the benzene layer was extracted twice with water. The combined water layers were extracted with chloroform, treated with concentrated HCl to pH 7, and again extracted with chloroform. The chloroform layer was dried and chromatographed on an alumina column made up with benzene (elution with chloroform) to give, upon distillation of the solvent and recrystallization of the residue from ethanol–chloroform, 0.4 g of **2**, mp 278–280°, identical with an authentic sample (mmp 277–279°).

2-(4-Pyridyl)-1,3-indandione (3). Method A.—1-(4-Pyridyl)-2-butanone[11] was condensed with compound **1** following the procedure above described for compound **2** (method A). Recrystallization from ethanol gave **3** as yellow crystals, mp 309–312°. The identity of **3** was established by mixture melting point determination with an authentic sample prepared from phthalide and picolinaldehyde (see method C).

Method B.—1-Phenyl-3(4-pyridyl)-2-propanone, prepared by the procedure above reported for 1-phenyl-3(2-pyridyl)-2-propanone, was condensed with compound **1** under the conditions above described for compound **2** (method B). Chromatography and recrystallization from ethanol gave **3** as yellow crystals, mp 313–316°, identical (mixture melting point) with an authentic sample.

Method C.—This method is similar to that used by Horton and Murdock for preparing 2-aryl-1,3-indandiones.[12] Sodium methoxide (14 g) was added slowly to a solution of phthalide (33.5 g) and picolinaldehyde (27 g) in ethanol (100 ml) under nitrogen, and the mixture was heated at reflux for 3 hr. The red precipitate formed on cooling was collected by filtration and dissolved in hot water (750 ml), and the solution was made slightly acid with concentrated HCl. The precipitate crystallized from ethanol gave a 40% yield of **3** as yellow crystals, mp 312–314°.

Anal. Calcd for $C_{14}H_9NO_2$: N, 6.28. Found: N, 5.91.

Reaction of Propiophenone with Phthalate 1.—A mixture of propiophenone (33.5 g) and compound **1** (48.5 g) was added to a dispersion of sodium hydride (50% in mineral oil, 12 g) in anhydrous benzene (500 ml). The reaction mixture was refluxed for 22 hr, cooled, and filtered. The red solid was washed with ether, dried *in vacuo*, and dissolved in water, (800 ml), and the solution was acidified with concentrated HCl. Chromatography of the resultant yellow oil on an alumina column made up with benzene–hexane (elution with chloroform) gave 11 g (27.5%) of 2-methyl-1,3-indandione as yellow solid, mp 78–80°.

Registry No.—**1**, 131-11-3; 3-pentanone, 96-22-0; 4-heptanone, 123-19-3; 3-hexanone, 589-38-8; 1-phenyl-2-butanone, 1007-32-5; propiophenone, 93-55-0.

Acknowledgment.—We gratefully acknowledge the valuable assistance of Dr. Mario F. Sartori in connection with this research.

(11) C. Osuch and R. Levine, *J. Org. Chem.*, **22**, 939 (1957).
(12) R. L. Horton and K. C. Murdock, *ibid.*, **25**, 938 (1960).

Heterocyclic Analogs of Fulvene and Fulvalene. III. $\Delta^{3,3'}$-Bi-3*H*-indazole

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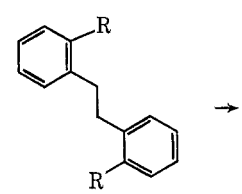
In an earlier part of this series we described the synthesis of $\Delta^{2,2'}$-bi-2*H*-benzimidazole (I).[1] Here we report the synthesis and properties of the remaining dibenzotetraazafulvalene, $\Delta^{3,3'}$-bi-3*H*-indazole (II). A common intermediate in all routes to this compound was 3,3′-bi-1*H*-indazole (III); the routes differed only in the method of synthesis of III and its subsequent oxidation.

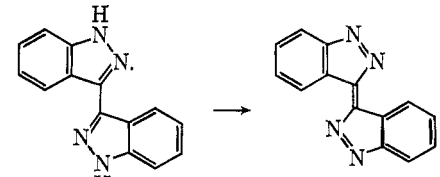
(1) J. H. M. Hill, *J. Org. Chem.*, **28**, 1931 (1963).

The most satisfactory of the several pathways to III investigated involved the direct synthesis of the biindazole from a suitably substituted bibenzyl derivative. 2,2′-Dinitrobibenzyl (IV) was simultaneously reduced and acetylated by catalytic hydrogenation in acetic anhydride, and the resulting 2,2′-diacetamidobibenzyl (V) was nitrosated with nitrosyl chloride. Nitrogen trioxide or nitrogen tetroxide was found to be less satisfactory in this particular case.[2] The resulting *N*,*N*′-dinitroso-2,2′-diacetamidobibenzyl (VI) was isomerized to bibenzyl-2,2′-diazoacetate (VII) by gentle warming in solution.[3] Cyclization of VII to III occurred when the temperature was raised to reflux.[4]

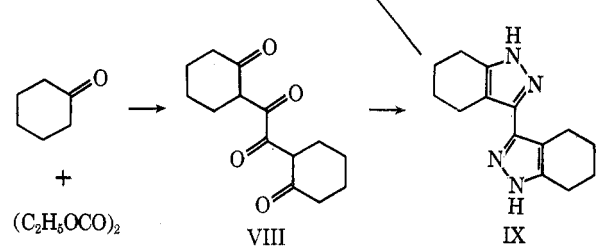
In this sequence all steps except the final ring closure proceeded with good yield. This last step gave erratic results and the reaction product was contaminated with appreciable amounts of tar, which was difficult to remove. Carrying out the rearrangement and cyclization in a variety of other solvents did not improve the yield or produce a cleaner product. The following yields are typical of those obtained in other solvents: C_6H_6, 29%; $CHCl_3$, 11%; CCl_4, 14%; *tert*-BuOH, 23%; C_6H_{12}, 14%.



IV, R = NO_2
V, R = $NHCOCH_3$
VI, R = $N(NO)COCH_3$
VII, R = N_2OCOCH_3



III II



$(C_2H_5OCO)_2$ VIII IX

A second successful stepwise route to III was developed: cyclohexanone condensed with ethyl oxalate to yield the tetraketone VIII. Examination of the –OH and –C=O absorbances in the infrared spectrum of VIII indicated that it was almost totally enolized. Treatment of VIII with hydrazine cyclized it to the bipyrazole (IX) which was aromatized to III by prolonged heating with palladium catalyst. Overall, this

(2) E. H. White, *J. Amer. Chem. Soc.*, **77**, 6008 (1955).
(3) The loss of the nitroso function was monitored by infrared; this was complete in about 5 hr.
(4) R. Huisgen and H. Nakaten, *Justus Liebigs Ann. Chem.*, **586**, 84 (1954).

route was less satisfactory than the former, as the initial condensation to produce VIII often gave a product contaminated with appreciable amounts of ethyl cyclohexanone-2-glyoxalate, which was difficult to remove.

Interestingly, it had earlier been claimed that IX was the product of the reaction of 2-cyanocyclohexanone semicarbazone with acid.[5] We repeated this reaction and found that the reaction product was, in fact, 1,2,-3,4-tetrahydroindazolo[3,2,-*b*]-1,2,3,4-tetrahydroquinazol-7-imine. Authentic material was made from the reaction of 2-cyclocyclohexanone azine with acid.[6,7]

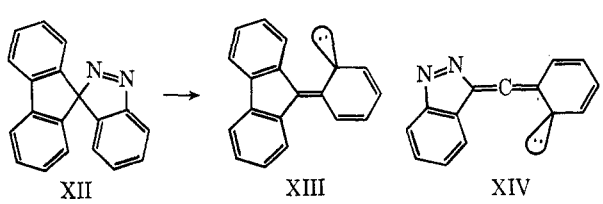
Oddo and Raffa claimed that oxidative dimerization of indole to 3,3′-biindole occurred when indole was heated with sulfur.[8] A similar experiment with indazole yielded a tarry product from which most of the indazole could be isolated unchanged. There was no evidence for the formation of III. The Ullmann reaction of 3-iodoindazole with copper in dimethylformamide also failed to yield any III; only the copper salt of 3-iodoindazole was isolated.

While the oxidation of 2,2′-bibenzimidazole to I was easily effected by lead peroxide in chloroform,[1] III was destroyed under these conditions, and from the reaction mixtures the only recognizable product isolated was a small amount of phenanthraquinone. We found, however, that lead tetraacetate in anhydrous acetonitrile,[9] containing sufficient magnesium oxide to ensure that the acetic acid liberated during the reaction would be removed rapidly, converted III into II which could be isolated as a deep red solid by low-temperature evaporation of the resulting crimson solution. A more satisfactory indirect oxidation involved treatment of III with *N*-bromosuccinimide, isolation of the relatively stable 1,1′-dibromo-3,3′-bi-1*H*-indazole (X), and its subsequent debromination with silver powder. In this way reasonably stable solutions of II were easily prepared in a variety of solvents and a crystalline product could be isolated by evaporation of the solvent *in vacuo* at low temperature. The intense color of X is surprising, as *N*-bromo compounds are usually colorless. An alternative formulation for X, which is consistent with the analytical and spectroscopic data, is that of a charge-transfer complex between molecular bromine and II. The fact that treatment of II with an equivalent amount of bromine results in the regeneration of X supports this suggestion.

The identity of products from both synthetic routes does not rule out completely the possibility that the cyclization steps in each case gave rise to the isomeric structure with fused six-membered rings. This being the case, II would be cinnolino[4,3-*c*]cinnoline (XI) and III would be the corresponding 6,12-dihydro derivative. In the absence of an available synthesis of XI or the unsubstituted dihydro derivative for comparison, the evidence appears to support the original formulation. Several substituted 6,12-dihydrocinnolino[4,3-*c*]cinnolines have been described in patent literature as highly colored compounds;[10] III is colorless and has an ultraviolet spectrum similar in both wavelength and absorbance to indazole. In the infrared III shows a peak at 6.18 μ which is also observed in indazole and several substituted indazoles. The observed photochemical and thermal lability of II and its facile, reversible conversion into III is inconsistent with an aromatic structure such as XI. Furthermore, it seems unlikely that the aromatization of VIII to III would stop at the dihydro stage and not continue to the fully aromatic structure XI. In fact, the ready conversion of II to III affords an efficient titrametric assay for II in solution. II reacts rapidly and quantitatively with hydroquinone to give *p*-benzoquinone and III.[11] End points are easily observed using the color of II.

At the inception of this work it was hoped that II would demonstrate some interesting photochemical and thermal properties, *e.g.*, benzocyclopropene formation.[12] This expectation has not been realized. Although II was rapidly photolyzed in a variety of solvents and at several wavelengths and temperatures, mainly polymeric products were formed. For example, photolysis in methanol under nitrogen yielded very small amounts of phenanthrene, and in air, in benzene, phenanthraquinone was the only isolable product. In both cases polymer constituted the bulk of the product. Photolysis at low temperature ($\sim -60°$) under the same conditions also yielded polymeric material. Heating II in solution or in the solid phase also produced a yellow polymer from which small amounts of phenanthraquinone and occasionally benzil could be obtained.

The polymer from II contained a negligible amount of nitrogen. Consequently, a process must operate by which nitrogen is lost sequentially or simultaneously from the indazole rings. An analogous compound, spiro[fluorene-9,3′-indazole] (XII), loses nitrogen, thermally or photochemically, *via* intermediate XIII, which is either a singlet or triplet diradical.[13,14] Similarly II could produce an intermediate XIV which, *via* an appropriate rotamer, could cyclize and rearrange and then yield the observed products phenanthrene, phenanthraquinone, or benzil by abstraction of hydrogen from solvent or reaction with molecular oxygen. Attempts to trap XIV by low-temperature photolysis in



XII XIII XIV

the presence of *N*-phenylmaleimide or cyclohexene yielded only a polymer whose infrared spectrum showed incorporation of the alicyclic group. No nonpolymeric material could be isolated.

Further attempts to characterize II showed that it was unreactive to dienes[9] and stable to bases. It re-

(5) K. V. Auwers, Th. Bahr, and E. Frese, *Justus Liebigs Ann. Chem.*, **441**, 82 (1925).
(6) A. Alemagna and T. Bacchetti, *Chem. Ind. (Milan)*, **45**, 709 (1963).
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(11) U. Mayer, H. Baumgartel, and H. Zimmerman, *Tetrahedron Lett.*, 5221 (1966).
(12) R. Anet and F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 525 (1964).
(13) G. Baum, R. Bernard, and H. Shechter, *ibid.*, **89**, 5307 (1967).
(14) Attempts to prepare the more directly analogous system, spiro[indazole-3,3′-indazole] by addition of benzyne to 3-diazoindazole have, to date, been unsuccessful.

acts rapidly with acids to regenerate moderate amounts of III.

Experimental Section

Infrared spectra were determined on a Beckman IR-8 spectrophotometer. Electronic spectra were obtained on a Beckman DB spectrophotometer. Nmr spectra were determined on a Varian T-60 spectrometer. Melting points were uncorrected and determined in sealed capillaries.

2,2′-Diacetamidobibenzyl (V).—A solution of 2,2′-dinitrobibenzyl (27.1 g, 0.1 mol) in a mixture of acetic anhydride (120 ml) and acetic acid (70 ml) containing 10% palladium-on-carbon catalyst (0.2 g) was hydrogenated at an initial pressure of 4 atm at room temperature. The exothermic reaction was complete in 40 min; hydrogen uptake ceased abruptly. The solution was filtered hot, concentrated *in vacuo* to 100 ml, and cooled to 0°. The crude product was recrystallized from glacial acetic acid to give V as white crystals (16.8 g, 57%): mp 268–269° (lit.[15] 249–250°); ir (Nujol) 6.12 μ (C=O); nmr (TFA) δ 7.2 (m, 8, aromatic), 3.05 (s, 4, $-CH_2CH_2-$), 2.31 (s, 6, CH_3CO) ppm.

***N,N′*-Dinitroso-2,2′-diacetamidobibenzyl (VI).**—A solution of V (38 g, 0.128 mol) in acetic acid (200 ml) containing acetic anhydride (70 ml) and sodium acetate (28 g) was stirred for 1 hr at room temperature and cooled to 0°; nitrosyl chloride was bubbled in for 4 hr, maintaining the temperature between 0 and 4°. The resulting dark red solution was stored at 0° for 10 hr and then added slowly to 1 l. of water and 500 g of crushed ice with stirring. The yellow oil which separated crystallized. This was dissolved in the minimum amount of hexane and stored at −20° overnight. VI separated as pale yellow crystals (21.4 g, 47%): mp 75° dec; ir (CCl_4) 5.81 (C=O), 6.62 μ (N=O); nmr ($CDCl_3$) δ 7.28 (m, 8, aromatic), 3.18 (s, 4, $-CH_2CH_2-$), 2.28 (s, 6, CH_3CO) ppm.

Anal. Calcd for $C_{18}H_{18}N_4O_4$: C, 61.01; H, 5.12; N, 15.81. Found: C, 60.86; H, 4.81; N, 16.04.

3,3′-Bi-1*H*-indazole (III).—A solution of VI (15.4 g, 0.044 mol) in benzene (800 ml) was maintained at 35° for 1 hr and at 45° for 7 hr. The solution went from pale yellow to light brown. After 10 hr at room temperature it was refluxed for 10 hr. The solvent was distilled *in vacuo* and the black residue was recrystallized three times from aqueous acetic acid using charcoal. III was obtained as tan crystals (3.1 g, 29%): mp 328–330°; uv (EtOH) 314 nm (log ε 4.27); ir (Nujol) 3.13 (N–H), 6.18, 7.46, 7.95 (aromatic C=C, C=N), 9.21, 9.96, 10.22, 11.21, 13.08, 13.68 μ; nmr (DMSO-d_6) δ 6.6–7.8 (m, aromatic) ppm.

An analytical sample was prepared by sublimation (120°, 0.1 mm).

Anal. Calcd for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30; N, 23.92. Found: C, 71.58; H, 4.33; N, 24.08.

Bis(2-oxocyclohexylidene)glyoxal (VIII).—To a slurry of sodium methoxide (35 g, 0.65 mol) in anhydrous ether (300 ml) was added, with vigorous stirring at 0°, a mixture of cyclohexanone (49 g, 0.5 mol) and ethyl oxalate (36.5 g, 0.25 mol). When addition was complete (1 hr) the mixture was stirred at room temperature for 2 days. The sodium methoxide dissolved initially to form an orange solution from which precipitated a solid. The solid was filtered, washed with ether, and dissolved in water (250 ml). The solution was extracted once with ether (100 ml), acidified to pH 3 with acetic acid, and extracted in a continuous extractor with ether. Washing of the ether (saturated aqueous NaCl), drying ($MgSO_4$), and evaporation yielded a yellow gum which could not be induced to crystallize. Some purification was effected by solution in aqueous base, extraction with ether, acidification, and reextraction. IX was obtained as a yellow gum (32.7 g, 52%): uv (EtOH) 288 nm (log ε 3.35), 236 nm (log ε 4.31); ir (film) 3.1 (enolic OH), 3.42 (C–H), 5.85 μ (C=O); nmr ($CDCl_4$) δ 1.72 (s, 12, $-CH_2-$), 2.42 (m, 4, $-CH_2-$), 9.4 (broad s, 2, enolic OH) ppm.

An analytical sample of IX was prepared by thick layer chromatography (SiO_2 with 1:1 methanol:methylene chloride elution).

Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.88; H, 7.39.

3,3′-Bi-4,4′,5,5′,6,6′,7,7′-tetrahydro-1*H*-indazole (IX).—A solution of IX (2.48 g, 0.01 mol) in ethanol (25 ml) was treated with hydrazine hydrate (1.0 g, 0.02 mol). After the exothermic reaction had ceased the solution was refluxed for 2 hr and then poured into water (200 ml); the gummy product was separated and triturated with benzene. The resulting white solid was sublimed (120°, 0.01 mm) to yield X (0.84 g, 33%): mp 320–322° dec; ir (Nujol) 3.08 (N–H), 6.33 (C=C or C=N), 7.72, 7.91, 8.08, 9.02, 10.15 μ; nmr (DMSO-d_6) δ 1.73 (broad s, 8, $-CH_2-$), 2.62 (broad s, 8, $-CH_2-$) ppm; nmr (TFA) 2.00 (broad s, 8, $-CH_2-$), 2.83 (d, 8, J = 14 Hz, $-CH_2-$) ppm.

Anal. Calcd for $C_{14}H_{18}N_4$: C, 69.39; H, 7.49; N, 23.12. Found: C, 69.08; H, 7.33; N, 22.87.

3,3′-Bi-1*H*-indazole (III).—A mixture of X (0.5 g, 0.002 mol) in decalin (10 ml) containing 10% palladium on carbon (0.5 g) was refluxed for 24 hr and filtered while hot. The filtrate was diluted with hexane (20 ml) and cooled to 0° for 12 hr. The precipitate (0.08 g) was purified by sublimation (140°, 0.1 mm) to yield III (0.04 g, 8%), mp 328–330°, identical in all respects with the material from the other synthetic route.

$\Delta^{3,3'}$-Bi-3*H*-indazole (II). Method A.—A solution of III (0.5 g, 0.002 mol) in anhydrous acetonitrile (50 ml) containing magnesium oxide (5 g) was treated at 0° under nitrogen with lead tetraacetate (2.0 g, 0.0045 mol) in small portions. The resulting deep red solution was stirred for 3 hr and poured into an ice-cold two-phase mixture of chloroform (50 ml) and 5% aqueous sodium bicarbonate (200 ml). The chloroform was separated, the aqueous phase was extracted with chloroform (two 50-ml portions), and the combined chloroform extracts were thoroughly washed with ice-cold 5% aqueous sodium bicarbonate, dried ($MgSO_4$), and evaporated *in vacuo* at 0° to yield II as an unstable deep red solid (0.17 g, 34%), which decomposed to a yellow polymer on warming: uv ($CHCl_3$) 442 nm (log ε 3.37); ir ($CHCl_3$) 3.30 (=CH), 6.28, 6.84, 7.05, 7.51, 7.82 μ (C=C or N=N); nmr ($CDCl_3$) δ 7.2–7.6 (m, aromatic) ppm.

Anal. Calcd for $C_{14}H_8N_4$: C, 72.40; H, 3.47; N, 24.12. Found: C, 72.06; H, 3.30; N, 23.80. (Nitrogen analysis was determined on separately prepared sample.)

Method B.—A suspension of III (0.234 g, 0.001 mol) in carbon tetrachloride (50 ml) containing magnesium oxide (2 g) was treated at room temperature with *N*-bromosuccinimide (0.356 g, 0.002 mol), added in small portions. The solution became deep red. After 2 hr the solution was filtered and cooled to −20°. Precipitation of X as brown crystals was complete in 3 hr. X was stable at −20° for several days without change. It was recrystallized by solution in carbon tetrachloride at 30° followed by cooling to −20° and was obtained as dark brown needles (0.18 g, 46%), no definite melting point: uv (EtOH) 457 nm (log ε 4.04); ir ($CHCl_3$) 6.25, 7.56 μ (C=C or C=N).

Anal. Calcd for $C_{14}H_8N_4Br_2$: C, 42.88; H, 2.05; N, 14.29. Found: C, 43.05; H, 2.28; N, 14.08.

XI (0.1 g, 0.00025 mol) was dissolved in distilled chloroform (25 ml), and silver powder (0.5 g) was added. The mixture was stirred at 0° for 2 hr, filtered, and evaporated *in vacuo* at 0° to yield II (0.053 g, 90%). The spectroscopic properties of this material were identical with the product from method A.

Photolysis of II.—The following is representative of several runs. A solution of II (0.464 g, 0.002 mol), in benzene, prepared by method B was photolyzed at 0° in a Rayonet photochemical reactor (360-nm lamps). The color faded in several minutes and a yellow solid precipitated. The solvent was evaporated and the residue sublimed (100°, 0.01 mm) to yield pale yellow crystals of phenanthraquinone (0.033 g, 8%), mp 207–208° (lit.[16] 208.5–210°), identical in all respects with authentic material. The nonsublimable material was insoluble in all common solvents. It showed ir (Nujol) 5.92 μ (C=O).

Thermolysis of II.—Solid II (0.100 g, 0.0004 mol) was placed in a sublimation apparatus and immersed in an oil bath at 100°. The color rapidly faded and a yellow solid remained. Vacuum was applied (0.01 mm) and a yellow solid sublimed. This was analyzed by tlc (silica gel G with benzene elution). Exposure of the plate to iodine vapor showed several spots; the major ones had R_f values identical with those of phenanthraquinone and benzil. Thick layer chromatography of the sublimate (0.009 g) with benzene elution afforded two main fractions which were phenanthaquinone (0.008 g, 6%) and benzil (0.001 g, 1%) identified by mixture melting points and ir comparison.

Registry No.—II, 28228-82-2; III, 28228-83-3; V, 28228-84-4; VI, 28228-85-5; VIII, 28228-86-6; IX, 28228-87-7; X, 28312-63-2.

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