles forming 2,2'-biindolyls have been investigated. 2-Iodo-N-methyl-indole and unactivated copper gave N,N'-dimethyl-2,2'-biindolyl whereas activated copper yielded N-methyl-indole and the symmetrical trisindolobenzene **5**. A mechanism involving the elimination of copper hydride to form a hetaryne intermediate is suggested.

Coupling of N-benzenesulfonyl-2-lithioindole with $CuCl_2$ yielded 2,2'-biindolyl after hydrolysis. N-methyl-2-lithioindole likewise gave N,N'-dimethyl-2,2'-biindolyl.

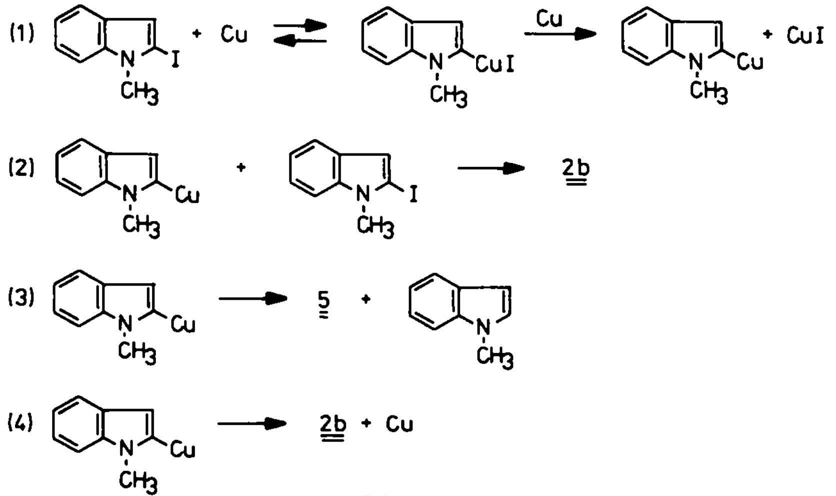
In spite of its relation to indigo (**1**), 2,2'-biindolyl (**2a**) and simple derivatives such as **2b** are relatively inaccessible compounds. All attempts[1,2] (e.g. Wolff–Kishner reduction) to convert **1** to **2**- have so far been unsuccessful. A rather capricious[3-6] Madelung cyclization of oxalyl-*o*-toluidide seems to be the only route available except for a two-fold Fischer cyclization of the bis-phenylhydrazone (**3b**) to impure N,N'-dimethyl-2,2'-biindolyl (**2b**) in a modest yield.[7] In our hands attempted cyclization of **3a** gave a complex mixture lacking **2a**.

Very few studies[3,8] of the chemical properties of 2,2'-biindolyls have been published and now we wanted to study some cycloadditions as well as interaction of reagents such as SeO_2, $SeOCl_2$ and $TeCl_4$, which might yield compounds of type **4** ($X = Se$ or Te). Such planar electron-rich systems might be of interest as donors in e.g. "organic metals".[9] A prerequisite for such studies is, however, ready access to the starting materials, and in this paper we report the results of some coupling reactions of simple indoles leading to 2,2'-biindolyls.

Copper promoted couplings. Iodination of N-methyl-2-lithioindole (a reagent often[10,11] used in synthetic indole chemistry) readily afforded 2-iodo-N-methylindole, which on coupling with unactivated copper gave N,N-dimethyl-2,2'-biindolyl (**2b**) whereas activated[12] copper afforded N-methylindole and the known[13] trimeric compound (**5**) in the relative ratio 3 : 1. Both reactions gave excellent yields.

These results might be explained using the reactions outlined in Scheme 1: With activated copper (in excess) 2-iodo-M-methylindole is quickly depleted in reaction (**1**). N-Methyl-2-indolyl copper is consumed in reaction (**3**) rather than reaction (4), which was corroborated by an independent experiment. The heating of N-methyl-2-indolyl copper, generated from 2-lithio-N-methylindole and cuprous bromide, gave **5** and N-methylindole. With unactivated copper N-methyl-2-indolyl copper is formed relatively slowly and reaction (2) can compete with reaction (3).

In accordance with this formulation iodobenzene was found to react with N-methyl-2-indolyl copper to give N-methyl-2-phenylindole. (For some related unsymmetrical Cu-promoted coupling reactions, see Refs 14–16). In reaction (3) the intervention of copper hydride seems not unlikely and in a separate experiment it was shown that heating of N-methyl-2-indolyl copper with copper hydride yielded N-methylindole. In this connection the reported[17] thermal decomposition of alkyl and vinyl copper derivatives into alkene and alkyne respectively and copper hydride is of interest. Furthermore the formation of copper hydride seemed to induce reductions.[17]



Scheme 1.

It should be noted that N-methyl-2-indolyl copper is represented as monomeric just for reasons of simplicity. From studies on related organocopper compounds[18,19] it seems likely that the best representation is a cluster of the general formula R_nCu_m, a fact which might have bearings on the facile trimerization.

N-Methyl-2-indolyl copper was found to be a relatively stable and rather insoluble compound that could be stored for several weeks at room temperature. In this connection the report of Müller[13] concerning several stable organometallic derivatives, such as Be, Mo and Tl of N-methyl-3-chloroindole is of interest. On the other hand N-methyl-3-chloro-2-indolyl copper was reported[13] to be comparatively unstable.

2-Iodo-N-methylindole (a low melting solid) is relatively unstable, especially in the presence of acids, and storage (even in refrigerator) resulted in the formation of the hydroiodide of N,N'-dimethyl-2,3'-bi-indolyl. Treatment with potassium hydroxide in ethanol readily gave the free base **6**. Interestingly Kunori[20] has made similar observations in connection with bromination studies of N-methylindole.

The high yield of the symmetrical trimeric compound **5** from N-methyl-2-iodoindole and copper is intriguing. No other haloarene studied so far in the Ullman reaction seems to have yielded triphenylenes. Certain dihaloarenes notably 1,2,3,4-tetrafluoro-5,6-diiodobenzene and 1-chloro-2-iodobenzene form triphenylenes in modest yield when treated with copper-bronze.[21] Dehydroarenes (arynes) have not been suggested as intermediates in these reactions. Although hetarynes with a 5-membered ring, including pyrrolyne[22] and N-methylindolyne[13] have frequently been suggested, questioned and recalled (*cf* ref. 23), it is tempting to imply such a species as an intermediate in the present case, because by donation–backdonation, according to the Dewar-Chatt-Duncanson model,[24,25] as indicated in Scheme 2, the intermediate should be stabilized considerably. Investigations on Cu(0)-ethylene complexes[26] support this view. A mechanism involving free radicals seems less likely in view of the relative cleanliness of the reactions.

The hetaryne-Cu complex might then undergo a stepwise trimerization yielding **5**. The unsymmetrical isomer (**7a**) is only formed in small amounts (<2%). Attempts to increase the yield of **7a** by addition of **2b** to the reactants failed. Furthermore, addition of derivatives of **2c** failed to yield **7b**. Thus we conclude that an "irregular" trimerization rather than a cyclo-addition of **2b** to a hetaryne, should account for the small amounts of **7a** formed. The unsymmetrical isomer **7a** has been synthesized by several routes (*cf* following paper).

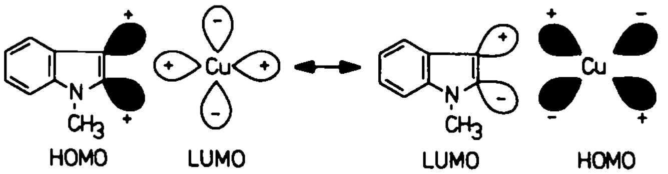
Müller[13] has made several attempts to "trap" N-methyl-indolyne. An example using tetraphenylcyclopentadienone (X) is given in Scheme 3. We have now found that addition of activated copper-bronze instead of (X) gave the symmetrical trimer **5** in good yield.

In connection with the discussion of the possible involvement of a N-methylindolyne-Cu complex in these reactions it should be mentioned that indirect evidence for the intervention of a benzyne-Ni complex has been obtained in connection with some carbon-nickel additions to benzyne.[27] Furthermore benzyne-Ag-olefin adducts have been suggested to account for unusual products from certain Ag-promoted benzyne-olefin cycloadditions[28] and recently Schrock *et al.*[28b] reported the synthesis and molecular structure of monomeric niobium- and tantalum benzyne complexes.

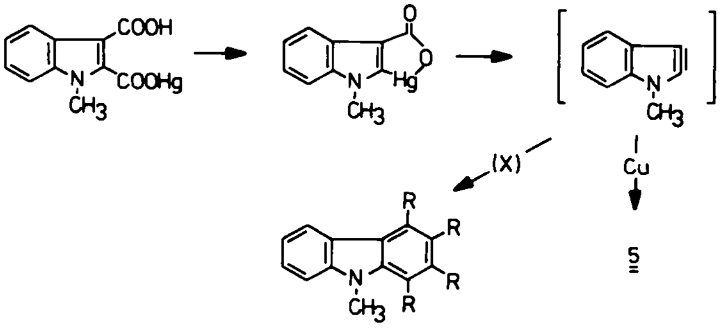
Coupling of Grignard-reagents and organolithium compounds with reagents such as Ag, $CuCl_2$ and $CoCl_2$ is a common procedure for the synthesis of biaryls,[29,30] which worked well in the present case. Some results are summarized in Scheme 4, where a mechanism involving a reductive elimination of a diarylated Cu(II)-species is indicated. In any case the intermediate cannot be identical with the species encountered in the reaction with N-methyl-2-lithioindole and cuprous bromide, because different products are obtained.

2,2'-Biindolyl (**2a**) could also be obtained by the route given in Scheme 4. Thus lithiation of N-benzenesulfonylindole (*cf* Ref. 31) followed by $CuCl_2$ afforded the coupled product **2d**, which on alkaline hydrolysis gave **2a**. In this connection it should be mentioned that the original synthesis due to Madelung,[3] was successful in our hands provided that the reaction temperature was kept at 320° rather than the indicated 360°.

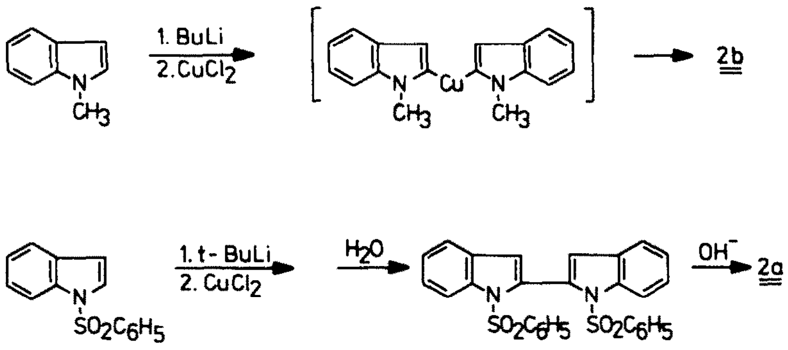
Couplings promoted by palladium acetate. Oxidative coupling promoted by palladium acetate has been used to convert benzofuran to 2,2'-bibenzofuranyl in a respect-



Scheme 2.



Scheme 3.

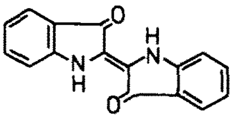


Scheme 4.

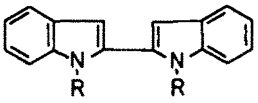
able yield.[32] Replacing benzofuran with N-methylindole did not, however, afford any shortcut route to **2b** or its 3,3'-isomer, because a very complex mixture including the 3,3'- and 2,3'-coupled products (*cf* Ref. 33) was obtained and **2b** was not formed at all. The main product (20%), which could be isolated by crystallization, was identified as **8a**. The methylene bridge must have been formed by oxidative demethylation to an equivalent of formaldehyde, which then condenses with N-methylindole to yield **8a**. The formation of **8b** could be detected by tlc. Interestingly N,N-dimethyl-aniline has been reported to undergo a similar oxidative demethylation yielding **9** with a wide range of reagents[34-38] including palladium acetate.[39] Oxidative coupling of indole with palladium acetate also gave a complex mixture, containing small amounts of 3,3'-biindolyl and 2,3'-biindolyl, but no 2,2'-biindolyl. In this connection a recent patent claiming good yields of 3,3'-biindolyl by oxidative coupling[40] of indole in pyridine induced by cupric sulfate is of interest.

N-Acylindoles were found to be a more suitable substrate in Pd(OAc)$_2$ induced couplings, thus e.g. N,N'-carbonylindole gave a respectable yield of **9**. Itahara and Sakakibara have recently [40a] reported similar intramolecular coupling reactions, e.g. the conversion of 3-benzoyl-N-methylindole in 60% yield to 5-methyl-5,10-dihydroindeno[1,2-b]indol-10-one. Alkaline hydrolysis of **9**, which also could be prepared from 2,2'-biindolyl and N,N'-carbonylimidazole, afforded 2,2'-biindolyl.

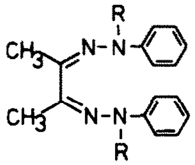
In some preliminary experiments to cyclise **2b** with SeOCl$_2$ and TeCl$_4$ respectively, the known[13] compound N,N'-dimethyl-3,3'-dichloro-2,2'-bi-indolyl was isolated rather than the desired compound of type **4**. An attempt to form 3,3'-diindolyl selenide by reaction with SeO$_2$ similar to the known[41] conversion of indole to 3,3'-biindolyl selenide resulted in a very complex mixture.



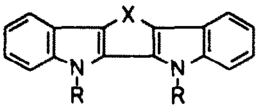
1



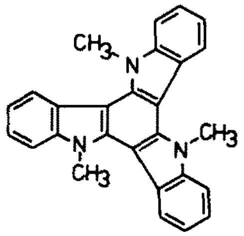
2 a R=H
b R=CH_3
c R=CD_3
d R=$SO_2C_6H_5$



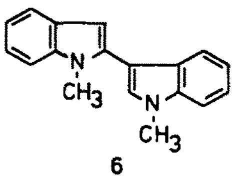
3 a R=H
b R=CH_3



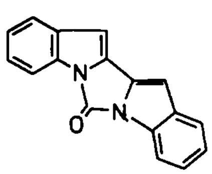
4



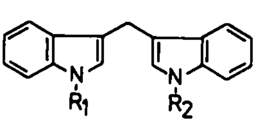
5



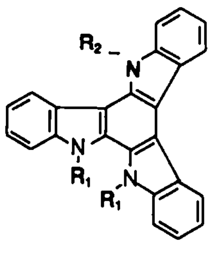
6



9



8 a $R_1 = R_2 = CH_3$
b $R_1 = H, R_2 = CH_3$



7 a $R_1 = R_2 = CH_3$
b $R_1 = CO_3, R_2 = CH_3$

EXPERIMENTAL

M.ps were determined on a micro hot stage m.p. apparatus and are uncorrected. IR spectra were recorded with a Perkin Elmer 421 IR spectrophotometer as KBr discs. ^{1}H-NMR spectra were recorded with a Varian-A60 instrument. All chemical shifts are related to TMS ($\delta_H = 0$). Mass spectra were recorded with LKB 9000 instrument (direct inlet, 70 eV).

2-*Iodo*-N-*methylindole*. BuLi (45 ml, 20% in hexane) was added under N_2 to a stirred soln of N-methylindole (13.1 g, 0.1 mol) in dry ether (300 ml) at 0°. After addition was complete the soln was refluxed for 3 hr, cooled to +15° and iodine (25.4 g, 0.1 mol) was added in portions. Na_2SO_3 (300 ml, aq. 5%) was then added and the ether phase separated, washed with water and dried. The oil obtained by evaporation was dissolved in light petroleum (40–60°) and when cooled to −25° produced crystals of 2-iodo-N-methyl-indole, yield 19.8 g (77%) m.p. 76–77°. MS[*m/e*(%*rel. int.*)]:258(M+1,10), 257(M, 100) 130(7), 129(11), 128.5(15), 115(7), 89(74), 63(10), 51(6), 39(7). Only peaks higher than 5% are listed.

N-*Methyl-2-indolyl copper*. N-Methylindole was lithiated as described (0.02 mol scale). Freshly prepared, dried cuprous bromide (2.87 g, 0.02 mol) was then added in portions to the stirred mixture at 25°. After 24 hr the light brown solid was collected, washed with dry ether and then stored under N_2 in the refrigerator.

Reaction of N-*methyl-2-indolyl copper with iodobenzene*. N-Methyl-2-indolyl copper (1.94 g) and iodobenzene (10.0 g) in pyridine (30 ml) were refluxed under N_2 for 4 hr. The solvent and an excess of iodobenzene were removed under reduced pressure. The residue was extracted with light petroleum. Cooling (finally to −30°) produced crystals of N-methyl-2-phenyl-indole, yield 1.2 g (60%) m.p. 100–101° (lit.[42] 100–101°).

Reaction of N-*methyl-2-indolyl copper with copper hydride*. N-Methyl-2-indolyl copper (1.94 g) and copper hydride[43] (5 g) were mixed and heated to 180° under N_2 for 30 min. The mixture was extracted with light petroleum and the extract evaporated and distilled to yield N-methylindole 1.1 g (83%).

N,N^1-*dimethyl-2,2′-biindolyl* (**2b**). N-Methylindole was lithiated, as described. Dry cupric chloride (6.92 g, 0.05 mol) was then added at 25° in portions to the well-stirred mixture. After addition was complete and after a period of reflux (1 hr) water was added. The ether phase was separated, dried (Na_2SO_4) and evaporated. The residue crystallized from EtOAc yielded 9.5 g (73%) m.p. 182–184° (lit.[7] 153–157°). A sample kindly provided by Dr. Fränkel was impure, but did contain N,N-dimethyl-2,2′-biindolyl, which could be isolated by preparative tlc. NMR ($CDCl_3$): δ_H 3.65(6, NCH_3, s), 6.62(2, 3-H s), 7.0–7.8(8, arom., m). MS [*m/e*(% rel. int.)]: 261(M+1, 20), 260(M, 100), 259(48), 258(7), 245(12), 243(9), 217(9), 144(7), 138(18), 129(7). Only peaks higher than 6% are listed, m*: 230.8(260→245).

Method B: 2-iodo-N-methylindole (2.57 g) and unactivated copper-bronze (15 g) were heated under N_2 for 15 min at 205°. The cooled mixture was extracted with hot EtOAc. Concentration and final cooling produced crystals, yield 0.86 g (66%) m.p. 182–184°.

Sym(*tris* N-*methylindolo*) *benzene* (**5**). Method A. Procedure B above was used (0.02 mol scale) with the exception that activated[12] copper–bronze was used, yield 0.52 g (81%) m.p. 265–267° (lit.[13] 267°). A sample kindly provided by Professor Wittig was identical with our product. The co-product, N-methylindole, could be isolated by distillation of the evaporated mother-liquor. MS: [*m/e*(% rel. int.]: 388(M+1, 28), 387(M, 100), 373(11), 372(28), 357(19), 342(10), 193.5(22), 186(11), 178.5(14). Only peaks higher than 9% are listed.

IR spectra: 3050(NH), 1575, 1480, 1330, 1250, 745, 720 cm^{-1}. NMR($CDCl_3$): δ_H 4.25(9, NCH_3, s), 7.0–7.8(12, arom., m). Method B. N-Methyl-2-indolyl copper (1.94 g) was heated (200°) under argon for 1 hr. The mixture extracted with EtOAc produced **5**, yield 0.24 g (75%) m.p. 265–267°. Method C. The mercury-containing compound[13] (3.74 g) and activated copper-bronze (10 g) were heated under N_2 for 1 hr at 205° and then extracted with EtOAc as described above, yield 0.72 g (56%) m.p. 265–267°.

N,N′*Diphenylsulphonyl-2,2′-biindolyl* (**2d**). t-BuLi (0.015 mol = 75 ml of a 2 molar soln in hexane) was added to a soln of N-phenylsulfonylindole 2.60 g (0.01 mol) in dry ether (200 ml). After stirring for 1 hr at room temp., dry fine-divided cupric chloride (3 g) was added and the mixture was refluxed for 2 hr. The mixture was poured into water (500 ml) and the organic layer was washed with water, dried and evaporated under reduced pressure. MeOH (10 ml) was added to the resulting yellow oil and the precipitated light brown crystals were filtred off, yield 0.60 g (23%). The crude product was purified by preparative tlc, using CH_2Cl_2 + 5% MeOH as eluent, producing white crystals, m.p. 229–231°. IR: 1440, 1375, 1185, 1090, 720, 680, 640. MS [*m/e* (% rel. int.)]: 512(M, 1.7), 256(100), 192(26), 191(69), 164(16), 163(16), 95.5(20). Only peaks higher than 15% above *m/e* 50 are listed (except M$^+$).

2,2′-*Biindolyl* (**2e**). Compound **2d** was hydrolysed in a mixture of MeOH 1 and 2 M NaOH (5 : 1) using the method described by Sundberg[31] for hydrolysis of N-phenylsulfonylindole. The resulting mixture was concentrated in vacuum and upon addition of water the crude 2,2-biindolyl separated as small light brown crystals. A pure sample was obtained by prep tlc using CH_2Cl_2 + 5% CH_3OH as eluent, m.p. 311–314° (lit.[5] 308–310°). IR: 3405(NH), 1445, 1400, 1343, 780, 755. MS [*m/s*(% rel. int.)]: 234(M+2, 1.8), 233(M+1, 18.0), 232(M, 100), 231(37.5), 230(90), 229(5.8), 204(13.8), 116(21.0), 115½(3.5), 115(5.8), 102½(3.5), 102(10.8), 101½(3.3), 90(5.0), 89(11.0), 88(4.0). Only peaks higher than 3% above *m/e* 70 are listed.

Reaction of N-*methylindole with* $Pd(OAc)_2$. N-Methylindole (1.31 g) and $Pd(OAc)_2$ (1.12 g) in AcOH (30 ml) were refluxed for 8 hr. The mixture was evaporated and residue extracted with hot MeOH and filtered. Upon cooling, crystals of **8a** were obtained, yield 0.24 g (26%) m.p. 112–113° (lit.[44] 112.5–113°).

N,N′,-*Dimethyl-3,3′-dichloro-2,2′-biindolyl*. To a soln of N,N′-dimethyl-2,2′-biindolyl (0.20 g) in dry ether (10 ml) an excess of $SeOCl_2$ (0.60 g) was added. The mixture was stirred at room temp. for 2 hr and then quenched with water. The organic phase was separated, washed with water, dried and evaporated to dryness. The residue was sublimed in vacuum, yield 0.08 g (32%) m.p. 189–191° (lit.[13] 183–191°). IR: 3050, 2930, 1460, 1325, 1234, 737. MS [*m/e*(% rel. int.)]: 330(M+2, 67), 328(M, 100), 293(32), 292(22), 258(70), 257(54), 256(23), 242(21), 164(22), 129(24). Only peaks higher than 20% above *m/e* 100 are listed. A sample kindly provided by Professor G. Wittig, and originally prepared by Müller,[13] was identical with our product.

N.N′-*Dimethyl-2,3′-biindolyl*. N-Methyl-2-iodoindole (10 g) stored for 6 months was dissolved in hot MeOH (100 ml) and water (10 ml) containing KOH (10 g). The mixture was filtered hot and the crystals obtained upon cooling were collected, washed with water and dried, yield 3.5 g (69%) m.p. 137–138° (lit. m.p. 134–135°,[20] 133–135°[45]). NMR ($CHCl_3$): δ_H 3.69(3, NCH_3, s), 3.79(3, NCH_3, s), 6.66(1, 3-H, s), 7.1–7.9(9, arom., m).

Synthesis of compound 9. N,N'-Carbonylindole[46] (1.30 g) and $Pd(OAc)_2$ (1.16 g) in AcOH (15 ml) was refluxed for 6 hr. The Pd(0) formed was filtered off and the filtrate concentrated to *ca* 5 ml: The crystals formed on cooling were collected washed with MeOH and dried, yield 1.08 g (84%), m.p. 293–294°. IR 1760 (C=0) (as compared[46] with 1708 cm^{-1} in the starting material). MS|*m*/*e*(% rel. int.)|: 259(M + 1, 25), 258(M, 100), 230(32), 144(14), 129(16), 116(22), 89(11). Only peaks higher than 10% above *m*/*e* 50 are listed. m*: 205.0(258 → 230).

Hydrolysis of compound 9. Compound 9 (258 mg) was refluxed in EtOH (15 ml), water (5 ml) and KOH (0.5 g) for 1hr. The solid formed on cooling was collected, dried (206 mg, 89%) and identified as 2,2'-biindolyl.

REFERENCES

[1a] W. Borsche and R. Meyer, *Ber. Dtsch. Chem. Ges.* **54**, 2854 (1921); [b] R. Meyer, *Diss.* Göttingen (1920).

[2] J. Bergman, B. Egestad and N. Eklund, *Tetrahedron Letters* 3147 (1978).

[3] W. Madelung, *Liebigs Ann.* **405**, 58 (1914).

[4] P. Seidel, *Ber. Dtsch Chem. Ges.* **77**, 788 (1944).

[5] S. A. Faseeh and J. Harley-Mason, *J. Chem. Soc.* 4141 (1957).

[6] H.-Ch. Steinmetzer, *Diss.* p. 41. Würzburg (1973).

[7] J. Fränkel, *Diss.* Aachen (1965).

[8] W. Madelung and F. Hager, *Ber. Dtsch. Chem. Ges.* **49**, 2039 (1916).

[9] E. M. Engler, V. V. Patel, J. R. Andersen, R. R. Schumaker and A. A. Fukushima, *J. Am. Chem. Soc.* **100**, 3769 (1978), and Refs therein.

[10] A. B. Levy, *J. Org. Chem.* **43**, 4684 (1978) and Refs therein.

[11] J. Kebrle, A. Rossi and K. Hoffmann, *Helv. Chim. Acta* **41**, 907 (1959).

[12] A. I. Vogel, *Practical Organic Chemistry* (3rd Edition), p. 192. Longmans, London (1956).

[13] H. Müller, *Diss.* Heidelberg (1964).

[14] C. Ullenius, *Diss.* Gothenburg (1973).

[15] N. Gjös, *Diss.* Lund (1971).

[16] Th. Kauffmann, *Angew. Chem.* **91**, 1 (1979).

[17] H. O. House and J. C. DuBose, *J. Org. Chem.* **40**, 788 (1975), and Refs therein.

[18] G. Costa, A. Puxeddu, A. Camus and N. Marsich, *J. Organometal Chem.* **160**, 353 (1978), and Refs therein.

[19] H. K. Hofstee, J. Boersma and G. J. M. van der Kerk, *J. Organometal Chem.* **144**, 255 (1978), and Refs therein.

[20a] M. Kunori, *Nippon Kaguku Zasshi* **83**, 836, 839 (1962); [b] J. A. Janke, *Diss.* p. 87. Univ. of Minnesota, Minneapolis (1970).

[21a] P. E. Fanta, *Synthesis* 9 (1974); [b] P. E. Fanta, *Chem. Rev.* **64**, 613 (1964); [c] P. E. Fanta, *Chem. Rev.* **38**, 139 (1946).

[22] R. H. Brown, *Diss.* New York University (1975).

[23] H. I. den Hertog and H. C. van der Plas, *Chemistry of Acetylene* (Edited H. G. Viehe), p. 1149. New York, Dekker (1969).

[24] J. Chatt and L. A. Duncanson, *J. Chem. Soc.* 2939 (1953).

[25] M. J. S. Dewar, *Bull. Soc. Chim. Fr* C71 (1951).

[26] H. Huber, D. McIntosh and G. A. Ozin, *J. Organometal. Chem.* **112**, C50 (1976).

[27] D. P. Kuhlman, *Diss.* University of North Dakota (1970).

[28a] P. Crews and M. Loffgren, *Tetrahedron Letters* 4697 (1971); [b] S. J. McLain, R. R. Schrock, P. R. Sharp, M. R. Churchill and W. J. Youngs, *J. Am. Chem. Soc.* **101**, 264 (1979).

[29] L. F. Elsom, J. D. Hunt and A. McKillop, *Organometal Chem. Rev.* **8A**, 135 (1972).

[30] K. Tamao, M. Kumada, S. Akutagawa and S. Otsuka, *Kagaku No Ryoki* **117**, 45 (1977).

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

[32] A. Kasahara, T. Izumi, M. Yodono, R. Saito, T. Takeda and T. Sugawara, *Bull. Chem. Soc. Jap.* **46**, 1220 (1973).

[33] E. S. Rudakov and V. M. Ignatenku, *Dokl. Akad. Nauk SSSR* **241**, 148 (1978).

[34] J. M. Bronsdijk, *Diss.* Leiden (1965).

[35] W. Michler and H. Walder, *Ber. Dtsch Chem. Ges.* **14**, 2175 (1881).

[36] C. Choo Yin and A. J. Deeming, *J. Organometal. Chem.* **144**, 351 (1978).

[37] A. G. Giumanini and M. M. Musiani, *Z. Naturforsch.* **32B**, 1314 (1977).

[38] A. Arnoldi, G. Galliani, B. Rindone and P. L. Beltrame, *Gazz. Chim. Ital.* **108**, 127 (1978).

[39] T. Sakakibara, J. Kotobuku and Y. Dogomori, *Chem. Lett.* 25 (1977).

[40a] Japan Kokai 76 19.764; *Chem. Absts.* **85**: 159874 (1976); [b] T. Itahara and T. Sakakibara, *Heterocycles* **12**, 148 (1979).

[41] J. Bergman, *Acta Chem. Scand.* **22**, 1883 (1968).

[42] H. M. Kissman, D. W. Farnsworth and B. Witkop, *J. Am. Chem. Soc.* **74**, 3948 (1952).

[43] J. A. Dilts and D. F. Shriver, *Ibid.* **90**, 5769 (1968).

[44] E. Leete, *Ibid.* **81**, 6023 (1959).

[45] A. Da Settimo and E. Nannipieri, *J. Org. Chem.* **35**, 2546 (1970).

[46] J. Bergman, R. Carlsson and B. Sjöberg, *J. Het. Chem.* **14**, 1123 (1977).