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THE INTERACTION OF ALKALI METALS WITH UNSATURATED HETEROCYCLIC COMPOUNDS

I. 2,3-DIPHENYLQUINOXALINE AND ITS CYCLODEHYDROGENATION TO DIBENZO[*a*,*c*]PHENAZINE

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SUMMARY

Sodium reduces 2,3-diphenylquinoxaline (I) to a dianion which was characterized by reaction with ethyl chloroformate, methyl iodide and 1,3-diiodopropane. The first reagent produced 1,4-bis(ethoxycarbonyl)-2,3-diphenyl-1,4-dihydroquinoxaline (III), the second a mixture of 1,2- and 1,4-dimethyl-2,3-diphenyl-1,4-dihydroquinoxalines [(V) and (VI)] and the third, 3*a*,4-diphenyl-1,2,3,3*a*-tetrahydropyrrolo-[1,2-*a*]quinoxaline (VIII).

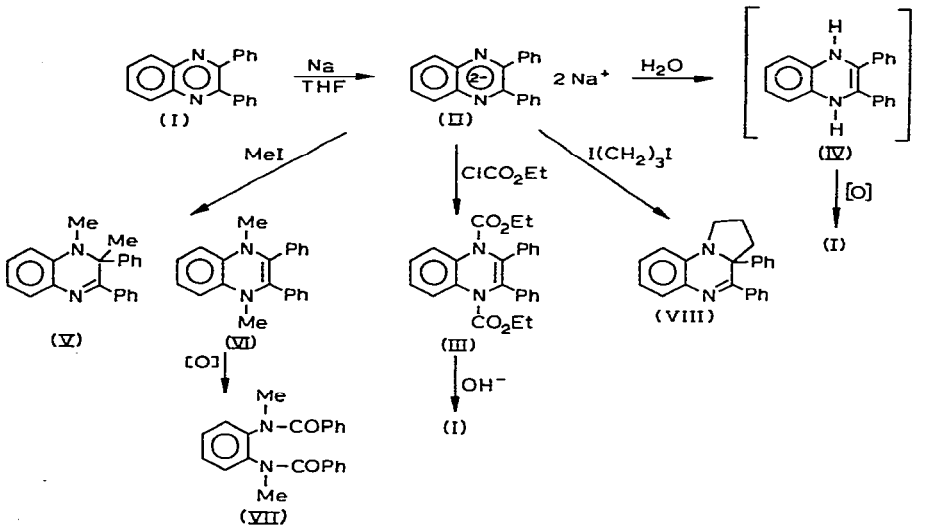
Treatment of (I) with lithium effected reduction and cyclodehydrogenation with the formation of the dibenzo[*a*,*c*]phenazine ring system. The lithium derivative so generated was compared in its chemical reactions to the lithium and sodium derivatives formed by reduction of dibenzo[*a*,*c*]phenazine itself by the alkali metal. With methyl iodide, the lithium and sodium derivatives gave 9,14-dimethyl-9,14-dihydrodibenzo[*a*,*c*]phenazine (XI). With ethyl chloroformate, the sodium derivative formed 9,14-bis(ethoxycarbonyl)-9,14-dihydrodibenzo[*a*,*c*]phenazine (XII) while the lithium derivative produced (XII) and 10,13-bis(ethoxycarbonyl)-9,14-dihydrodibenzo[*a*,*c*]phenazine (XIV). Additional products were isolated when excess ethyl chloroformate was added to the lithium derivative formed via the cyclodehydrogenation of (I). The formation of these by-products is traced to the presence of lithium hydride, a co-product of the cyclodehydrogenation reaction.

Recently[1,2] we have reported that lithium effects cyclodehydrogenation of benzil dianil to *N*,*N*′-diphenyl-9,10-diaminophenanthrene. This reaction appeared worthy of further investigation since it offers two advantages; a convenient conversion of simple, easily accessible compounds to products containing complex ring systems and the ability to functionalize these cyclodehydrogenated derivatives since they are formed as reactive dianions. 2,3-Diphenylquinoxaline (I) is a convenient molecule for a continuation of this study since it has a more rigid geometry than our earlier example and offers increased possibilities for delocalization of the anionic charges.

Reduction of (I) with sodium generated a dianion (II). Several reactions were used to characterize (II) including alkylation with iodomethane and 1,3-diiodo-

SCHEME 1

REACTIONS OF THE DIANION OF 2,3-DIPHENYLQUINOXALINE



propane, acylation with ethyl chloroformate and protonation. (see Scheme 1) With ethyl chloroformate, the sole product isolated was identified as 1,4-bis(ethoxycarbonyl)-2,3-diphenyl-1,4-dihydroquinoxaline (III). This identification was based on the equivalency of the carbethoxy groups in the NMR spectrum and on the formation of (I) when (III) was hydrolyzed. The expected product from the hydrolysis, 2,3-diphenyl-1,4-dihydroquinoxaline (IV) is readily oxidized to the parent compound (I) as is apparent from the behaviour of the protonation product. The original crude product was red in colour but during purification the colour faded and only (I) was isolated.

In contrast to the relatively clean acylation reaction, alkylation with iodomethane produced a complex mixture. The products showed a sensitivity to oxygen but chromatography provided two products, 1,2-dimethyl-2,3-diphenyl-1,2-dihydroquinoxaline (V) and *N,N'*-dimethyl-*N,N'*-dibenzoyl-*o*-phenylenediamine (VII). Structure (V) was indicated by the presence of a C=N in the IR spectrum and by the non-equivalency of the methyl groups in the NMR spectrum. The mass spectrum was also indicative of 1,2-substitution since initial fragmentations involve loss of either methyl or phenyl radicals by β-cleavage. The latter compound, (VII), was identified initially by spectral evidence and its structure confirmed by synthesis of an authentic sample.

Alkylation with iodomethane must produce both the 1,2- and 1,4-dimethylated products [*i.e.* (V) and (VI)]. While the former is sufficiently stable for isolation, the latter, because of its electron rich enediamine structure[3,4], oxidizes readily to the bisamide (VII).

An extension of the ring system was accomplished by treating the dianion with 1,3-diiodopropane. The product isolated, 3*a*,4-diphenyl-1,2,3,3*a*-tetrahydropyrrolo[1,2-*a*]quinoxaline (VIII), showed an NMR spectrum compatible with the proposed structure and a UV spectrum very similar to (V). In addition, the mass

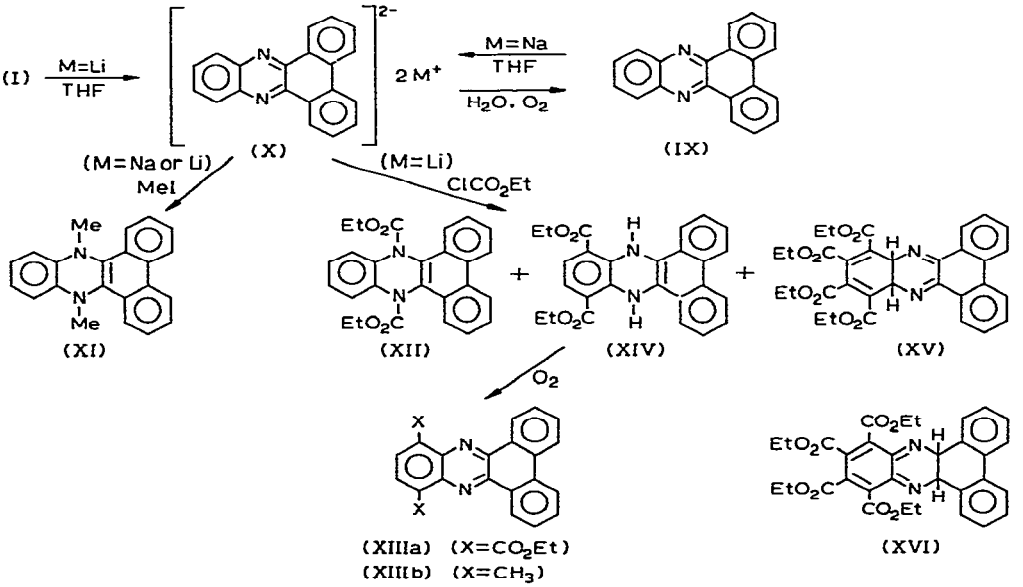
spectrum exhibited a fragmentation pattern closely related to that of (V). The formation of the isomeric *N,N'*-dialkylated product is undoubtedly precluded in this case by the difficulty in forming a 7-membered ring.

In the presence of excess lithium, (I) reacted rapidly to form a dianion and then more slowly to give a solution which titrated for 4 lithium atoms per mole of (I). Treatment of the solution at this point with a protonating agent induced vigorous foaming. The organic product of the reaction was a brown solid which oxidized during isolation and purification to provide dibenzo[*a,c*]phenazine (IX). As in the case of benzil dianil[1,2], cyclodehydrogenation had occurred forming a dianion of (IX) [(X)].

Characterization of the anion (X) generated in this reaction was accomplished by reaction with iodomethane and ethyl chloroformate (see Scheme 2). The alkylation reaction produced in good yield a compound showing two equivalent methyl groups in its NMR spectrum. Since its UV spectrum was quite unlike that of (I) in that the long wavelength bands were much less intense, the product was considered to be 9,14-dimethyl-9,14-dihydrodibenzo[*a,c*]phenazine (XI). This same product was formed by alkylation of the dianion generated by reduction of (IX) with sodium.

SCHEME 2

REACTIONS OF THE DIANION OF DIBENZO[*a,c*]PHENAZINE



In contrast to the alkylation reaction, acylation with ethyl chloroformate proved to be a complex reaction. With 2 moles of ethyl chloroformate, two products were isolated. The first showed two equivalent carbethoxy groups in its NMR spectrum, and a UV spectrum similar to that of (XI). Hydrolysis resulted in loss of the ester groups to produce (IX). Consequently, its structure is 9,14-bis(ethoxycarbonyl)-9,14-dihydrodibenzo[*a,c*]phenazine (XII). This compound was produced in excellent yield from the disodium adduct of (IX).

Accompanying this material was a deep purple solid whose insolubility pre-

vented an NMR spectrum from being obtained. Elemental analysis indicated the molecular formula to be $C_{26}H_{22}N_2O_4$ and the IR spectrum showed the presence of NH and ester groups with apparent hydrogen bonding of the carbonyl groups. This material was found to oxidize slowly in refluxing chlorinated solvents to a compound $C_{26}H_{20}N_2O_4$ whose UV spectrum was almost identical to that of (IX) and whose two carbethoxy groups were equivalent in the NMR spectrum. It was apparent that this material contained two ester groups somewhere on the aromatic rings. On the basis of chemical shifts of the aromatic protons in the NMR spectrum, the structure assigned was 10,13-bis(ethoxycarbonyl)dibenzo[*a*,*c*]phenazine (XIIIa). This region of the spectrum showed the characteristic 3 multiplets of the phenanthrene ring system[5] plus a singlet equivalent to two protons.

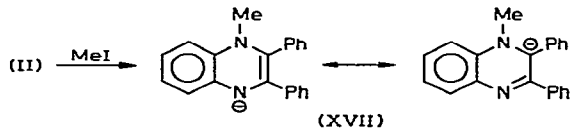
Attempts to synthesize (XIIIa) involved preparation of 2,3-dinitro-*p*-xylene and attempted oxidation to 2,3-dinitroterephthalic acid. While one methyl group could be successfully oxidized, attempts to complete the oxidation resulted in decarboxylation. However, the 10,13-dimethyldibenzo[*a*,*c*]phenazine (XIIIb) was prepared and its NMR spectrum showed the same aromatic proton pattern as (XIIIa) except for the chemical shift of the 2 proton singlet.

Thus, the original purple solid must be 10,13-bis(ethoxycarbonyl)-9,14-dihydrodibenzo[*a*,*c*]phenazine (XIV).

In an attempt to improve the yield of (XII) and/or (XIV), the effect of an excess of ethyl chloroformate was examined. The yield of both (XII) and (XIV) decreased and two additional compounds were isolated. One could not be purified satisfactorily (unknown *A*). The NMR spectrum of the second compound showed four equivalent carbethoxy groups per mole and in addition the characteristic phenanthrene type aromatic system with the addition of a non-aromatic 2 proton singlet. Microanalytical and mass spectral data established the molecular formula as $C_{32}H_{30}N_2O_8$. These data suggest structure (XV) for this compound. The alternative structure (XVI) is considered to be less likely since the UV spectrum of the compound resembles that of (XIIIa) and (IX).

DISCUSSION

As might be expected from the structural analogy between (I) and benzil dianil, the dianion (II) formed by reduction of the compound with sodium has the charge density largely localized on the nitrogen atoms. With reactive reagents such as ethyl chloroformate, functionalization at these positions is observed. With the less reactive reagent, iodomethane, a mixture of two alkylation products arises, one of which (VI) oxidizes during isolation. It is suggested that with this latter reagent, the reaction proceeds stepwise providing a mono-anion (XVII) with a discrete life span. With one



(XVII)

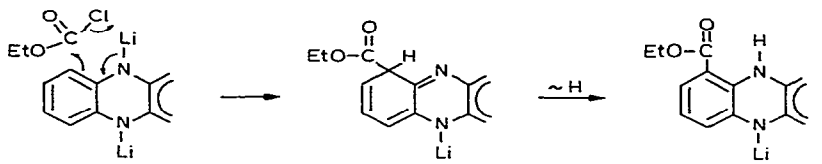
anionic center removed delocalization within the remaining aza-allylic anion occurs more easily. The second alkyl group may then be introduced in two positions.

In the cyclodehydrogenated ring system, the normal situation again finds the

negative centers of anion (X) confined to the nitrogen atoms. Alkylation and acylation proceeds at these sites provided the counterion is sodium. Presumably, the lack of 1,2-alkylation in this system is due to the enhanced stability of the phenanthrene system *vs.* the two isolated phenyl groups which exist in the quinoxaline anion (II).

Deviations from this behavior were observed with lithium as the counter ion and these took two forms; ring acylation and tetraacylation. Differences between lithium and sodium salts of ambident anions have been observed elsewhere[6]. For example, the lithium salt of pyrrole undergoes more extensive alkylation[7,8] and acylation[9] at carbon (rather than at nitrogen) than does the sodium salt. Similar results have been reported for the alkali metal salts of phenols[10].

This effect is usually attributed[7,10] to the coordinating ability of lithium which enables a transition state such as (XVIII) to be established. Such a transition state provides mutual stabilization of the charges on the cation and on the developing halide ion.



(XVIII)

In a control experiment, the dianion (X) (M = Li) generated from dibenzo-[*a,c*]phenazine (IX) when treated with excess ethyl chloroformate produced (XII) and (XIV) and only traces of unknown *A* and (XV). It must be concluded that the lithium hydride formed as a coproduct in the cyclodehydrogenation of (I) is responsible for the formation of the by-products unknown *A* and (XV). Probably, it converts the primary product (XIV) to a dilithio salt which then undergoes additional acylation with the excess ethyl chloroformate to form (XV).

EXPERIMENTAL

Melting points are uncorrected and were determined in open capillaries using a Mel-temp melting point apparatus. NMR spectra were recorded on a Varian T-60 spectrometer and are reported in ppm downfield (δ) from tetramethylsilane as internal standard. IR spectra were recorded on a Beckman IR-10 spectrophotometer and were calibrated with polystyrene film. UV spectra were obtained on a Unicam SP-800 instrument. Mass spectra were obtained on a Hitachi–Perkin–Elmer RMU-6E single focussing mass spectrometer. Tetrahydrofuran (THF) was dried at reflux over lithium aluminum hydride under nitrogen and was used freshly distilled. Solutions were dried over anhydrous sodium sulfate. In column chromatography, silica gel (70–325 mesh A.S.T.M.) purchased from E. Merck was used. Microanalyses were performed by M.H.W. Laboratories, Garden City, Michigan.

Preparation of alkali metal adducts

The alkali metal adducts were prepared by shaking THF solutions of 2,3-diphenylquinoxaline[11,12], (I), m.p. 123–124°, (0.01 or 0.005 mole), or dibenzo[*a,c*]-phenazine[13,14], (IX) m.p. 224–226° (0.005 mole), with excess alkali metals in modified

Schlenk tubes. Details of this procedure and of the measurement of metal uptake have been reported elsewhere[15,16].

Reactions of disodium adduct of 2,3-*diphenylquinoxaline* (*I*)

(*i*). *Uptake of metal and protonation.* The reaction of (I) with excess sodium resulted in two equivalents of metal reacting in ca. 6 h; no further reaction occurred in the following 24 h. Solutions of the sodium adduct were prepared by shaking (I) and sodium for 16 h.

Quenching the purple solution with water/ethanol gave a red solid, which decolourized on melting at the m.p. of (I). Attempted crystallization of this material led to rapid fading of the red colour and quantitative recovery of (I).

(*ii*). *Iodomethane.* Iodomethane (2.83 g, 0.02 mole) was added to the sodium adduct of (I) (2.82 g, 0.01 mole) at room temperature and the resulting solution stirred until the colour had discharged (1 h). After diluting with water, the mixture was extracted with ether, the extracts evaporated and the residue chromatographed on silica gel (150 g). Elution of the column with benzene/petroleum ether (4/1) gave a yellow solid (0.58 g) from which benzil, m.p. 91–92° (0.13 g) was isolated by crystallization. This was followed by a fluorescent oil (ca. 1.2 g), from which yellow, fluorescent crystals, m.p. 102–105° (0.80 g), were isolated by crystallization from cyclohexane. Two further crystallizations from cyclohexane gave an analytical sample of 1,2-dimethyl-2,3-diphenyl-1,2-dihydroquinoxaline (V); m.p. 107–108°; IR (CCl_4), 2870, 2820, 1600, 1475 cm^{-1}; NMR $\delta(C_6D_6)$, 1.55 (s, 3H), 2.01 (s, 3H), 6.3–7.8 ppm (m, 14H); UV (CH_3OH), 244 nm (log ε 4.45), 261 (sh, 4.32), 290 (sh, 3.77), 392 (3.42); mass spectrum (70 eV), *m/e* (rel. intensity), 312 (21), 311 (4), 297 (100), 235 (35), 217 (30), 208 (20), 194 (11), 118 (17), 77 (14), *m** (parent, daughter), 282.7 (312, 297), 177.0 (312, 235), 138.7 (312, 208). (Found: C, 84.63; H, 6.42; N, 8.86. $C_{22}H_{20}N_2$ calcd.: C, 84.58; H, 6.45; N, 8.97%.)

Continuing the elution with benzene/ether gave a white solid, *N,N'*-dimethyl-*N,N'*-dibenzoyl-*o*-phenylenediamine (VII) (0.32 g), m.p. 160–161° after recrystallization from benzene/hexane; IR, ($CHCl_3$) 3500, 1640 cm^{-1}; NMR $\delta(C_6D_6)$, 2.6–3.0 (broad s, 6H), 6.8–7.7 ppm (m, 14H); mass spectrum, *m/e* (rel. intensity), 344 (24), 327 (7), 239 (20), 223 (100), 133 (10), 105 (25), 77 (66), *m** (parent, daughter), 207.2 (344, 267), 166.0 (344, 327), 208.1 (239, 223), 56.4 (105, 77). (Found: C, 76.61; H, 5.54; N, 8.00. $C_{22}H_{20}N_2O_2$ calcd. C, 76.70; H, 5.85; N, 8.17%.)

The compound was also identified by comparison with an authentic sample (see below).

Weight balance in this reaction was poor. Hydrolysis and oxidation of the reaction products were undoubtedly occurring as indicated by appreciable darkening of the material while on the chromatography column, by the isolation of (VII) [rather than (VI)] and by the isolation of benzil.

(*iii*). 1,3-*diiodopropane.* 1,3-Diiodopropane (1.63 g, 0.055 mole) was added to the sodium adduct of (I) (1.41 g, 0.005 mole) at room temperature, and the resulting solution stirred for 1 h. The crude product was isolated as described above and chromatographed on silica gel (80 g). Elution with benzene/petroleum ether (1/1) gave a yellow oil (1.4 g). Crystallization from cyclohexane gave a greenish-yellow, fluorescent product (0.43 g), m.p. 147–150°. Two further crystallizations from cyclohexane gave an analytical sample of 3*a*,4-diphenyl-1,2,3,3*a*-tetrahydropyrrolo[1,2-*a*]-

quinoxaline (VIII); m.p. 149–150°, IR (CCl_4), 1601, 1475, 1375 cm^{-1}; NMR δ($CDCl_3$), 2.0–3.0 (m, 4H), 3.57 (t, J 7 Hz, 2H), 6.5–7.1 (m, 2H), 7.1–7.8 ppm (m, 12H); UV (CH_3OH), 249 nm (log ε 4.39), 261 (sh, 4.29), 291 (sh, 3.87), 404 (3.54); mass spectrum, *m/e* (rel. intensity), 324 (12), 247 (100), 220 (33), 77 (8), *m** (parent, daughter), 188.2 (324, 247). (Found: C, 85.02, 85.35; H, 6.43, 6.35; N, 8.73, 8.48. $C_{23}H_{20}N_2$ calcd.: C, 85.15; H, 6.21; N, 8.63%.)

(*iv*). *Ethyl chloroformate.* Ethyl chloroformate (2.17 g, 0.02 mole) was added to the chilled solution (−65°) of the sodium adduct of (I) (2.82 g, 0.01 mole). The resulting solution was stirred for 6 h during which time the temperature was allowed to rise to ca. 20°. Dilution with water and ether extraction provided the crude product which was crystallized from benzene/hexane to give 1,4-bis(ethoxycarbonyl)-1,4-dihydroquinoxaline (III), m.p. 138–140° (1.9 g). Three crystallizations of this product from ethanol gave an analytical sample; m.p. 146.5–147.5°; IR ($CHCl_3$), 1713 cm^{-1}; NMR δ($CDCl_3$), 0.90 (t, J 8 Hz, 6H), 4.03 (q, J 8 Hz, 4H), 7.0–7.6 (m, 12H), 7.7–7.9 ppm (m, 2H); UV (CH_3OH), 227 nm (log ε 4.31), 264 (4.13); mass spectrum, *m/e* (rel. intensity), 428 (76), 400 (0.4), 383 (1), 356 (26), 311 (99), 283 (100), 281 (25), 205 (38), 179 (21), 178 (14), 77 (21), 76 (19), 29 (26), *m** (parent, daughter), 296.1 (428, 356), 257.5 (311, 283), 224.9 (356, 283). (Found: C, 73.09, 72.78; H, 5.62, 5.43; N, 6.34. $C_{26}H_{24}N_2O_4$ calcd.: C, 72.86; H, 5.64, N, 6.56%.) The filtrate from the 1.9 g of (III) was chromatographed on 100 g of silica gel to provide 0.29 g of (I) (3/1 benzene/petroleum ether) and 1.0 g of additional (III) (total crude yield 2.9 g, 67%).

Reactions of the disodium adduct of dibenzo[a,c]phenazine (IX)

(*i*). *Metal uptake.* Titration of aliquots from a solution of (IX) (1.39 g) with sodium (0.66 g) in THF (98.35 g) showed two equiv. metal reacting in ca. 6 h with no further change after 24 h. The colour of the solution was deep red.

(*ii*). *Ethyl chloroformate.* Ethyl chloroformate (0.7 g) was added to the disodium adduct of (IX) (0.003 mole) at −65°. The solution was stirred for three h, during which time it was allowed to come to room temperature. Water was added, and the products isolated by ether extraction. The extracts were dried, evaporated, and the residue crystallized from ethanol to give crude 9,14-bis(ethoxycarbonyl)-9,14-dihydrodibenzo[*a,c*]phenazine (XII), m.p. 223–226° (0.978 g, 83%), mixture m.p. 222–225° with a sample of (XII) isolated from other reactions (see below). The NMR spectrum was indistinguishable from that of the analytical sample.

(*iii*). *Iodomethane.* Iodomethane (1.4 g, 0.01 mole) was added to the disodium adduct of (IX) (1.40 g, 0.005 mole) in THF (ca. 100 ml), at room temperature. Within a few minutes the deep red colour had faded to yellow. Stirring was continued for 30 min, water was added, and the product was isolated by ether extraction. Evaporation of the dried extracts gave an oil (1.54 g) from which crude product, m.p. 134–144° (0.9 g), crystallized on the addition of cyclohexane. Two recrystallizations from cyclohexane gave 9,14-dimethyl-9,14-dihydrodibenzo[*a,c*]phenazine (XI), m.p. and mixture m.p. 148–150° (dec.) with the analytical sample of (XI) (see below). The NMR spectrum of this sample was superimposable on that of the product obtained from the reaction of the lithium adduct of (I) with iodomethane.

Reactions of the lithium adduct (X) derived from (I)

(*i*). *Metal uptake and protonation.* Titration of aliquots from reactions of (I)

with lithium metal indicated a rapid reaction of 2 equiv. metal in 4–5 h giving a purple solution identical to that from the reaction with sodium. Continued shaking and titration of aliquots showed a slower, but steady uptake of additional lithium which reached 4 equiv. of metal in ca. 24 h. Uptake of lithium did not cease but slowly continued. The colour at 24 h was orange-brown and when quenched with ethanol/water the only product isolated was (IX) identified by IR and mixture m.p. However, the initial brown product is probably the dihydro derivative, since a sample of the crude product gave analytical figures which correspond to those of a mixture of (IX) and a dihydro derivative. For subsequent runs, (I) (1.41 g, 0.005 mole), lithium (ca. 0.5 g), and THF (ca. 100 ml) were shaken for 24 h.

(ii). Ethyl chloroformate. The following is a description of the procedure for one reaction where ethyl chloroformate (4.2 g, 0.04 mole) was added at $-65°$ to the lithium adduct.

After addition of the ethyl chloroformate, the reaction mixture was stirred for ca. 4 h during which time it was allowed to come to room temperature. Water (ca. 5 ml) was gradually added through the syringe cap (vigorous reaction with gas evolution). After the reaction had subsided, the reaction mixture was further diluted with water and extracted with benzene. The purple solid which formed in the organic phase was filtered off and the filtrate was dried and evaporated. The purple solid was crystallized from benzene to give material, m.p. 233–245° (100 mg). Two crystallizations from benzene gave 10,13-bis(ethoxycarbonyl)-9,14-dihydrodibenzo[*a,c*]phenazine (XIV); m.p. 243–245°; IR (KBr), 3290 (NH), 1665 (C=O), 1230 cm^{-1}; UV (C_6H_{12}), 243 nm (sh, log ε 4.76), 249 (4.89), 267 (sh, 4.65), 279 (sh, 4.48); (C_6H_6), 299 (4.29), 324 (sh, 3.51), 450 (3.62), 470 (3.78), 504 (3.94), 543 (4.06), 590 (4.03). (Found: C, 73.38; H, 5.16; N, 6.45. $C_{26}H_{22}N_2O_4$ calcd.: C, 73.22; H, 5.20; N, 6.57%.) The compound was too insoluble for an NMR spectrum.

The residual reaction mixture was chromatographed on silica gel (90 g). Elution with benzene/petroleum ether (3/1) gave (IX) (329 mg, 23%) from which purified material, m.p. and mixture m.p. 224–226° (250 mg), was isolated by crystallization from benzene.

Elution with benzene gave an oil (875 mg) which contained two products. The first of these was insoluble in acetonitrile and was filtered off (71 mg). It was recrystallized from acetonitrile to give 10,13-bis(ethoxycarbonyl)dibenzo[*a,c*]phenazine (XIIIa); m.p. 171–172°; IR (KBr), 1730, 1690 cm^{-1}; NMR $\delta(CDCl_3)$, 1.58 (t, *J* 7 Hz, 6H), 4.68 (q, *J* 7 Hz, 4H), 7.5–7.8 (m, 4H), 8.2–8.4 (m, 2H), 8.20 (s, 2H), 9.1–9.3 ppm (m, 2H); $\delta(CF_3CO_2H)$, 1.68 (t, *J* 7 Hz, 6H), 4.88 (q, *J* 7 Hz, 4H), 7.9–8.5 (m, 4H), 8.92 (s, 2H), 8.65–9.2 ppm (m, 4H); UV (CH_3OH), 248 nm (log ε 4.78), 250 (4.78), 276 (4.41), 282 (4.42), 299 (4.06), 312 (4.26), 363 (sh, 3.91), 371 (sh, 4.00), 379 (4.11), 398 (4.13); mass spectrum, *m/e* (rel. intensity), 424 (50), 352 (100), 280 (30), 279 (30). (Found: C, 73.46; H, 4.86; N, 6.51. $C_{26}H_{20}N_2O_4$ calcd.: C, 73.57; H, 4.76; N, 6.60%.)

Crystallization of the acetonitrile soluble material of this fraction from ethanol gave material (unknown *A*), m.p. 115–120° dec. to a black tar (18%), which did not give a reasonable melting point after eleven crystallizations. Unknown *A* has IR (KBr), 1720, 1250 cm^{-1}; NMR $\delta(CDCl_3)$, 1.0–1.9 (m, 6 or 7H), 3.38 (d, *J* 5 Hz, 1H), 4.2–4.7 (m, 4–5H), 7.2–9.5 ppm (m, 8–9H). Decoupling experiments show the doublet at 3.38 to be coupled with protons at 7.3 ppm. No structure is proposed for this compound.

Elution with ether/benzene (3/97) gave a fraction containing two components (900 mg). Fractional crystallization from ethanol gave a white solid, m.p. 222–224° (452 mg, 21%). Crystallization from ethanol gave pure 9,14-bis(ethoxycarbonyl)-9,14-dihydrodibenzo[*a*,*c*]phenazine (XII); m.p. 223–224°, IR ($CHCl_3$), 1715, 1260 cm^{-1}; NMR $\delta(CDCl_3)$, 1.15 (t, *J* 7 Hz, 6H), 4.28 (q, *J* 7 Hz, 4H). 7.2–8.2 (m, 10H), 8.5–8.8 ppm (m, 2H); UV (CH_3OH), 224 nm (log ε 4.56), 250 (4.63), 257 (4.62), 271 (sh, 4.32), 298 (4.00), 308 (4.00); mass spectrum, *m/e* (rel. intensity), 426 (41), 354 (5), 353 (14), 310 (19), 309 (69), 281 (100), 280 (60), 279 (29). (Found: C, 72.96, 73.04; H, 5.21, 5.07; N, 6.53, 6.65. $C_{26}H_{22}N_2O_4$ calcd.: C, 73.22; H, 5.20 N, 6.57%.)

The residual solution from the first ethanol crystallization of this fraction was concentrated, and water was added to give a white solid (0.5 g), m.p. 141–150°. Eight crystallizations from ethanol/water gave compound *B* (XV); m.p. 146–148°; IR (KBr), 1730, 1250 cm^{-1}; NMR $\delta(CDCl_3)$, 1.27 (t, *J* 7 Hz, 12H), 4.37 (q, *J* 7 Hz, 8H), 6.67 (s, 2H), 7.5–7.7 (m, 4H), 8.3–8.6 (m, 2H), 9.0–9.3 ppm (m, 2H); UV (CH_3OH), 235 nm (log ε 4.52), 249 (sh, 4.76), 255 (4.86), 279 (4.15), 291 (4.01), 309 (4.03), 345 (4.01), 361 (4.11), 3.90 (2.85); mass spectrum, *m/e* (rel. intensity), 570 (4), 453 (11), 425 (27), 407 (5), 379 (29), 352 (9), 280 (100), 279 (50). (Found: C, 67.44; H, 5.31; N, 4.60. $C_{32}H_{30}N_2C_8$ calcd.: C, 67.36; H, 5.30; N, 4.91%.)

The results using different ratios of ethyl chloroformate to adduct (X) will be found in Table 1.

TABLE 1

PRODUCTS AND YIELDS FROM THE REACTION OF ETHYL CHLOROFORMATE AND THE LITHIUM DERIVATIVE OF 2,3-DIPHENYLQUINOXALINE (I)

Mole ratio $ClCO_2Et$/(I)	*Product, yield*[a] (%)					
	(*IX*)	(*XII*)	(*XIV*)	*Unknown A*	(*XV*)	(*XIIIa*)
1	48[c]	Trace	27			Trace
2	17[c]	56	32			
4	25[c]	19	9	15	25	
8	23[c]	27	5	18	20	0.4
2[b]	8[c]	52	10			

[a] Yields are corrected (except where indicated) for the formation of (IX).
[b] Reaction mixture quenched with aqueous HCl.
[c] Based on (I).

Two equiv. (1.1 g) of ethyl chloroformate were added to the lithium adduct of (I) at ca. 20° and (XIV) was isolated in 12% yield (252 mg). (See Table 1 for the results from the reaction at −65°) An NMR spectrum of the residue was that of (XII) with very little of any other component present.

(*iii*). *Iodomethane.* Iodomethane (1.4 g, 0.01 mole) was added to the adduct at room temperature and the resulting solution stirred for 4 h. Water (ca. 5 ml) was added through the syringe cap (vigorous reaction with gas evolution). After further dilution, the product was isolated by ether extraction, (appreciable darkening of the extracts occurred during this operation). After drying and evaporating the extracts, the residue was chromatographed on silica gel (60 g). Elution with benzene/petroleum

ether (3/2) gave in the first 250 ml of eluent a yellow solid (1.24 g) which decomposed to a purple substance either on silica gel or in chloroform solution. Crystallization of this fraction from cyclohexane gave material, m.p. 139–143° (0.86 g). Two further crystallizations from cyclohexane gave greenish-yellow, fluorescent crystals of 9,14-dimethyl-9,14-dihydrodibenzo[*a,c*]phenazine (XI); m.p.148–150° (see above), NMR $\delta(C_6D_6)$, 3.13 (broad s, 6H), 6.98 (s, 4H), 7.2–7.6 (m, 4H), 8.2–8.8 ppm (m, 4H); UV (CH_3OH), 243 nm (sh, log ε 4.77), 249 (4.95), 269 (sh, 4.30), 291 (sh, 4.05), 352 (3.58); mass spectrum, *m/e* (rel. intensity), 310 (42), 295 (100), 280 (27), 279 (13). (Found: C, 85.28; H, 5.90; N, 9.00. $C_{22}H_{18}N_2$ calcd.: C, 85.13; H, 5.84; N, 9.03%.)

Continued elution with benzene/petroleum ether (3/2) gave in the next 500 ml of eluent 0.14 g of solid which on recrystallization from benzene gave (IX), m.p. and mixture m.p. 224–226°.

Reactions of the lithium adduct of dibenzo[a,c]phenazine (IX) with ethyl chloroformate

The following reactions were carried out with solutions of the adduct prepared from (IX) (1.40 g, 0.005 mole), lithium (ca. 0.5 g) and THF (ca. 100 ml) by shaking for 24 h.

(*i*). Ethyl chloroformate (1.1 g, 0.01 mole) was added to the adduct at −65°. Work-up under conditions identical to those for the reactions with (X), gave (XIV) (0.51 g, 24%) and by crystallization of the residue from ethanol, (XII) (0.90 g, 42%).

(*ii*). Ethyl chloroformate (2.2 g, 0.02 mole) was added to the adduct at −65°. Work-up gave (XIV) (89 mg, 4%) and the NMR spectrum of the residual reaction mixture was almost identical to that of (XII) showing only traces of unknown *A* and (XV) in contrast to the corresponding reaction of 4 equiv. of ethyl chloroformate with the lithium adduct (X) derived from (I) (see Table 1).

Hydrolysis of 1,4-*bis*(*ethoxycarbonyl*)-1,4-*dihydroquinoxaline* (*III*)

A solution of (III) (0.73 g, 0.017 mole) in 10% aq. NaOH/dioxane (10/1, 55 ml) was heated at reflux with stirring for three days. After cooling, the solution was acidified and the solid which precipitated was recrystallized from ethanol/water to give (I) (200 mg), identified by m.p., mixture m.p. and IR spectrum.

Hydrolysis of 9,14-*bis*(*ethoxycarbonyl*)-9,14-*dihydrodibenzo*[*a,c*]*phenazine* (*XII*)

A mixture of (XII) (0.49 g, 0.011 mole), 20% aq. NaOH (50 ml) and dioxane (5 ml) was refluxed for 4 days. The solution was cooled, acidified and the solid which precipitated recrystallized from benzene/ethanol to give (IX) (200 mg, 65%), m.p. and mixture m.p. 224–226°.

Oxidation of 10,13-*bis*(*ethoxycarbonyl*)-9,14-*dihydrodibenzo*[*a,c*]*phenazine* (*XIV*)

A chloroform solution (250 ml) of (XIV) (0.83 g, 0.019 mole) was refluxed with occasional cooling until the purple colour of the solution faded to yellow (ca. 3 days). The chloroform was evaporated and the product chromatographed on silica gel (60 g). Elution with benzene gave a yellow solid (0.64 g, 77%) which was crystallized from acetonitrile to give (XIIIa) m.p. 164–165°. The NMR and IR spectra of this sample were superimposable on those of the sample previously described.

N,N'-Dibenzoyl-o-phenylenediamine

This compound was prepared from benzoyl chloride and *o*-phenylenediamine

under Schotten–Baumann reaction conditions. The crude product was recrystallized from dimethylformamide to give a 61% yield of *N,N'*-dibenzoyl-*o*-phenylenediamine; m.p. 317–319° [lit.[17] m.p. 301°]; NMR $\delta(CF_3CO_2H)$, 7.5–7.7 (m, 10H), 7.8–8.1 (m, 4H), 9.50 ppm (b, 2H); IR (KBr), 1653, 3280 cm^{-1}.

N,N'-Dibenzoyl-N,N'-dimethyl-o-phenylenediamine

A mixture of *N,N'*-dibenzoyl-*o*-phenylenediamine (3.2 g, 0.01 mole), sodium hydride (1.06 g of 50% dispersion in mineral oil, 0.022 mole) and dry dimethylformamide was stirred at ca. 50° for 5 min. Iodomethane (3.12 g, 0.022 mole) was added to the mixture and stirring was continued for 5 min. The reaction mixture was then poured into water (150 ml), the crude product filtered and twice recrystallized from benzene/hexane to give *N,N'*-dibenzoyl-*N,N'*-dimethyl-*o*-phenylenediamine, m.p. and m.p. 160–161°, and superimposable NMR spectrum with the material previously described.

10,13-*Dimethyldibenzo[a,c]phenazine* (*XIIIb*)

(*i*). 2,3-*Dinitro-p-xylene.* Nitration of 2-nitro-*p*-xylene[18] was carried out by a previously described method[19]. The required 2,3-dinitro isomer was isolated by recyrstallization of the crude product from ethanol. This removed the 2,6- and some 2,5-isomer* and evaporation of the filtrate provided a product enriched in 2,3-dinitro-*p*-xylene. The solid isolated from this filtrate was further enriched in the 2,3-isomer by recrystallization from acetonitrile and finally purified by recrystallization from ethanol to give material; m.p. 92–93° (lit.[20] m.p. 93°); NMR $\delta(CDCl_3)$, 2.43 (s, 6H), 7.42 ppm (s, 2H).

(*ii*). 2,3-*Diamino-p-xylene.* A solution of 2,3-dinitro-*p*-xylene (9.8 g, 0.05 mole), stannous chloride dihydrate (67.5 g, 0.3 mole) in conc. HCl (80 ml) was stirred overnight. The solid that precipitated was filtered, washed with ether, taken up in aq. sodium hydroxide and the solution extracted with chloroform. The extracts were dried, and evaporated to give 3 g product (44%), NMR $\delta(CDCl_3)$, 2.10 (s 6H), 3.30 (s, 4H), 6.53 ppm (s, 2H) which was used in the next step without purification.

(*iii*). 10,13-*Dimethyldibenzo[a,c]phenazine* (*XIIIb*). This compound was prepared from phenanthraquinone and 2,3-diamino-*p*-xylene by the procedure of Noelting[21] in 81% yield; m.p. 289–290°, (lit.[21] m.p. 285–286°); NMR $\delta(CF_3CO_2H)$, 3.17 (s, 6H), 7.9–8.5 (m, 4H), 8.10 (s, 2H), 8.5–8.8 (m, 2H), 8.9–9.0 ppm (m, 2H).

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