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CHEMICAL SYNTHESES WITH BERGMANN–SCHLENK ADDUCTS—VIII

THE CYCLODEHYDROGENATION OF BENZIL DIANIL

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Abstract—Treatment of benzil dianil with lithium metal in THF effects the initial formation of N,N'-dilithio-α,α'-dianilinostilbene in a manner similar to sodium. In the presence of excess lithium, this dianion undergoes a cyclodehydrogenation to form N,N'-dilithio-9,10-dianilinophenanthrene and lithium hydride. This new dianion is characterised by protonation, alkylation with methyl iodide or allyl bromide and acylation with ethyl chloroformate. The formation of lithium hydride is established by treatment with deuterium oxide and identification of HD. It is suggested that the cyclodehydrogenation proceeds through a radical trianion which stabilizes itself by eliminating lithium hydride.

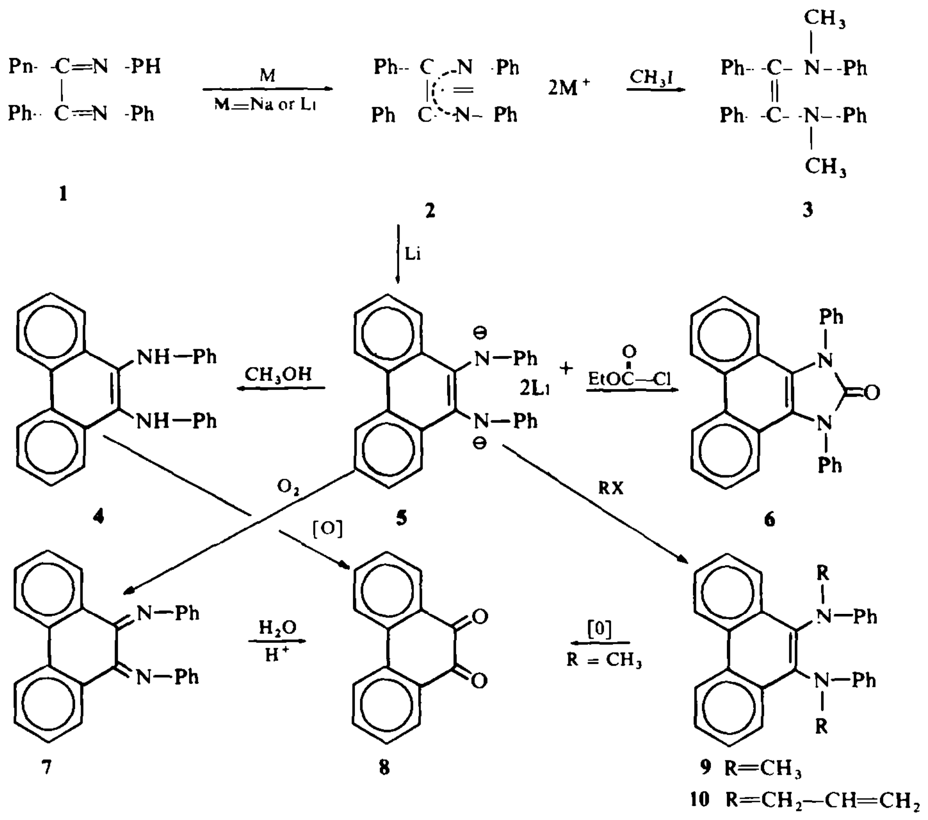
Our previous investigation[1] of the reduction of benzil dianil, **1**, with sodium metal has been extended to the related reaction with lithium. As reported in an earlier communication,[2] the dianil behaved in an unexpected manner towards the latter alkali metal.

In the presence of excess lithium metal, with THF as solvent, an extensive reduction of benzil dianil, **1**, occurred. Titration of the solution of reaction products indicated that 10–11 g-atoms of lithium per mole of **1** had reacted. On quenching such solutions in water, considerable amounts of hydrogen were evolved. Evidently, the reduction of **1** was accompanied by hydride elimination and additional studies concentrated on delineating the steps involved in the reaction.

By limiting the amount of lithium to 2 g-atom per mole of **1** or by taking advantage of the characteristic colour change which occurred at this composition, N,N'-dilithio-α,α'-dianilinostilbene, **2**, was formed. Alkylation of the dilithio salt with methyl iodide furnished evidence for the formation of **1** by producing N,N'-dimethyl-α,α'-dianilinostilbene, **3**, and demonstrated that in the early stages of the reduction, the same dianion **2** was formed by both sodium[1] and lithium.

By restricting the lithium metal to 4 g-atoms per mole of **1** and permitting the reaction to continue until the metal was consumed, a product **5** differing from **2** was formed. Characterization of **5** was accomplished by protonation and by alkylation with methyl iodide. The products obtained in these reactions were not identical to those obtained in the corresponding reactions of dianion **2**.

A comparison of the spectra of these new products with those of the products isolated from the reaction of **2** showed that major changes had occurred in the aromatic ring system. In the NMR spectra, two aromatic protons appeared at a position further downfield than expected for a substituted phenyl ring. The UV spectra showed several absorption maxima with large extinction coefficients. Both of these observations are compatible with the presence of a phenanthrene ring in the products. Final confirmation of this was obtained by oxidizing these two compounds with sodium dichromate in aqueous acetic acid to phenanthraquinone, **8**. The two compounds (Scheme 1) were thus established as 9,10-dianilinophenanthrcne **4** and 9,10-bis(N-methylanilino)phenanthrene, **9**.



Scheme 1. The chemical reactions of the Dianions from Benzil Dianil

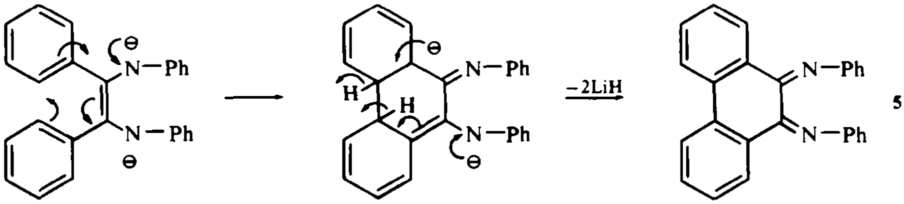
In additional reactions, the dianion **5**—now established as N,N'-dilithio-9,10-dianilinophenanthrene—was treated with allyl bromide to form 9,10-bis(N-allylanilino)phenanthrene, **10**, and with ethyl chloroformate to form 1,3-diphenyl-4,5-(9,10–phenanthro)-2-imidazolinone, **6**. Alkylation with 1,3-dibromopropane provided a complex reaction mixture from which no definite product could be isolated.

A further confirmation of the formation of a phenanthrene ring was obtained by oxidizing the dianion **5** with dry oxygen. This reaction produced the deep red 9,10-phenanthraquinone dianil, **10** and hydrolysis of this generated 9,10-phenanthraquinone, **8**.

The formation of the phenanthrene ring during the reaction requires the loss of two aromatic protons. Since the reaction of benzil dianil with metal is carried out in sealed tubes, the evolution of hydrogen gas would be readily observed. The lack of any pressure in the tubes at the conclusion of the reactions indicated that the loss of hydrogen occurred with the formation of lithium hydride.

In order to prove this, the dianion, **5**, was protonated and the evolved gas, which was collected, amounted to 2 moles of hydrogen per mole of benzil dianil. The possibility that the gas arose from metallic lithium remaining suspended in solution was eliminated by repeating the reaction using deuterium oxide. The collected gas was examined by mass spectrometry and shown to be largely HD, the expected product from lithium hydride, and not D_2, the expected product from lithium metal.

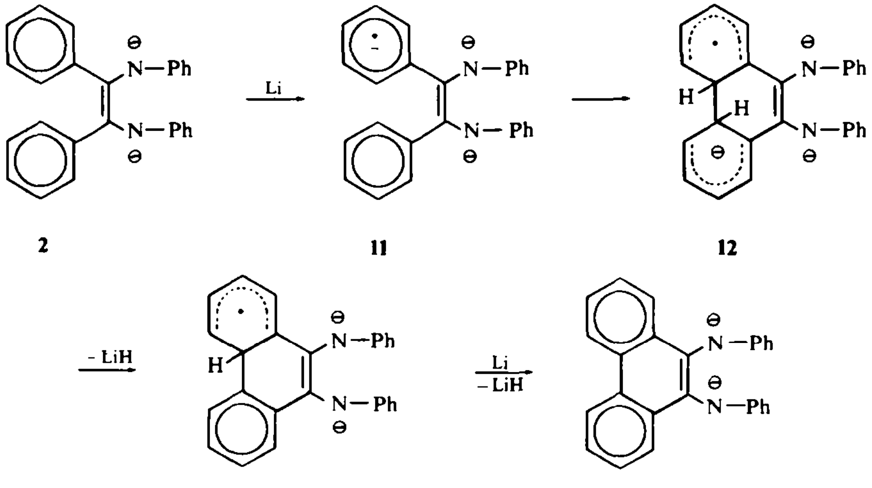
One possible explanation of the phenanthrene ring formation is the elimination of hydride ion from the dianion **2** to form phenanthraquinone dianil **7**. Subsequent reduction of this material with the excess lithium would produce the observed cyclized dianion **5**. However, the lithium salt of α,α′-dianilinostilbene, was prepared



2 **7**

and during the time interval required for the formation of **5**, it showed no tendency to spontaneously produce the phenanthrene derivative.

Only under the influence of excess lithium metal does the cyclization occur. It would appear that the dianion, **2**, is converted to a trianion-radical (eg. **11**) by the excess lithium and that this induces a coupling of one phenyl to the other spatially accessible ring. Such coupling reactions are well-known occurrences in the Pschorr synthesis[3] and in the photochemical reactions of stilbene derivatives.[4]



5

The cyclized radical trianion **12** may then stabilize itself by the elimination of a hydride ion either stepwise, as shown, or simultaneously on reaction with lithium, to give the observed product.

Additional examples of similar cyclodehydrogenations in the presence of alkali metals are known. For example, benzil is converted to phenanthrene derivatives by potassium,[5] binaphthyl to perylene by lithium,[6,7] tetraphenylallene to a dibenzocycloheptatriene by lithium,[8] and *o*-terphenyl to triphenylene by lithium.[9] From these reports it is not unwarranted to suggest that lithium may well prove to be a valuable cyclodehydrogenating agent for the synthesis of fused aromatic ring systems.

EXPERIMENTAL

M.ps are uncorrected and were determined with a Mel-temp apparatus. The NMR spectra were recorded on a Varian T-60 or a 100 Mc spectrometer using TMS as an internal standard. The IR spectra were recorded on a Beckman IR-10 and the UV spectra on a Cary spectrophotometer. Eastman Kodak pre-coated silica gel sheets were employed for TLC. Microanalyses were performed by A. Gygli, Toronto, Ontario.

The THF was dried with LAH, stored under nitrogen over the same reagent and distilled from it immediately before use. The Bergmann–Schlenk adducts were prepared in Schlenk tubes and drained from any unreacted metal into the reaction flask under nitrogen.

Preparation of 9,10-*dianilinophenanthrene*, **4**. A soln of the dianion **5** prepared from 1·44 g (·004 m) of benzil dianil and 0·138 g (·0199 g atom) Li in 100 ± 10 ml THF was treated with 2·0 ml MeOH injected through a septum. The reaction flask was connected to a gas collecting tube so that the H_2 which evolved on addition of the MeOH could be measured. A total of 174 ml of gas (corrected to STP, ·008 m) was liberated.

The mixture was treated with water and the product isolated by an ether extraction. Removal of the solvent left an oil which crystallized on adding a few ml ether. Filtration gave 1·26 g of **4** (88%) white solid mp 205–210°. Recrystallization from degassed acetonitrile raised the mp to 213–215° (sealed tube); IR (KBr) 3480 cm^{-1} (NH); UV max (95% EtOH) 252 mμ (ε 64,800), 335 (ε 9,900); NMR ($CDCl_3$ degassed and sealed δ 5·1 (broad, 2H, NH), 6·7–8·2 (m, 16H, aromatics), 8·6 (complex d, 2H, aromatics); mass spectrum (70 eV) *m/e* (rel intensity), 361 (38), 360 (100, M^+), 345 (35), 282 (19), 267 (20). Found: C, 86·89; H, 5·77; N, 7·80. Calcd for $C_{26}H_{20}N_2$: C, 86·62; H, 5·60; N, 7·77%).

A soln of 500 mg of **4** in 15 ml glacial AcOH was treated with 1·0 g sodium dichromate dihydrate. After 2 hr heating at 100°, the mixture was diluted with water and extracted with benzene. Evaporation of the dried extracts gave 300 mg of a brown solid which on recrystallization from glacial AcOH gave 200 mg (69%) 9,10-phenanthraquinone mp 204–205°, undepressed on admixture with an authentic sample.

Deuteration of the dianion **5** was performed in the manner described using the dianion prepared from 0·234 g (·0336 g–atoms) Li, 2·412 g (·0067 m) of benzil dianil in 100 ml THF. Addition of 2·0 ml D_2O generated 290 ml of gas (corrected to STP, ·0134 m). Mass spectral analysis gave an *m/e* (rel intensity) of 2 (1), 3 (10), 4 (1) establishing it as predominantly HD.

Isolation of the reaction product gave 2·0 g (84%) of **4**.

Preparation of 9,10-*bis*(N-*methylanilino*)*phenanthrene*, **9**. The adduct from 0·189 g (·0272 g-atoms) Li, 1·944 g (·0054 m) benzil dianil and 100 ml THF was treated at −60° with 3·07 g (·0216 m) MeI. The mixture was allowed to warm to room temp, stirred 12 h, quenched with water and extracted with ether. Evaporation of the dried extracts gave an oil which crystallized from cold n-hexane. The yellow solid **9** amounted to 1·5 g (72%), mp 175–176°. Recrystallization from abs EtOH raised the mp to 179–181° (sealed tube); IR (KBr) 2890, 2920 (aliphatic CH), 2810 cm^{-1} ($N–CH_3$); UV max (95% EtOH) 255 mμ (ε 81,700), 275 (shoulder, ε 17,000), 285 (ε 14,300), 298 (ε 12,900), 350 (ε 4.800); NMR (C_6D_6, degassed and sealed) δ 2·85 (s, 6H, $N–CH_3$), 6·3–8·0 (m, 16H, aromatics), 8·6 (complex d, 2H, aromatics); mass spectrum (70 eV) *m/e* (rel intensity) 389 (31), 388 (M^+, 100), 282 (52), 281 (27), 280 (37), 267 (30). (Found: C, 86·74; H, 6·34; N, 7·15. Calcd for $C_{28}H_{24}N_2$: C, 86·55; H, 6·24; N, 7·21%).

The material was oxidized in the manner described for **4**. A 63% yield of 9,10-phenanthraquinone mp 204–206° was obtained.

Preparation of 9,10-*bis*(N-*allylanilino*)*phananthrene*, **10**. The dianion **5** prepared from 0·144 g (·0208 g atoms) Li, 1·512 g (·0042 m) benzil dianil and 100 ml THF was treated at −60° with 2·54 g (·021 m) allyl bromide. The product was isolated as described for **9**. The crude yellow oily solid was taken up in anhyd ether, cooled and filtered to provide 1·55 g (84%) of the yellow solid **10** mp 198–201°. Recrystallization from EtOH did not raise the mp; IR (KBr) 2990, 2920 and 2890 cm^{-1} (aliphatic CH); UV max (95% EtOH 249 mμ (shoulder, ε 76,500), 255 (ε 94,400), 275 (shoulder, ε 20,800), 286 (ε 17,000), 294 (ε 16,000)

347 (ε 5,900); NMR (C_6D_6) δ 4·15 (complex d, 4H —CH_2—), 5·0 (complex t, 4H, =CH_2) 6·1 (m, 2H, —CH=), 6·5–7·5 (m, 16H, aromatics), complex doublets at 8·0 and 8·5 (2H, aromatics): mass spectrum (70 eV) *m/e* (rel intensity), 440 (M^+, 100), 399 (26), 372 (32), 371 (100), 307 (27), 306 (35)m 280 (25), 267 (20), 165 (22), 106 (73), 77 (80). (Found: C, 87·18: H, 6·68; N, 6·35. Calcd for $C_{32}H_{28}N_2$: C, 87·25; M, 6·42; N, 6·35%).

Preparation of 4,5-(9,10-*phenanthro*)-1,3-*diphenyl*-2-*imidazolinone*, **6**. The adduct **5**, prepared from 0·196 g (·0283 g atom) Li, 2·052 g (·0057 m) benzil dianil and 100 ml THF, was treated at −60° with 3·03 g (·028 m) ethyl chloroformate. Rapid decolorization occurred and after reaching room temp the mixture was diluted with water and the product isolated by a benzene extraction. Evaporation of the dried extracts, trituration of the residue with n-hexane and filtering gave 1·6 g (73%) of **6**, mp 330–340° (sealed tube). Recrystallization from nitromethane gave a faintly yellow solid mp 338–342° (sealed tube): IR (KBr) 1690 cm^{-1} (C=O); UV max 95% EtOH) 265 mμ (ε 51,000), 315 (shoulder, ε 11,800), 327 (ε 13,000), 360 (ε 1,600) 375 (ε 1,600); NMR ($CDCl_3$) 7·2–7·8 (m, 16H, aromatics) 8·15 (d, 2H, aromatics); mass spectrum (70 eV) *m/e* (rel intensity) 387 (60), 386 (M^+, 100), 266 (16), 149 (17), 77 (19). (Found: C, 84·14; H, 4·82; N, 7·16. Calcd for $C_{27}H_{18}N_2O$: C, 83·91; H, 4·70; N, 7·25%).

Preparation of α,α′-*bis*(N-*methylanilino*)*stilbene*, **3**. Benzil dianil (1·8 g, ·005 m) in 100 ml THF was shaken with an excess of Li metal until the colour changed from opaque red-brown to transparent light red (about 1 hr). The soln was immediately drained from the excess metal, cooled to −60° and treated with 1·42 g (·01 m) MeI. Isolation and purification of the product as previously described[1] gave 1·8 g (90%) of yellow-green **3** mp 174°.

This experiment was repeated with 2·30 g (·0064 m) benzil dianil, ·089 (·0128 g atom) Li in 100 ml THF and 24 hr shaking. The reaction conditions with MeI (1·86 g, ·0128 m) and the isolation and purification of the product were as previously described; 2·1 g (84%) of **3**, mp 173° were obtained.

Preparation of 9,10-*phenanthraquinone dianil*, **7**. A soln of **5** prepared from 0·205 g (·0296 g atom) Li and 2·131 g (·00592 m) benzil dianil in 100 ml THF was treated with dry O_2 at room temp. The colour changed from dark red-brown to orange in a few min. Water was added and the product extracted with ether. Evaporation of the dried extracts gave an oily red solid which was triturated with n-hexane and filtered to give 1·8 g (85%) of a red solid mp 133–136°. Recrystallization from EtOH raised the mp of **7** to 137–138°; (IR KBr) 1635 cm^{-1} (C=N); UV max (95% EtOH) 251 mμ (ε 43,900), 362 (ε 6,760); NMR ($CDCl_3$) complex aromatic proton band δ 6·0–8·3; mass spectrum (70 eV) *m/e* (rel intensity) 359 (26), 358 (79, M^+), 282 (46), 281 (100). (Found: C, 87·21; H, 5·27; N, 7·96. Calcd for $C_{26}H_{18}N_2$: C, 87·3; H, 5·07; N, 7·82%).

A 200 mg sample of **7** was refluxed with 20 ml of 20% HCl for 1/2 hr. The resulting mixture was cooled, extracted with chloroform and evaporated to give a dark brown solid. Recrystallization from glacial AcOH acid gave 90 mg (78%) of 9,10-phenanthraquinone, mp 206°, undepressed on admixture with an authentic sample.

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