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1,3-DIPHENYLISOINDOLES[1]

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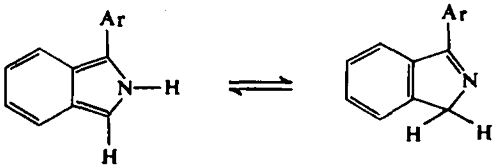
Abstract—1,3-Diphenylisoindole and 1,3-diphenyl-2-methylisoindole have been prepared by Leuckart reactions of *o*-di-benzoylbenzene and ammonia or methylamine. 1,3-Diphenylisoindole gives stable Diels-Alder addition products with acetylene dicarboxylic ester and benzyne, but the adduct with maleic anhydride readily reverts to the starting materials. 1,3-Diphenylisoindole can also be prepared by base treatment, in dimethyl sulfoxide, of N-*p*-toluenesulfonyl-1,3-diphenylisoindoline.

INTRODUCTION

1-ARYLISOINDOLES not substituted on the nitrogen (2-position), have recently been synthesized[3] and found to exist in tautomeric equilibrium with the corresponding isoindolenines:



A similar equilibrium, but with phenyl groups migrating between the 2- and the 3-positions, was found by Theilacker[4] when he heated 1,3,3-triphenylisoindolenine to 300°. We were interested in the position of the isoindole–isoindolenine equilibrium in the case of 1,3-disubstituted isoindoles, as well as in their behaviour as dienes in the Diels-Alder addition reaction.

The reported reactions of isoindoles with dienophiles do not appear to follow a consistent pattern. N-substituted isoindoles without substituents in the 1- and 3-positions[5-7] as well as the parent compound isoindole itself[8] react with maleic anhydride to give Diels-Alder adducts, solutions of which seem not to be noticeably dissociated into their components. 1-Methyl-3-phenylisoindole behaves similarly,[7] while 1-benzyl-2-methylisoindole[9] undergoes additive substitution in the 3-position, as does 1-phenylisoindole.[3] Finally, 1,3-diphenyl-2-methylisoindole[10] and 1-phenylisoindole-3-(N,N-diethyl)propionamide[3] form Diels-Alder adducts with maleic anhydride

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[1] Part of this work was communicated in *Chem. Comm.* 272 (1965).

[2] Present address: Unilever Research Ltd., Sharnbrook, Bedford, Bedfordshire, England.

[3] D. F. Veber and W. Lwowski, *J. Amer. Chem. Soc.* **86**, 4152 (1964).

[4] W. Theilacker, H.-J. Bluhm, W. Heitmann, H. Kalenda and H.-J. Meyer, *Liebigs Ann.* **673**, 96 (1964).

[5] G. Wittig, H. Tenhaeff, W. Schoch and G. Koenig, *Liebigs Ann.* **572**, 1 (1951).

[6] R. Kreher and J. Seubert, *Angew. Chem.* **76**, 682 (1964).

[7] G. Wittig, G. Closs and F. Mindermann, *Liebigs Ann.* **594**, 89 (1955).

[8] R. Kreher and J. Seubert, *Z. Naturforsch.* **20b**, 75 (1965).

[9] G. Wittig and H. Streib, *Liebigs Ann.*, **584**, 1 (1953).

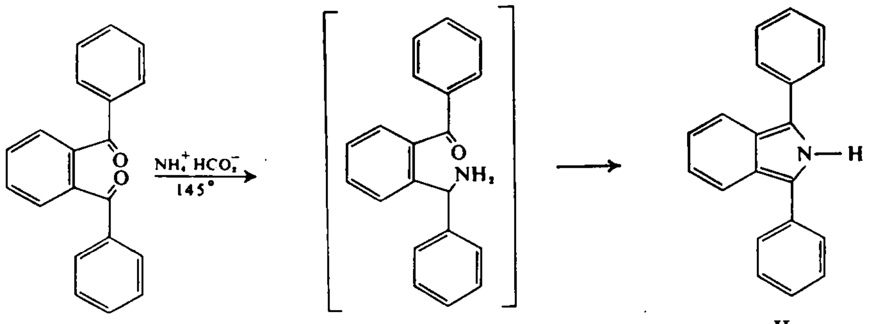
[10] W. Theilacker and W. Schmidt, *Liebigs Ann.* **597**, 95 (1957).

which revert easily to the starting materials. 1,2,3-Triphenylisoindole did not react with maleic anhydride.[11]

To study the tautomeric equilibrium and the reactivity in the Diels-Alder reaction of 1,3-diarylisoindoles, a synthetic path leading to these compounds had to be chosen. Three alternatives seemed inviting: An extension of our first synthesis of N-unsubstituted isoindoles,[3] a modification of this approach creating an intermediate *o*-aminoalkylbenzophenone by a method different from that previously used, and base-induced elimination of toluenesulfinic acid from a N *p*-tosylisoindoline. The last method had been proposed by Fenton and Ingold[12] and has recently been used successfully by Kreher.[8]

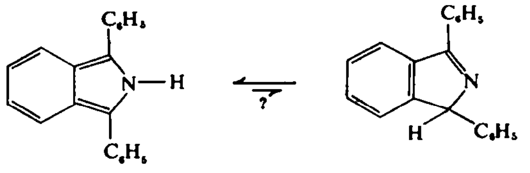
RESULTS AND DISCUSSION

Extension of our synthesis of 1-arylisoindoles would have called for preparing 2-(α-phthalimidobenzyl)benzophenone and cyclizing it by treatment with hydrazine in ethanol. However, the synthesis of the phthalimido compound would have required seven steps and it was decided to try first a Leuckart reaction on *o*-dibenzoylbenzene:



I II

Reaction of *o*-dibenzoylbenzene with ammonium formate at 145°, followed by chromatography of the crude product, indeed gave a 44% yield of 1,3-diphenylisoindole (II) which forms pale yellow needles, mp. 148–150°. Its NMR spectrum in deuteriochloroform shows a broad NH signal at 0·7 τ and aromatic protons at 2·0–3·2 τ. The absence of any other detectable CH signals indicates that the tautomeric isoindolenine (III) is either absent or present only in rather small concentration. The IR spectrum shows a single sharp NH band at 3445 cm^{-1}, as compared to 3460 cm^{-1} in 1-phenylisoindole.



II III

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[11] W. Theilacker and W. Schmidt, *Liebigs Ann.* **605**, 43 (1957).

[12] G. W. Fenton and C. K. Ingold, *J. Chem. Soc.* 3295 (1928).

The Leuckart reaction has been used for the reductive alkylation of primary amines as well as ammonia and it seemed to be of interest to ascertain whether N-substituted isoindoles can be prepared this way. Reaction of I with methylammonium formate at 145°, followed by chromatography and recrystallization, gave a 28% yield of 1,3-diphenyl-2-methylisoindole (IV). Its IR spectrum and m.p. are in complete agreement with the published data.[10]

The UV spectra of our isoindoles show much more detail than those of pyrroles with corresponding patterns of substitution. Nevertheless, the differences between these isoindoles are similar to the differences between correspondingly substituted pyrroles, as far as the long wavelength absorption band is concerned. Table 1 gives the spectral data for our isoindoles, and, in the last lines, shows the differences in absorption maxima and extinction coefficients for the isoindoles and corresponding pyrroles.

TABLE 1. UV SPECTRA IN ETHANOL
Absorption maxima and (log ε)

a	II	IV	b[13]	c[13]	d[14]	
—	228 sh	228	—	—	—	mμ
	(4·24)	(4·47)				(log ε)
—	237	—	—	—	—	mμ
	(4·27)					(log ε)
272	268 sh	268 sh	—	—	—	mμ
(3·86)	(4·22)	(4·13)				(log ε)
282	273	276	—	—	—	mμ
(3·92)	(4·27)	(4·20)				(log ε)
314 sh	322	—	—	—	—	mμ
(3·87)	(4·13)					(log ε)
325	335	332	—	—	—	(log ε)
(3,99)	(4.16)	(4.01)				
357	387	371	307	330	287	mμ
Δλ	30	16		23	43	Δmμ
(4·10)	(4·37)	(4·27)	(4·31)	(4·43)	(4·30)	(log ε)
(Δ log ε)	(+0·27)	(0·10)		(0·12)	(0·13)	(Δ log ε)

[a] 1-phenyl-isoindole
II: 1,3-diphenyl-isoindole
IV: 1,3-diphenyl-2-methyl-isoindole
[b] 2,5-diphenyl-1-methyl-pyrrole
[c] 2,5-diphenyl-pyrrole
[d] 2-phenyl-pyrrole

The changes caused by introducing another phenyl group, or an N-methyl group into the pyrroles and the isoindoles are very similar as far as the absorption maxima are concerned. The extinction coefficients also change in the same direction and order of magnitude for analogous structural changes.

After the products of the Leuckart reaction had been shown to indeed be isoindoles, the scope of the synthesis was investigated. Reactions of *o*-dibenzoylbenzene, formic acid and aniline or ethyl carbamate failed to give products with the characteristic UV spectrum of isoindoles. 1,1-Dimethylhydrazine reacted with loss of dimethylamine to give a good yield of 1,3-diphenylisoindole (II). When *o*-acetylbenzophenone[15] was treated with ammonium formate under Leuckadt conditions, instead of the expected 1-methyl-3-phenylisoindole, a brown solid, m.p. 246–247°, giving intense blue solutions,

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[13] S. M. King, C. R. Bauer and R. Lutz, *J. Amer. Chem. Soc.* **73**, 2253 (1951).

[14] B. Elpern and F. C. Nachod, *J. Amer. Chem. Soc.* **72**, 3379 (1959).

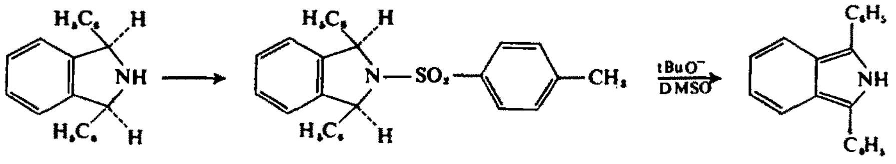
[15] A. F. Harms and W. Th. Nauta, *Rec. Trav. Chim.* **73**, 892 (1954).

was obtained. The IR spectrum showed neither NH nor C=O absorption, and the UV spectrum was not that of an isoindole. The same substance was obtained from the treatment of *o*-acetylbenzophenone with ammonium hydroxide and acetic acid at 80°; thus the reaction seems to involve an acid-catalysed condensation of the ketone with ammonia. The compound was almost insoluble in all solvents at hand.

Reactions of 1,3-*diphenylisoindole*. When exposed to the atmosphere, II decomposes slowly in the solid state at room temperature, and more rapidly in solution, Compound II and its solutions can easily be handled under nitrogen. On shaking solutions of II with air, a pale yellow solid deposits. Its IR spectrum shows no longer a NH band and elemental analysis indicates that a polymer of II has been formed without incorporation of oxygen. No solvent for the polymer could be found, and it was not investigated further.

Reduction of II with coppered zinc dust in acetic acid according to the method of Carpino[16] gave *cis*-1,3-diphenylisoindoline (*V*) mp. 108–109°, in agreement with the literature value.[17] The spectral data (Experimental) confirm the structure V.

Treatment of IV with *p*-toluenesulfonyl chloride in piperidine gave the known sulfonamide.[17] This, when treated with potassium t-butoxide in a dimethylsulfoxide—benzene solution,[8] gave a 38% yield of 1,3-diphenylisoindole (II):



V II

Thus, the route to isoindole suggested by Fenton and Ingold[12] and successfully modified by Kreher[8] may be generally applicable.

1,3-Diphenylisoindole (II) reacted with maleic anhydride in ether at room temperature to give a 72% yield of a 1:1-adduct, which, in solution, showed the characteristic blue fluorescence of II. This indicated that the adduct in solution is in equilibrium with the starting materials, as is the case with the maleic anhydride adduct of 1-phenyl-isoindole-3-(N,N-diethyl)propionamide.[3] The IR spectrum (in KBr) is in accord with the formulation VI as a Diels-Alder adduct. The UV spectrum in acetonitrile, however, indicated the presence of II. A comparison of the extinction coefficients with those of pure II showed the adduct formation to be almost totally reversed in dilute acetonitrile solution.

Compound II reacted with diethyl acetylenedicarboxylate to give a 72% yield of a 1:1-adduct. Analysis and spectra show this to be a Diels-Alder adduct (VII) No isoindole (II) could be detected in solutions in ethanol and acetonitrile by UV spectrometry, even in concentrated solutions. In the UV spectrum, the characteristic absorption of the benzene rings is obscured by the strong absorption of the maleic ester moiety.[18] The NMR spectrum (Experimental) is in accord with structure VII.

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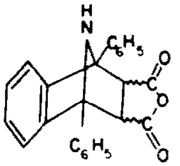
[16] L. A. Carpino, *J. Amer. Chem. Soc.* **84**, 2196 (1962).

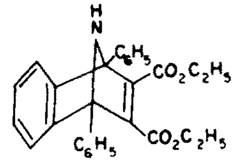
[17] D. R. Boyd and D. E. Ladhams, *J. Chem. Soc.* 2089 (1928).

[18] W. D. Closson, S. Brady, E. Kosower and P. Huang, *J. Org. Chem.* **28**, 1161 (1963).

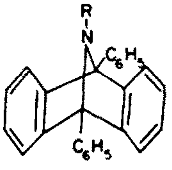
Benzyne, generated from *o*-bromofluorobenzene and magnesium in tetrahydrofuran,[19] reacted with II to give a 43% yield of a 1:1-adduct. Analysis, NMR, IR and UV spectra indicate the structure VIII. The UV spectrum in ethanol shows λ_{max} (log ε) of 284 (3·30), 277 (3·17) and 257 sh (3·26), and closely resembles the spectrum of 7,7-dimethyldibenzonorbornadiene (IX).[20] Benzyne adducts to N-Methyl- and N-phenylisoindoles have previously been prepared by Wittig.[21]



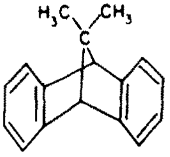
VI



VII



VIII R = H
X R = $CO_2C_2H_5$



IX

Attempts to acylate the nitrogen atom in 7-aza-1,4-diphenyl-dibenzo norbornadiene (VIII) with ethyl chloroformate and potassium carbonate, pyridine, triethylamine, or lithium hydride failed. The carbamate (X) was obtained, however, by treating VIII first with butyl lithium in hexane and then with ethyl chloroformate. Compound X was isolated in 72% yield and exhibited dimorphism. The structural assignment is based on analysis and spectra (Experimental). The NMR signals of the carbethoxy group are shifted upfield relative to the positions in other ethyl carbamates: the CH_2 quartet appears at 6·4 τ vs. 5·93 τ in N-cyclohexylurethan, the CH_3 triplet of X appears at 9·49 τ vs. 8·80 τ in cyclohexylurethan.[22] This must be due to the influence of the benzene rings.

We had hoped that thermolysis or photolysis of X would cause extrusion of carbethoxynitrene[22] and formation of 9,10-diphenylanthracene (XI). However, photolysis of X in cyclohexane or cyclohexene, using a medium pressure mercury arc, did not give XI as shown by the absence of its characteristic UV spectrum. Also, the products to be expected from carbethoxynitrene and the solvents could not be detected by VPC of the reaction mixture. Thermolysis of X in cyclohexane (saturated with nitrogen) at 215° for 48 hr caused little or no decomposition. When, however, X was heated to the same temperature in commercial cyclohexane through which nitrogen had not

[19] E. Woltkins, B. Bossenbroek, G. DeWall, E. Geels and A. Leegwater, *J. Org. Chem.* **28**, 148 (1963).
[20] J. A. Berson and M. Pomerantz, *J. Amer. Chem. Soc.* **86**, 3896 (1964).
[21] G. Wittig, E. Knauss and K. Niethammer, *Liebigs Ann.* **630**, 10 (1960).
[22] W. Lwowski and T. W. Mattingly, Jr. *J. Amer. Chem. Soc.* **87**, 1947 (1965).

been passed, decomposition occurred to yield a dark tar from which 9,10-diphenylanthracene precipitated upon addition of ether. Its m.p.,[23] IR spectrum[24] and UV spectrum[25] were identical with those reported in the literature. VPC of the reaction mixture did not indicate the presence of N-cyclohexyl urethan. Thus, the formation of 9,10-diphenylanthracene agrees with our structural assignments, but the extrusion of the moiety N—COOEt in form of the nitrene was not demonstrated. The thermal stability of the benzyne adduct X (in the absence of oxygen) is remarkable. The extent to which retro-Diels-Alder reaction occurs must be very small at the most, because even a small equilibrium concentration of II would have led to much decomposition. The 7-aza-benzonorbornadiene system seems to be much more stable than the 7-azabenzonorbornene system, as indicated by the ready reversal of the addition to II of maleic anhydride, compared with the stability of the adducts with acetylendicarboxylate and benzyne. The 7-azanorbornadiene system—without the benzene ring condensed at the 5 and 6 positions—is apparently not very stable.[26]

EXPERIMENTAL

Instruments. IR spectra were taken on a Perkin–Elmer model 421 spectrometer, UV spectra on a Cary model 11s, and NMR spectra on a Varian A-60 instrument. VPC was carried out on an Aerograph model A-90-P chromatograph.

o-Dibenzoylbenzene (I) was at first prepared by air oxidation of 1,3-diphenylisobenzofuran[27] according to Allen.[28] However, oxidation with potassium ferricyanide gave comparable yields in a shorter time when the method of Blicke[29] was used with the slight modification of dissolving the diphenylisobenzofuran in dioxan and extraction with benzene after oxidation.

1,3-*Diphenylisoindole* (II). Formic acid (45 g; 0·9 mole) was added dropwise with stirring to a 28% NH_4OHaq (54 g; 0·9 mole). Water was then distilled until the temp in the liquid had risen to 150°. The solution was allowed to cool to 130°, the system was flushed with N_2 and *o*-dibenzoylbenzene (9 g; 0·3 mole) was added in one portion. The mixture was stirred and heated to 145° under N_2 for 4 hr. After cooling, the mixture was made alkaline by adding 2N NH_4OH, and extracted with benzene until all of the brown, tarry solid had dissolved. The benzene solution was dried and concentrated and chromatographed on acid-washed alumina, using benzene as the eluent. A fraction containing 3·77 g (44% yield) of 1,3-diphenylisoindole was obtained. It formed yellow needles, m.p. 148–150° under N_2 with dec. For the UV spectrum, see Table 1. IR spectrum: Sharp NH at 3445 cm^{-1}, ring vibration at 1595 cm^{-1}. The NMR spectrum showed a broad NH peak at 0·7 τ, complex aromatic proton signals at 2·0 to 3·2 τ and no trace of a signal at higher τ values, even at increased gain. (Found: C, 89·31; H, 5·69; N, 5·06. Calc. for $C_{20}H_{15}N$: C, 89·18; H, 5·61; N, 5·20%.)

Polymerization of II. 1,3-Diphenylisoindole (0·1 g), purified by chromatography, was dissolved in a mixture of benzene and ether. The solution was exposed to the atmosphere for 1 day. The lemon-yellow precipitate was washed with ether and dried (0·08 g). The product was insoluble in all solvents at hand. (Found: C, 89·58; H, 5·22; N, 5·02. Calc. for $(C_{40}H_{28}N_2)_n$: C, 89·53; H, 5·26; N, 5·22%.)

1,3-*Diphenyl-2-methylisoindole* (IV) was prepared from formic acid (7·5 g; 0·15 mole), methylamine (11·6 g; 0·15 mole) and *o*-dibenzoylbenzene (1·5 g; 0·005 mole) in the same way as was II. After chromatography on alumina using benzene as the eluent, the product was recrystallized from EtOH to give yellow needles (0·28 g; 28% yield), mp. 149·5–150°; cf. Ref. 10. UV spectrum: see

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[23] C. K. Ingold and P. G. Marshall, *J. Chem. Soc.* 3080 (1926).

[24] API IR spectrum No. 2243.

[25] cf. H. H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy* p. 325; Wiley, New York (1962).

[26] cf. R. M. Acheson, *Advances in Heterocyclic Chemistry* (Edited by A. R. Katritzky) Vol. 1; p. 125ff. Academic Press, New York (1963).

[27] M. S. Newman, *J. Org. Chem.* **26**, 2630 (1961).

[28] C. F. H. Allen and J. A. VanAllen, *J. Amer. Chem. Soc.* **70**, 2069 (1948).

[29] F. F. Blicke and R. A. Patelski, *J. Amer. Chem. Soc.* **58**, 276 (1936).

Table 1 NMR spectrum: aromatic protons from 2·0 to 3·0 τ, sharp CH_3 at 6·25 τ, ratio of aromatic to aliphatic protons: 14·3. (Found: C, 89·33; H, 6·00; N, 4·54. Calc. for $C_{21}H_{17}N$: C, 89·01; H, 6·05; N, 4·94%.)

cis-1,3-*Diphenylisoindoline* (V) was prepared in 86% yield by reduction of 1,3-diphenylisoindole with coppered Zn dust according to Carpino.[16] A sample, recrystallized from aqueous EtOH, m.p. 108–109°. The IR spectrum shows NH at 3365 cm^{-1}, the NMR spectrum (in CCl_4) shows the aliphatic CH at 4·32 τ and NH at 7·7 τ. The UV spectrum shows a benzene pattern with a long wavelength absorption maximum at 265 mμ, lgε 3·1.

N-p-*Toluenesulfonyl*-cis-1,3-*diphenylisoindoline* was prepared by heating a solution of V and *p*-toluenesulfonyl chloride in pyridine to 70° for 15 min then adding water. The product precipitated and melted, after 3 recrystallizations from MeOH–benzene, at 238–239°; (lit.[17] 255°).

Treatment of N-p-*toluenesulfonyl*-1,3-*diphenylisoindoline with base.* A solution of potassium t-butoxide (0·25 g; 0·24 mole) in dry dimethyl sulfoxide (10 ml) was added dropwise with stirring to a solution of the tosylate (0·50 g; 0·0012 mole) in dimethyl sulfoxide (15 ml) and benzene (10 ml). The mixture was stirred for 30 mins, 45 ml of water was then added with stirring and cooling and the benzene layer separated. The aqueous layer was twice extracted with benzene, the combined benzene solutions were twice washed with water and dried. Removal of the benzene and chromatography gave 0·12 g (38% yield) of 1,3-diphenylisoindole, identical in all respects with the material prepared above.

Maleic anhydride adduct of II (VI). A solution of maleic anhydride (0·60 g; 0·006 mole) in 10 ml ether was added to a solution of 0·84 g (0·003 mole) of II in 10 ml of ether, under N_2. The resulting deep brown solution was allowed to stand for 24 hr. The adduct VI was filtered off and washed with ether to give 0·82 g (72% yield of almost white needles, m.p. 140–145° (dec). IR spectrum (in KBr); NH at 3280, anhydride C═O 1835 and 1770, C—O—C at 1230 cm^{-1}. UV spectrum in acetonitrile, λ_{max} (log ε): 387 (4·34); 333 (4·13); 320 (4·12); 270 (4·30); 236 (4·32). (Found: C, 78·68; H, 4·93; N, 3·99. Calc. for $C_{24}H_{17}NO_3$: C, 78·46; H, 4·66; N, 3·81%.)

Diethyl acetylenedicarboxylate adduct of II (VII). Compound II (1 g; 0·0037 mole) was dissolved in 3 g of diethyl acetylenedicarboxylate under an atmosphere of N_2 and allowed to stand for 24 hr at room temp. A 74% yield (1·2 g) of a crystalline adduct was filtered off. Recrystallization from benzene–EtOH gave prisms, m.p. 169–170°. The IR spectrum (in KBr) shows NH at 3260 cm^{-1}, C═O at 1720 and 1705 cm^{-1}. The UV spectrum in EtOH and in acetonitrile shows only end absorption, and no isoindole pattern could be discerned. The NMR spectrum in $DCCl_3$ showed aromatic protons at 2·2 to 3·1 τ (14), NH at 6·42 τ (1), OCH_2 at 5·87 τ (4) and CH_3 at 8·89 τ (6). (Found: C, 76·29; H, 5·78; N, 3·40. Calc. for $C_{28}H_{25}NO_4$: C, 76·52; H, 5·73; N, 3·19%.)

Benzyne adduct of 1,3-*diphenylisoindole* (VIII). A solution of 5 g of 1,3-diphenylisoindole (0·019 mole) and 5·6 g (0·013 mole) of bromofluorobenzene in dry tetrahydrofuran (120 ml) was added dropwise, with stirring, to activated Mg turnings (0·84 g; 0·035 mole) covered with refluxing tetrahydrofuran in a N_2 atmosphere. After addition, the mixture was heated to reflux for 2 hr, cooled, decomposed with NH_4Cl and extracted with benzene. After washing with water, the benzene solution was dried and the solvent evaporated under red. press. The residual solid was recrystallized from ethyl acetate. 2·78 g (43% yield) of white needles, m.p. 249–257° of VIII was obtained. The IR spectrum shows a sharp NH band at 3228 cm^{-1}, aromatic CH at 3060 and 3030 cm^{-1}. The NMR spectrum in $DCCl_3$ shows 18 aromatic protons at 1·84–3·17 τ and a broad NH signal at 6·25 τ, corresponding to one proton. The UV spectrum in EtOH had maxima (lg ε) at 284 (3·30); 277 (3·17) and 257 (shoulder) (3·26). (Found: C, 90·09; H, 5·68; N, 4·24. Calc. for $C_{26}H_{19}N$: C, 90·40; H, 5·54; N, 4·06% Mol. wt. Calc: 345; Found: 361.)

1,4-*Diphenyl-7-carbethoxy-7-azadibenzonornadiene* (X). 15·2% solution of butyllithium (1·89 g, 0·005 mole) in hexane was added dropwise with stirring to a solution of 1·05 g (0·003 mole) of VIII in 45 ml of dry benzene. The temp. was maintained at ca. 15°, and the solution was stirred for 10 min. Then a solution of 0·45 g (0·0042 mole) of ethyl dichloroformate in 10 ml of benzene was added over a period of 30 min. After another 30 min at room temp the mixture was washed with water and dried. The benzene phase left an oily residue which solidified upon addition of hexane to give 0·92 g (72% yield) of 1,4-diphenyl-7-carbethoxy-7-aza-dibenzo-norbornadiene. Recrystallization from ethyl acetate gave white, rhombic, crystals which melted first at 143–145°, then resolidified to melt again at 155–160°. Further recrystallization gave needles, m.p. 158–160°. The NMR spectrum shows a symmetrical pattern due to the aromatic protons from 1·67 to 3·33 τ (18), almost identical to the pattern in VIII. The carbethoxy group gives rise to a quartet at 6·4 τ (2) and a triplet at 9·49 τ(3).

The UV spectrum showed a maximum at 287 mμ (3·10 and a shoulder at 255 mμ (3·3). Needles and plates had identical UV spectra. (Found: C, 83·13; H, 5·48; N, 3·44. Calc. for $C_{29}H_{23}NO_2$: C, 83·43; H, 5·55; N, 3·36%.)

Decomposition of X

Photolysis of 0·7 g of X in silica vessels, using the light of medium press. Hg arcs, in cyclohexane and in cyclohexane (40 ml) for 19 hr gave no detectable amount of 9,10-di-phenylanthracene, as shown by absence of its characteristic UV spectrum. After 30 min of irradiation 50% of the starting material was recovered. After 19 hr only a yellow oil remained upon removal of the solvent. No addition or insertion products from solvents and carbethoxynitrene could be detected by VPC of the residue. The products obtained from the solvents and authentic carbethoxynitrene[12] were used to calibrate the VPC analysis.

Thermolysis In a sealed tube 4 g (0·009 moles) of X in 90 ml of cyclohexane was heated to 215° for 48 hr. After removal of the solvent and addition of ether to the residue, a yellow precipitate was obtained and shown to be 9,10-diphenylanthracene (1·1 g; 33% yield). A sample, recrystallized from hexane-EtOH melted at 250–251°. The dark brown filtrate contained at least seven products, none of which was cyclohexylurethan. The reaction was repeated using cyclohexane saturated with nitrogen. Little or no decomposition of the starting material X was observed.

Attempted preparation of 1-*methyl*-3-*phenylisoindole*. *o*-Acetylbenzophenone (0·55 g, 0·02 mole) was added to ammonium formate (from 7·6 g formic acid and 9 g NH_4OH) at 80°. An intense blue color immediately developed. After heating to 140° for 3 hr, the reaction mixture was worked up as described for II. Chromatography on alumina gave 0·07 g glistening light-brown crystals, m.p. 246–247°, sparingly soluble in cold benzene and almost totally insoluble in other common solvents, including dimethyl sulfoxide. The IR spectrum (in KBr) showed strong absorptions only at 1610, 1590, 1250, 1062, 800, 745 and 690 cm^{-1}. The UV spectrum in EtOH shows a benzene pattern at 252, 257 and 264 mμ, and further maxima at 288, 205 and 335 mμ. The visible spectrum in benzene showed maxima at 342 (shoulder) and 593 mμ.

The same blue color was produced when *o*-acetylbenzophenone was heated to 80° with NH_4CH and acetic acid. (Found: C, 87·20; H, 5·27; N, 7·55%.)

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