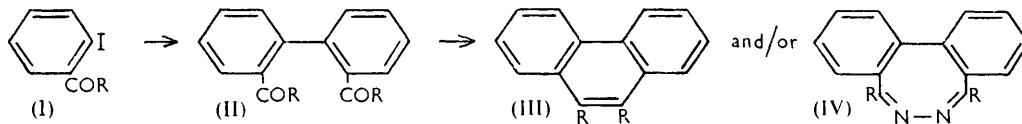


277. *Cyclisations with Hydrazine. Part II.* Conversion of 2:2'-Diacyldiphenyls into Compounds of the Phenanthrene and 4:5-6:7-Dibenzo-1:2-diazocine Series.*

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2:2'-Diacyldiphenyls are converted by hydrazine into phenanthrenes or 4:5-6:7-dibenzo-1:2-diazocines containing alkyl (or aryl) substituents in the 9:10- and 3:8-positions respectively. The influence of reaction conditions on the nature of the product is reported for the cyclisation of diacetyl-, dipropionyl-, and dibenzoyl-diphenyl. The stability of the dibenzodiazocines indicates that in general they are unlikely to be intermediates in the formation of the phenanthrenes. The ultraviolet and infrared absorption spectra of the dibenzodiazocines are discussed and compared with those of open-chain azines, $\text{Ar}\cdot\text{CR}\cdot\text{N}\cdot\text{N}\cdot\text{CRAr}$.

In Part I and in an earlier note¹ we referred to differences between diketones of type (II) and the corresponding aldehydes ($\text{R} = \text{H}$) in their reactions with hydrazine. In cases which we have so far examined, both classes of compound undergo reductive cyclisations to phenanthrenes (III), but only the diketones also yield 3:8-dialkyl(or -diaryl)-4:5-6:7-dibenzo-1:2-diazocines (IV). We now report details of these reactions for three diketones ($\text{R} = \text{Me}$, Et, and Ph) and describe some properties of the resulting diazocines.



Diketones (II), also obtainable from phenanthraquinone,^{2,3} were prepared in 60–75% yield by an Ullmann reaction on *o*-iodophenyl ketones (I), derived from *o*-iodobenzoyl chloride. The latter gave *o*-iodobenzophenone by a Friedel–Crafts reaction⁴ and gave *o*-iodoacetophenone, in high yield, on treatment with diethyl ethoxymagnesiummalonate. This reagent, used in similar cases by Walker and Hauser⁵ and by Bowman,⁶ proved superior to ethyl sodioacetoacetate.^{7,8} The homologous *o*-iodopropiophenone was obtained similarly from diethyl ethoxymagnesiummethylmalonate. Under appropriate conditions, described below, yields of up to 70% were obtained in the conversion of the diketones into the diazocines (IV), which may thus be synthesised from *o*-iodobenzoyl chloride in three steps and with overall yields of up to 40%. Only in one experiment (Table 3) was a high yield of a phenanthrene (III) obtained; yields were more commonly 20–30%.

Cyclisation of 2:2'-diacetyldiphenyl with hydrazine occurred readily in polar solvents (Table 1). The best yields of the diazocine were obtained at 0°, but even so a little reductive cyclisation to 9:10-dimethylphenanthrene occurred. Moderate yields of the hydrocarbon were obtained at ~80–180°, but diazocine formation was a strongly competitive reaction under nearly all conditions. Both reactions occurred in acidic media but, in contrast to the case of diphenyl-2:2'-dialdehydes (Part I), only resins were

* Part I, preceding paper.

¹ Bacon and Lindsay, *Chem. and Ind.*, 1956, 1479.

² Zincke and Tropp, *Annalen*, 1908, **363**, 302.

³ Hall, Ladbury, Lesslie, and Turner, *J.*, 1956, 3475.

⁴ Wachter, *Ber.*, 1893, **26**, 1744.

⁵ Walker and Hauser, *J. Amer. Chem. Soc.*, 1946, **68**, 1386.

⁶ Bowman, *J.*, 1950, 322.

⁷ Thorp and Brunskill, *J. Amer. Chem. Soc.*, 1915, **37**, 1258.

⁸ Rapson and Shuttleworth, *J.*, 1941, 487.

formed under alkaline conditions. The sensitivity of 2:2'-diacetyldiphenyl towards alkali was noted by Turner and his co-workers during their study³ of the anomalous behaviour of this diketone with various reducing agents. They too observed the dual reaction with hydrazine in warm ethanol, obtaining the diazocine and 9:10-dimethylphenanthrene in yields of 53% and ~4% respectively.

From 2:2'-dipropionyl-diphenyl and hydrazine in ethanol or carboxylic acids, 3:8-diethyl-4:5-6:7-dibenzo-1:2-diazocine was obtained exclusively, the best yield being at the lowest temperature (Table 2). 9:10-Diethylphenanthrene was obtained, together with the diazocine, by using excess of anhydrous hydrazine in diethylene glycol, a technique recommended for Wolff-Kishner reductions of hindered ketones.⁹

2:2'-Dibenzoyldiphenyl proved much more resistant to hydrazine (Table 3). In ethanol, or preferably in acetic acid, reduction could be achieved in pressure vessels at 200–280°, the product being 9:10-diphenylphenanthrene exclusively. The hydrocarbon was obtained more conveniently, and in high yield, by using excess of anhydrous hydrazine in hot diethylene glycol at atmospheric pressure. When hydrazine hydrate was employed in this medium the main product was 3:8-diphenyl-4:5-6:7-dibenzo-1:2-diazocine. Other instances are known in which reduction by anhydrous hydrazine gives a different product from reduction by the hydrate. For example, Dutt and Sen obtained phenanthrene from phenanthraquinone with anhydrous hydrazine, but obtained 9:10-dihydroxyphenanthrene with the hydrate.¹⁰

It might be supposed that the phenanthrenes arise by loss of nitrogen from the diazocines, just as stilbenes are formed from aromatic aldazines, $\text{Ar}\cdot\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{CHAr}$. However, aldazine decompositions require a relatively high temperature (280–300°),¹¹ and yields are poor. For aromatic ketazines, $\text{Ar}\cdot\text{CR}\cdot\text{N}\cdot\text{N}\cdot\text{CRAr}$, it is reported that even higher temperatures (300–350°) are required for decomposition and that stilbenes are not produced.¹² Dimethyl- and diethyl-diazocines had considerable stability. They yielded no phenanthrenes in the molten state above 300° or on prolonged boiling in acetic acid. The dimethyl- but not the diethyl-compound gave a trace of the phenanthrene in boiling diethylene glycol. In the presence of excess of hydrazine there was very slow conversion of diazocines into phenanthrenes (10–20% in 24 hr.) in boiling diethylene glycol or acetic acid. Comparison of such data (see Experimental section) with those in Tables 1, 2, and 3 suggests that the diazocines do not contribute as intermediates to an important degree, except, probably, with excess of hydrazine present at the higher temperatures. Turner and his co-workers concluded that 9:10-dimethylphenanthrene was unlikely to have been formed *via* the diazocine under their conditions. Similar comparative experiments were not possible when conversions of diphenyldialdehydes were studied (Part I), since no conditions have yet been discovered for obtaining the related diazocines.

Construction of three-dimensional ("Catalin"-type) molecular models for the 1:2-diazocines showed that formation of the central ring necessitates *cis*-linkages (in relation to the rings of the diphenyl system) at both $\cdot\text{CR}\cdot\text{N}\cdot$ bonds, as shown in Fig. 1. The diazocines are diazacyclooctatetraenes and the "tub" form possessed by the eight-membered ring in this model is similar to that preferred by Pitzer and his co-workers for cyclooctatetraene itself.¹³ The twist in the chain of four bridge atoms fixes the benzene rings at an inclination to each other of ~67° and the model can be constructed in enantiomorphous forms. The resolution of 4:5-6:7-dibenzo-1:2-diazocine derivatives has yet to be attempted; a derivative of the isomeric 5:6-7:8-dibenzo-1:4-diazocine system has already been resolved.¹⁴

A related carbocyclic compound, 1:2-3:4-dibenzocyclooctatetraene, could not be

⁹ Barton, Ives, and Thomas, *J.*, 1955, 2056.

¹⁰ Dutt and Sen, *J.*, 1923, 3420; Dutt, *J.*, 1925, 2971.

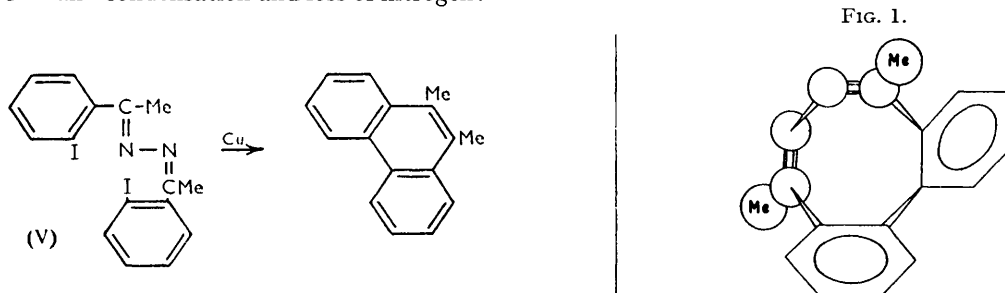
¹¹ Cf., e.g., Pascal and Normand, *Bull. Soc. chim. France*, 1911, **9**, 1029, 1059; 1912, **11**, 21.

¹² Howard and Hilbert, *J. Amer. Chem. Soc.*, 1932, **54**, 3628.

¹³ Person, Pimentel, and Pitzer, *ibid.*, 1952, **74**, 3437.

¹⁴ Bell, *J.*, 1952, 1527.

obtained by Rapson and Shuttleworth⁸ by treating 1:4-di-*o*-iodophenylbuta-1:3-diene with copper; cyclisation would presumably be assisted by a *cis-cis*-diene structure. We likewise failed to convert *o*-iodoacetophenone azine (V) into the diazocine (IV; R = Me), but we did obtain some 9:10-dimethylphenanthrene in a reaction involving both an Ullmann condensation and loss of nitrogen:



We have also examined some spectroscopic properties of the diazocines. In the near-ultraviolet region the effects of 2:2'-bridges on the characteristic diphenyl peak (249 m μ) have previously been studied for more than thirty tricyclic compounds,¹⁵ but in few of these cases does the bridge contain more than three linking atoms. A saturated chain of four

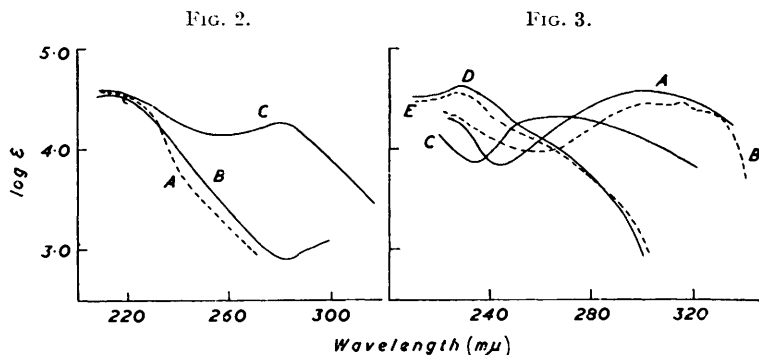


FIG. 2. Spectra of: (A) 3:8-dimethyl-4:5-6:7-dibenzo-1:2-diazocine, (B) 3:8-diethyl-4:5-6:7-dibenzo-1:2-diazocine, (C) 3:8-diphenyl-4:5-6:7-dibenzo-1:2-diazocine.

FIG. 3. Spectra of: (A) benzaldehyde azine, (B) *o*-iodobenzaldehyde azine, (C) acetophenone azine, (D) *o*-iodoacetophenone azine, (E) *o*-iodopropiophenone azine.

carbon atoms causes a displacement of the peak to shorter wavelengths and a reduction in intensity, indicating reduced conjugation in the benzene rings, which are thought to be inclined at 60–80° to each other.¹⁶ On the other hand, in *apogalanthamine*,¹⁷ containing the bridge CH₂·CH₂·NMe·CH₂, and in phenyl(or methyl)dihydrothebaine,¹⁸ containing the bridge CH₂·CHR·NMe·CH₂·CH₂, a band of reduced intensity appears at longer wavelengths.* The ultraviolet absorption spectrum for Turner's 3:8-dimethyl-4:5-6:7-dibenzo-1:2-diazocine³ was recently recorded by Beaven and Johnson.¹⁹ Our own spectra for this and for the diethyl- and diphenyl-compounds are shown in Fig. 2. The spectra of

* Comparison is complicated in these cases because an *o*-hydroxyl group is also present.

¹⁵ Beaven, Turner, and their co-workers, *J.*, 1952, 854, and later papers; Braude and Waight in Klyne's "Progress in Stereochemistry," Vol. I, Butterworths, London, 1954; Truce and Emrick, *J. Amer. Chem. Soc.*, 1956, **78**, 6130 (earlier data are there collected).

¹⁶ Beaven, Bird, Hall, Johnson, Ladbury, Lesslie, and Turner, *J.*, 1955, 2708.

¹⁷ Kobayashi and Uyeo, *J.*, 1957, 638.

¹⁸ Small, Sargent, and Bralley, *J. Org. Chem.*, 1947, **12**, 839; cf. Bentley and Robinson, *J.*, 1952, 947.

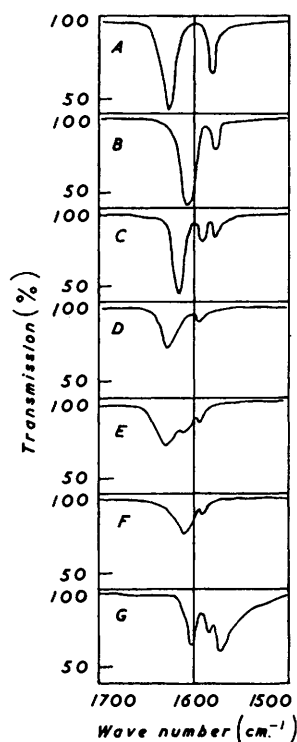
¹⁹ Beaven and Johnson, *J.*, 1957, 651.

the two dialkyl derivatives, with peaks ($\sim 215 \text{ m}\mu$) at much shorter wavelength than diphenyl, are similar to those of 2:2'-linked diphenyl derivatives containing the bridge $\text{CH}_2\cdot\text{AsR}\cdot\text{CH}_2$, in which the estimated deviation²⁰ of the benzene rings from coplanarity is $\sim 63^\circ$.

Comparison may also be made with the absorption spectra of open-chain azines, $\text{Ar}\cdot\text{CR}\cdot\text{N}\cdot\text{N}\cdot\text{CRAr}$ ($\text{R} = \text{H}$, alkyl, or aryl). We were led to examine some spectra in this series (Fig. 3) on observing the absence of the usual yellow colour in some available *o*-iodo-substituted azines. Other investigators have considered both steric and polar factors in interpreting the spectroscopic characteristics of series of nuclear-substituted aromatic

FIG. 4.
Spectra of:

- (A) Benzaldehyde azine.
- (B) Acetophenone azine.
- (C) *o*-Iodobenzaldehyde azine.
- (D) *o*-Iodoacetophenone azine.
- (E) 3:8-Dimethyl-4:5-6:7-dibenzo-1:2-diazocine.
- (F) 3:8-Diethyl-4:5-6:7-dibenzo-1:2-diazocine.
- (G) 3:8-Diphenyl-4:5-6:7-dibenzo-1:2-diazocine.



azines.²¹ *ortho*-Substituted ketazines may be expected to show a particularly strong disturbance of conjugation between the $\text{CR}\cdot\text{N}\cdot\text{N}\cdot\text{CR}$ group and attached benzene rings, since there will be difficulty in accommodating the R groups and the *ortho*-substituents in a coplanar $\text{Aryl}\text{-C=N-}$ structure. When compared with that in benzaldehyde azine (λ_{max} 300 $\text{m}\mu$), the peak in the *o*-iodo-derivative differs chiefly in being split into two subsidiary bands (Fig. 3), as has been noted in some related cases.^{21a,b} On the other hand, the spectrum of acetophenone azine (λ_{max} 265 $\text{m}\mu$) differs greatly from those of *o*-iodoacetophenone azine and *o*-iodopropiophenone azine (Fig. 3), which show maxima at much shorter wavelength (λ_{max} 225 $\text{m}\mu$) and resemble the spectra of the dialkyldiazocines (Fig. 2). The curve for the diphenyldiazocine resembles those of the dialkyldiazocines in the 210—230 $\text{m}\mu$ region, but it shows an extra band at 280 $\text{m}\mu$, presumably due, as in open-chain ketazines, to conjugation in the group $\text{Ph}\cdot\text{C}\cdot\text{N}\cdot\text{N}\cdot\text{CPh}$.

Infrared absorption spectra²² have been reported by Blout, Fields, and Karplus²³ for

²⁰ Beeby, Mann, and Turner, *J.*, 1950, 1923.

²¹ (a) Blout and Gofstein, *J. Amer. Chem. Soc.*, 1945, **67**, 13; (b) Blout, Eager, and Gofstein, *ibid.*, 1946, **68**, 1983; (c) Ferguson and Goodwin, *ibid.*, 1949, **71**, 633; (d) Barany, Braude, and Pianka, *J.*, 1949, 1898; (e) Szmant and Planinsek, *J. Amer. Chem. Soc.*, 1950, **72**, 4981.

²² Cf. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 226.

²³ Blout, Fields, and Karplus, *J. Amer. Chem. Soc.*, 1948, **70**, 194.

several aldazines containing the group $\text{CH:N}\cdot\text{N}\cdot\text{CH}$ in conjugation with ethylenic bonds or furan rings. A sharp peak due to the $\text{C}=\text{N}$ stretching vibration occurred in the range $1580\text{--}1670\text{ cm.}^{-1}$ and showed a displacement towards lower frequency in proportion to the degree of conjugation in the compound; it was accompanied by neighbouring subsidiary peaks. The characteristics of our compounds are shown for this region of the spectrum in Fig. 4. The interrelations here observed are reminiscent of those discussed above for the ultraviolet region: benzaldehyde azine, acetophenone azine, and *o*-iodobenzaldehyde azine resemble one another in giving sharp peaks at $1610\text{--}1630\text{ cm.}^{-1}$ and sharp, less intense peaks at $\sim 1580\text{ cm.}^{-1}$; *o*-iodoacetophenone azine and the two dialkyl-substituted diazocines are alike in exhibiting broad peaks in the $1610\text{--}1630\text{ cm.}^{-1}$ region, with the subsidiary peak reduced to a shoulder; in the diphenyl-substituted diazocine a strong peak reappears at 1570 cm.^{-1} .

EXPERIMENTAL

o-Iodoacetophenone.—Reaction of *o*-iodobenzoyl chloride (75 g.) and diethyl ethoxy-magnesiummalonate (from 0.5 g.-atom of magnesium), as described for the preparation of *o*-chloroacetophenone,⁶ gave the ketone (54 g., 78%), b. p. $144^\circ/15\text{ mm.}$ It was obtained in only 25% yield by reaction of *o*-iodobenzoyl chloride and ethyl sodioacetoacetate⁸ and was then accompanied by much ethyl *o*-iodobenzoate. The ketone was characterised as the semi-carbazone,⁸ m. p. 179° , and as the *azine*, which crystallised from ethanol in colourless needles, m. p. 124° (Found: C, 39.2; H, 2.7; N, 5.4; I, 51.9. $\text{C}_{16}\text{H}_{14}\text{N}_2\text{I}_2$ requires C, 39.3; H, 2.9; N, 5.7; I, 52.0%).

2 : 2'-Diacetyldiphenyl.—*o*-Iodoacetophenone (49 g.) was heated under reflux in dimethylformamide (70 ml.) with copper bronze (40 g.) for 6 hr. The mixture was extracted with chloroform, and the extract distilled at $134^\circ/0.4\text{ mm.}$, giving solid 2 : 2'-diacetyldiphenyl (14 g., 59%), which crystallised from hexane in needles, m. p. 92.5° (Found: C, 80.7; H, 5.5. Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_2$: C, 80.7; H, 5.9%); Hall *et al.*³ give m. p. $93\text{--}94^\circ$. In 3 hr. at $180\text{--}200^\circ$, in the absence of dimethylformamide, the diketone was obtained in 45% yield, together with acetophenone (10%).

Reaction of 2 : 2'-Diacetyldiphenyl with Hydrazine.—The data summarised in Table 1 (as also in Tables 2 and 3) were usually obtained with 0.5—2.0 g. of the diketone and 50—200 ml. of solvent. The following are the best conditions so far found for preparing the diazocine and 9 : 10-dimethylphenanthrene respectively.

TABLE 1. Reaction of hydrazine and 2 : 2'-diacetyldiphenyl.

	Temp.	Time (hr.)	Medium *	Molar ratio, N_2H_4 : diketone	Dimethylphenanthrene (yield %)	Diazocine (yield %)
(i)	-20°	96	EtOH	1.2 : 1	2	72
(ii)	0	72	EtOH	1.2 : 1	2	70
(iii)	20	24	EtOH	1.2 : 1	2	66
(iv)	78	2—6	EtOH	1.5—3 : 1	8—19	50—52
(v)	78	2	EtOH + 10N- H_2SO_4 (10 ml.)	1.1 : 1	8—12	38—42
(vi)	78	1	EtOH + KOH (0.1 g.)	3 : 1	0	0
(vii)	78	1	EtOH + NaOEt (0.2 g.)	3 : 1	0	0
(viii)	117	1	AcOH	3 : 1	21	28
(ix)	117	1	AcOH	3 : 1	21	20
(x)	136	3	Et· CO_2H	3 : 1	28	0
(xi)	180	0.5	$\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$	3 : 1	21	0
(xii)	180	2	Diethylene glycol (+ anhyd. N_2H_4)	30 : 1	25	30
(xiii)	180	2	Diethylene glycol + 10N- H_2SO_4 (10 ml.)	1.1 : 1	13	35

* 60% or 100% Hydrazine hydrate was used in (i)—(iv) and (vi)—(xi), anhydrous hydrazine in (xii) only, hydrazine sulphate in (v) and (xiii). The hydrazine (in 10 ml. of solvent) was added dropwise in (ii), (iv)—(viii), and (xii).

(a) 2 : 2'-Diacetyldiphenyl (2.0 g., 0.0084 mole) in ethanol (200 ml.) was treated at -20° with 100% hydrazine hydrate (0.50 g., 0.010 mole) and after 1 hr. the mixture was transferred to a refrigerator and kept for 4 days at -5° . Ethanol was then evaporated under reduced

pressure at room temperature and the residue chromatographed on alumina. Elution with benzene gave a little 9 : 10-dimethylphenanthrene (0.04 g., 2%), and ether gave colourless prisms of 3 : 8-dimethyl-4 : 5-6 : 7-dibenzo-1 : 2-diazocine (1.44 g., 72%), m. p. 165°, raised to 168° by recrystallisation from hexane (Hall *et al.*³ give m. p. 167—168°) (Found: C, 82.0; H, 6.1; N, 11.6. Calc. for $C_{16}H_{14}N_2$: C, 82.0; H, 6.0; N, 12.0%).

(b) 2 : 2'-Diacetyldiphenyl (0.50 g., 0.0021 mole) and 60% hydrazine hydrate (0.50 g., 0.006 mole) were heated for 2 hr. under reflux in propionic acid (30 ml.). Evaporation, followed by chromatography on alumina, yielded 9 : 10-dimethylphenanthrene (0.12 g., 27%) and yellow resin (0.30 g.) but no diazocine. The hydrocarbon had m. p. 143.5—144° after recrystallisation from methanol (Found: C, 92.9; H, 7.0. Calc. for $C_{16}H_{14}$: C, 93.2; H, 6.8%) and formed a picrate, m. p. 193—194°; Bradsher and Amore²⁴ give m. p. 142.5—143° and 193—194°, respectively.

Conversion of o-Iodoacetophenone Azine into 9 : 10-Dimethylphenanthrene.—2.0 g. (0.0041 mole) of the azine (see above) was heated with copper bronze (2.0 g.) at 210° for 1.5 hr. and the product extracted with ether. Chromatography of the extract (0.58 g.) on alumina gave resins and a crystalline fraction (0.07 g., 8%), which was 9 : 10-dimethylphenanthrene, m. p. and mixed m. p. 141—142°; no diazocine was detected.

Stability of 3 : 8-Dimethyl-4 : 5-6 : 7-dibenzo-1 : 2-diazocine.—Samples were treated under the following conditions and the products examined by chromatography.

(a) After 15 min. at 370—380° or for 24 hr. at 220°, unchanged diazocine (65% and 55% respectively) was recovered, but no 9 : 10-dimethylphenanthrene obtained.

(b) 90% of the diazocine was recovered after 36 hr. in refluxing acetic acid (0.20 g. in 20 ml.), but when the diazocine (0.20 g.) and 100% hydrazine hydrate (0.50 g., 12 mol.) were heated for 48 hr. in refluxing acetic acid (50 ml.), the unchanged diazocine (70%) was accompanied by 9 : 10-dimethylphenanthrene (23%). A similar mixture, irradiated by a 250w mercury-vapour lamp for 16 hr. at the b. p., gave 85% of unchanged diazocine and 11% of 9 : 10-dimethylphenanthrene.

(c) The diazocine (0.20 g.), after 24 hr. at 240° in diethylene glycol (25 ml.), was recovered (65%), together with 9 : 10-dimethylphenanthrene (6%). Under similar conditions, but with 100% hydrazine hydrate (2.5 mol.) also present, the recovery was 55% and the yield of hydrocarbon 23%.

(d) Heating the diazocine with hydrazine (1 mol.) in 5*N*-aqueous sulphuric acid gave only resins.

(e) Attempted hydrogenation with platinum or palladium catalyst at ordinary temperature and pressure gave unchanged diazocine as the only crystalline product. Only resins resulted from treatment with lithium aluminium hydride in ether at room temperature or with sodium amalgam and ethanol at 50°.

o-Iodopropiophenone.—A solution of diethyl ethoxymagnesiummethylmalonate was prepared from 0.5 g.-atom of magnesium and was treated by Bowman's procedure⁶ with *o*-iodobenzoyl chloride (0.37 mole). *o*-Iodopropiophenone was obtained (72%; b. p. 96°/0.3 mm., n_D^{25} 1.5978) (Found: C, 41.6; H, 3.5. C_9H_9OI requires C, 41.5; H, 3.5%). The derived azine crystallised from ethanol in colourless plates, m. p. 107.5° (Found: C, 41.6; H, 3.4; N, 5.3. $C_{18}H_{18}N_2I_2$ requires C, 41.85; H, 3.5; N, 5.4%).

2 : 2'-Dipropionylidiphenyl.—*o*-Iodopropiophenone (65 g., 0.25 mole) and copper bronze (50 g.) were heated for 2 hr. in refluxing dimethylformamide (80 ml.), and the product taken up in chloroform. Distillation yielded 2 : 2'-dipropionylidiphenyl (22 g., 66%), b. p. 122—123°/0.001 mm., n_D^{25} 1.5807 (Found: C, 81.3; H, 6.5. $C_{18}H_{18}O_2$ requires C, 81.2; H, 6.8%).

Reaction of 2 : 2'-Dipropionylidiphenyl with Hydrazine.—Procedures (a) and (b) below represent the best conditions so far found (see Table 2) for preparing the diazocine and 9 : 10-diethylphenanthrene respectively. Only unchanged diketone (84%) was found when reaction was attempted with 100% hydrazine hydrate and Raney nickel W-2 in boiling ethanol, as described by Balcom and Furst²⁵ for the reduction of nitro-compounds.

(a) A solution of 2 : 2'-dipropionylidiphenyl (1.00 g., 0.0038 mole) and 100% hydrazine hydrate (0.21 g., 0.0042 mole) in ethanol (75 ml.) was left for 3 days at room temperature. Solvent was removed under reduced pressure and the residue chromatographed with benzene on alumina, yielding colourless prisms of 3 : 8-diethyl-4 : 5-6 : 7-dibenzo-1 : 2-diazocine (0.70 g.,

²⁴ Bradsher and Amore, *J. Amer. Chem. Soc.*, 1944, **66**, 1280.

²⁵ Balcom and Furst, *ibid.*, 1953, **75**, 4334.

70%), m. p. 126.5°, unchanged by recrystallisation from hexane (Found: C, 82.3; H, 6.6; N, 10.8. $C_{18}H_{18}N_2$ requires C, 82.4; H, 6.9; N, 10.7%).

(b) Anhydrous hydrazine (2.0 g., 0.063 mole), prepared as described by Barton, Ives, and Thomas,⁹ in redistilled diethylene glycol (10 ml.) was added to 2 : 2'-dipropionyl-diphenyl (1.00 g.) in redistilled diethylene glycol (40 ml.), and the mixture refluxed for 2 hr. The solution

TABLE 2. Reaction of hydrazine and 2 : 2'-dipropionyl-diphenyl.

	Temp.	Time (hr.)	Medium *	Molar ratio, N_2H_4 : diketone	Diethylphenanthrene (yield %)	Diazocine (yield %)
(i)	15°	72	EtOH	1.1 : 1	0	71
(ii)	78	5	EtOH	3.2 : 1	0	55
(iii)	117	3	AcOH	3.2 : 1	0	39
(iv)	136	2	Et·CO ₂ H	1.3 : 1	0	42
(v)	180	2	Diethylene glycol (anhyd. N_2H_4)	16 : 1	31	48
(vi)	180	2	Diethylene glycol (anhyd. N_2H_4)	16 : 1	12	51

* 100% Hydrazine hydrate was used in (i)—(iv) and was added dropwise, in 10 ml. of solvent, in (ii)—(iv); the diketone, in 10 ml. of solvent, was added dropwise to the hydrazine solution in (vi).

was poured into water, the product extracted with ether, the solvent evaporated, and the residue chromatographed on alumina. 9 : 10-Diethylphenanthrene (0.27 g., 30%) was eluted with benzene and the diazocine (0.48 g., 48%) was eluted with ether. The 9 : 10-diethylphenanthrene had m. p. 103° when recrystallised from methanol; Zincke and Tropp² give m. p. 105—106° (Found: C, 92.3; H, 7.9. Calc. for $C_{18}H_{18}$: C, 92.3; H, 7.7%). Difficulty was experienced in preparing a picrate but the *styphnate* was obtained in orange needles, m. p. 155.5° from benzene-hexane (Found: C, 60.0; H, 4.3; N, 9.0. $C_{24}H_{21}O_8N_3$ requires C, 60.1; H, 4.4; N, 8.8%).

Stability of 3 : 8-Diethyl-4 : 5-6 : 7-dibenzo-1 : 2-diazocine.—A solution of the diazocine (200 mg., 0.76 mmole) and excess of 100% hydrazine hydrate (500 mg., 0.01 mole) in diethylene glycol (25 ml.) was kept for 24 hr. at 210°. Dilution with water, extraction with ether, and chromatography yielded unchanged diazocine (150 mg.) and 9 : 10-diethylphenanthrene (20 mg., 11%). In the same solvent, in 24 hr. at 240°, but without hydrazine, no hydrocarbon was obtained and 160 mg. of diazocine were recovered.

o-Iodobenzophenone.—*o*-Iodobenzoyl chloride (50 g.) in dry benzene (200 ml.) was gradually treated with powdered anhydrous aluminium chloride (28 g.), and the mixture refluxed for 2 hr. After hydrolysis of the complex, *o*-iodobenzophenone was obtained as a nearly colourless liquid (34 g., 59%), b. p. 143°/0.3 mm., which solidified and gave needles, m. p. 32.5°, from hexane (Found: C, 51.0; H, 3.0. Calc. for $C_{13}H_9OI$: C, 50.6; H, 2.9%); Montagne²⁶ gives b. p. 210—211°/13 mm., m. p. 32°.

2 : 2'-Dibenzoyldiphenyl.—*o*-Iodobenzophenone (20 g., 0.065 mole), copper bronze (18 g.), and dimethylformamide (40 ml.) were heated under reflux for 2 hr., the product was taken up in chloroform, the solvents were removed, and the solid residue was recrystallised from light petroleum (b. p. 100—120°), yielding 9.0 g. (76%) of 2 : 2'-dibenzoyldiphenyl in needles, m. p. 167°, raised to 171° by further recrystallisation from cyclohexane (Found: C, 86.1; H, 4.9. Calc. for $C_{26}H_{18}O_2$: C, 86.2; H, 5.0%); De Tar and Sagmanli²⁷ give m. p. 166.5—168°.

Reaction of 2 : 2'-Dibenzoyldiphenyl with Hydrazine.—Procedures (a) and (b) below represent the best conditions so far found (see Table 3) for converting the diketone into the diazocine and 9 : 10-diphenylphenanthrene respectively.

(a) 2 : 2'-Dibenzoyldiphenyl (0.50 g., 0.00138 mole) and 100% hydrazine hydrate (2.0 g., 0.04 mole) were heated in diethylene glycol (40 ml.) at 180° for 72 hr. The cooled solution was diluted with water and extracted with ether and the extract was chromatographed with benzene on alumina. 9 : 10-Diphenylphenanthrene (0.12 g., 26%) was obtained, followed by 3 : 8-diphenyl-4 : 5-6 : 7-dibenzo-1 : 2-diazocine (0.30 g., 60%), in colourless prisms, m. p. 228—229°, raised to 232° by recrystallisation from hexane (Found: C, 87.3; H, 5.0; N, 7.9. $C_{26}H_{18}N_2$ requires C, 87.2; H, 5.0; N, 7.8%).

(b) 2 : 2'-Dibenzoyldiphenyl (0.50 g.) and anhydrous hydrazine⁹ (2.0 g., 0.063 mole) in redistilled diethylene glycol (40 ml.) were kept at 180° for 48 hr. and the product was treated as in (a). 9 : 10-Diphenylphenanthrene was obtained as needles (0.39 g., 86%); m. p. 238°.

²⁶ Montagne, *Rec. Trav. chim.*, 1915, **34**, 156.

²⁷ DeTar and Sagmanli, *J. Amer. Chem. Soc.*, 1950, **72**, 965.

unchanged by recrystallisation from hexane (Found: C, 94.7; H, 5.2. Calc. for $C_{26}H_{18}$: C, 94.6; H, 5.4%); Schoepfle and Ryan²⁸ give m. p. 235°.

TABLE 3. Reaction of hydrazine and 2 : 2'-dibenzoyldiphenyl.

	Temp.	Time (hr.)	Conditions *	Mol. ratio, N_2H_4 : diketone	Diketone recovered (%)	Diphenyl-phenanthrene (yield %)	Diazocine (yield %)
(i)	78°	5	Boiling EtOH	1.3 : 1	97	0	0
(ii)	117	20	Boiling AcOH	1.5 : 1	98	0	0
(iii)	180	72	Diethylene glycol	30 : 1	0	26	60
(iv)	180	48	Diethylene glycol; anhyd. N_2H_4	45 : 1	0	86	0
(v)	200	24	EtOH; 100 ml. stainless-steel autoclave	2.6 : 1	58	9	0
(vi)	270—290	24	AcOH; 100 ml. stainless-steel autoclave	2.2 : 1	0	18	0
(vii)	200	6	AcOH; 100 ml. stainless-steel autoclave	7.2 : 1	0	22	0
(viii)	200	12	AcOH; sealed Pyrex tube	3.6 : 1	0	35	0
(ix)	280—290	5	AcOH; sealed Pyrex tube	3.6 : 1	0	29	0
(x)	200—230	6	AcOH; sealed Pyrex tube	7.2 : 1	44	20	0

* 100% Hydrazine hydrate was used except in (iv).

Spectra.—Ultraviolet absorption spectra (Fig. 1 and 2) were examined in a Unicam S.P. 500 quartz spectrometer, for solutions in *n*-hexane or cyclohexane. Infrared absorption spectra were examined in a Perkin-Elmer double-beam spectrometer, for 5% solutions in carbon disulphide and in carbon tetrachloride, and also for pressed potassium bromide discs. Strong peaks were recorded as follows: benzaldehyde azine, at 1630, 1580, 1496, 1451, 747, and 685 cm^{-1} ; acetophenone azine, at 1609, 1579, 1500, 1450, 1361, 754, and 686 cm^{-1} ; *o*-iodobenzaldehyde azine, at 1616, 1585, 1560, 1460, 1436, and 744 cm^{-1} ; *o*-iodoacetophenone azine, at 1626, 1434, 1363, and 753 cm^{-1} ; 3 : 8-dimethyl-4 : 5-6 : 7-dibenzo-1 : 2-diazocine, at 1628, 1435, 1371, and 746 cm^{-1} (weaker bands at 767, 760, 753, and 735 cm^{-1}); 3 : 8-diethyl-4 : 5-6 : 7-dibenzo-1 : 2-diazocine, at 1611, 1477, 1461, 1440, 1375, and 738 cm^{-1} (weaker bands at 767, 762, 753, and 744 cm^{-1}); 3 : 8-diphenyl-4 : 5-6 : 7-dibenzo-1 : 2-diazocine, at 1602, 1570, 1558, 1445, 743, and 683 cm^{-1} (weaker bands at 771, 762, 753, and 738 cm^{-1}).

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²⁸ Schoepfle and Ryan, *J. Amer. Chem. Soc.*, 1932, **54**, 3687.