[1939]

279. cis-Azo-compounds. Part II.

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An earlier preliminary study of the preparation of some cis-azo-compounds has been extended to the chromatographic separation and preparation of substituted azobenzenes, azonaphthalenes, and polyazo-compounds in labile cis-modifications. Most previous possible instances of such isomerism have another explanation than cis-trans isomerism, but the isomeric p-azophenols exhibit a phenomenon of a new type. The known electronic nature of the substituents is not sufficient to account for differences in lability observed among cis-azo-compounds although these differences are parallel to those observed among the diazo-cyanides. The azo-linkages in polyazo-compounds are capable of independent isomerisation to give more than one labile isomeride. Orientations of the isomerides of bisbenzeneazobenzene and bisbenzeneazodiphenyl are deduced.

IN Part I (J., 1938, 876) one of us showed that a solution of irradiated azobenzene could be easily resolved into *cis*- and *trans*-isomerides by the preferential adsorption of the former on a column of active alumina and the generality of this type of isomerism was indicated by the preparation of several substituted azobenzenes in *cis*-modifications. Shortly afterwards a similar separation was announced by Zechmeister and his co-workers (*Naturwiss.*, 1938, 26, 495). We now report the extension of this study to further substituted (methyl-, halogeno-, hydroxy-, methoxy-, and nitro-) azobenzenes, azonaphthalenes, and to bisazocompounds.

Although o-methylazobenzene could not be isomerised to a cis-form (the trans-modification is a low-melting oil), yet fresh preparations of the m-isomeride contained a considerable proportion of the cis-form. The compound termed "m-azotoluene" in Part I was o-azotoluene supplied in error by the manufacturer; these isomerides possess similar m. p.'s (54°, 56°) but the azoxy-compound of m. p. 59° previously isolated has now been

1310 Cook and Jones: cis-Azo-compounds. Part II.

shown to be identical with *trans-o*-azoxytoluene. Repeated experiments have confirmed the impossibility of isolating by the adsorption technique a *cis*-isomeride of *o*-azotoluene but *cis*-m-*azotoluene* was readily obtained by irradiation of the normal form although it was not so stable as the monomethyl compound. Both p-methyl- (as shown previously) and pp'-dimethyl-azobenzenes exhibit considerable stability in the *cis*-form.

Of the differences in stability among the isomerides under discussion the most remarkable were exhibited by the isomeric nitroazo-compounds :

Nitroazobenzene.	Stability.
o-, oo'-, pp'-	Isomerides not detected.
p-, mm'-	Normal stability.
m-	Very stable.

Normal stability indicated that the *cis*-isomeride reverted to the *trans*-form on standing for 1—2 days in absence of light or on gentle warming in a solvent. cis-m-*Nitroazobenzene* not only occurred in our crude preparations, from which it is removed by crystallisation, but when isolated by chromatographic means it remained unchanged after standing in petroleum solution in diffuse light for several days and only reverted to the normal *trans*-form (m. p. 95°) after melting (m. p. 70°) several times. As shown in the following paper, *cis-m*-nitroazobenzene shows an absorption spectrum with the finest structure of all *cis*-azo-compounds so far examined. The cis-mm'-*dinitroazobenzene* had an apparent m. p. which was somewhat lower (144°) than that of the *trans*-compound (150°) but it reverted to the more stable configuration on standing overnight. pp'-Dinitroazobenzene had previously been prepared (Meigen and Normann, *Ber.*, 1900, **33**, 2716) by the oxidation of p-nitro-aniline with sodium hypochlorite. By this procedure we obtained finally chlorinated azo- and azoxy-compounds, but pp'-dinitroazobenzene prepared by oxidising p-nitroaniline with potassium persulphate failed to isomerise on irradiation.

Particular interest is attached to the isomerism of pp'-dihydroxyazobenzene reported by Willstätter and Benz (Ber., 1906, 39, 3492; 1907, 40, 1578). Not only is the isomerism unexpected in view of the hitherto insuperable difficulty of obtaining a pure cis-p-benzeneazophenol, or indeed of any hydroxy- or amino-azo-compound, but if these forms of p-azophenol are really isomerides of this kind, then both are so stable that that having the cis-configuration is the most stable cis-azo-compound yet known. Willstätter and Benz record, for example, that each form is soluble in concentrated sulphuric acid and may be precipitated unchanged after a moderate interval, and Robertson indicates that their interconversion in alkali is even less readily effected than was supposed by Willstätter and Benz. Our experiments confirm the conversion of the β - into the α -compound at the fusion point, and we find that on subliming the hydrated forms in high vacuum $(170^{\circ}/0.002 \text{ mm.})$ only the anhydrous forms of the α -modification result. Similarly, both azophenols yield the same hydrated *picrate*, m. p. 183°. In their reluctance to undergo interconversion, α - and β -p-azophenols are quite unlike any authentic pair of cis-trans-azo-isomerides. We have re-examined the absorption spectra of the α - and β -hydrates and anhydrous forms and find no noticeable difference between the spectra of the hydrated and anhydrous forms of one series, and only minor differences between the α - and β -series both in the wave-length of the band-heads and in the extinction coefficients (Part III). However, our doubt of the *cis-trans* nature of the isomerides under discussion was strengthened by the fact that they preserved their spectroscopic individuality unchanged even after continuous irradiation in ultra-violet light for 24 hrs., whereas all authentic cis-azo-compounds have been prepared from the trans-compounds by exposure to light. We examined also the diacetates, claimed by Willstätter and Benz to be isomeric, without detecting any definite difference between them. The absorption bands are not sharp in light petroleum solution, but the maxima were at nearly the same wave-lengths, and the intensity of the main band (3310 A) of the "cis"compound increased to that of the "trans"-compound on crystallising, probably owing to the removal of non-absorbing impurity.

Since *cis-p*-benzeneazophenol is not so stable as its ethers, *cis-* and *trans-p*-azoanisoles should possess an even greater range of stability than the alleged isomeric azophenols, but methylation of both phenols, by means of methyl sulphate or even of diazomethane,

[1939] Cook and Jones: cis-Azo-compounds. Part II. 1311

yields the same dimethyl ether. This result was not, however, at once conclusive, because methylation of both isomerides with diazomethane was considerably slower than was expected even in the presence of small amounts of methanol which would assist the reversion of any *cis*-form to the more stable *trans*-isomeride. Although methylation proceeded still more slowly in the complete absence of methanol—an observation recalling the similar finding of Kuhn and Bär when methylating benzeneazo- β -naphthol (*Annalen*, 1935, 516, 143)—again only one dimethyl ether was obtained. On the other hand, this dimethyl ether isomerised normally on irradiation to give what must be regarded as an authentic cis-*pazoanisole* with the expected instability. It was shown by chromatographic analysis that none of the products of direct methylation of the isomeric azophenols contained any detectable proportion of the true *cis*-azoanisole. Although the physical and chemical evidence therefore does not of itself exclude the possibility of Willstätter's isomerides being related as *cis*- and *trans*-modifications, yet comparison with a large number of other azo-compounds, including *p*-benzeneazophenol and azoanisoles most of which have been obtained in *cis*forms, indicates that α - and β -*p*-azophenols represent a phenomenon of another type.

Attempts to prepare further pairs of isomeric pp'-azophenols (e.g., 4:4'-dihydroxybenzeneazo- α -naphthalene) through quinoneazines were unsuccessful. We were unable to find any difference, as claimed by Willstätter and Benz (*Ber.*, 1906, **39**, **3501**), between normal *o*-azophenol and that which had been distilled in a vacuum, and we find the reported isomerides of phenolazophloroglucinol (Weselsky and Benedikt, *Ber.*, 1879, **12**, 227) to be physical and not stereoisomerides.

A number of methyl ethers of azophenols (2:4- and 2:6-dimethoxyazobenzene, benzeneazo- α -naphthyl and substituted benzeneazo- β -naphthyl methyl ethers) were obtained in cis-*modifications*. These *cis*-methyl ethers present no marked differences in stability among themselves, although it is noteworthy that, whereas *cis*-azobenzene is more stable than most of its *cis*-substituted derivatives (*e.g.*, those containing methyl or methoxyl groups), yet in the benzeneazonaphthalene and azonaphthalene series the *cis*azo-hydrocarbons are too unstable to be isolated but usually their methoxyl derivatives (*e.g.*, benzeneazo- α -naphthyl methyl ether) are comparatively stable in the *cis*-form and only rarely (as with the β -naphthyl ether) is this form unobtainable. Even in such cases a single *o*-substituent (*o*-iodo-) in the benzene ring was able to stabilise the *cis*-form.

In Part I (*loc. cit.*) the isomerisation of p-chloroazobenzene to an oily *cis*-isomeride was described. This, as well as the p-*bromo*- and p-*iodo*-compounds have now been obtained in crystalline *cis*-modifications which revert to the more stable *trans*-form on heating. The three *cis*-*p*-halogenoazobenzenes form a series of increasing stability, the iodo-compound remaining substantially unchanged after 2 weeks in absence of light. We have not systematically examined dihalogenated azobenzenes, but in one attempt to prepare *oo*'-di-iodoazobenzene by reducing *o*-iodonitrobenzene with sodium stannite, a product of the composition of oo'-*di*-*iodoazoxybenzene* was isolated which on further mild reduction with sodium amalgam was converted into unsubstituted azobenzene.

The *cis*-configuration of all the new modifications here described is based on analogy with previous examples and on the fact that all revert with ease to the *trans*-modification on melting. A rigid proof of the configuration assigned awaits the determination of their dipole moments. In inert solvents they are stable at room temperature and in absence of light for periods varying from a few hours (as with the *cis-cis*-form of bisbenzeneazobenzene; p. 1312) to at least several weeks (as with p-iodo- and p-bromo-azobenzenes). In one or two instances (m-nitroazobenzene) only slight illumination is needed to establish the cis-trans-equilibrium in the solid form, and appreciable quantities of the cis-modification may be obtained directly from crude or old preparations by the selective adsorption process. Although the increasing stability of the p-halogenoazobenzenes in passing from the chloroto the iodo-compound might be due to the decreasing op-directing effect of the halogen atoms, the azo-compounds so far obtained in cis-forms provide several instances which are contrary to such a simple conception (e.g., cis-m-nitroazobenzene, so far from being less stable in the *cis*-form than azobenzene, is one of the most stable *cis*-azo-compounds yet prepared); further, any such electronic explanation does not make it apparent why, when a single substituent will sometimes stabilise a *cis*-form, two such substituents

symmetrically placed will frequently make it impossible to isolate a *cis*-modification. Clearly, there are superposed on these direct electronic effects further factors which remain obscure, but it is noteworthy that Hantzsch found similar differences in stability among the normal and *iso*-diazocyanides which are regarded as *cis-trans*-isomerides.

All the compounds so far discussed possess one azo-linkage. For ordinary azobenzene the trans-configuration is now established (Robertson et al., Proc. Roy. Soc., 1936, A, 154, 187; cf. this vol., p. 232) and appears to be the normally stable orientation of the C·N:N·C group. To bisbenzeneazobenzene therefore is ascribed a *trans-trans-configuration*. two other (cis-trans- and cis-cis-) isomerides, (I) and (II), being envisaged, if the azo-linkages



are capable of independent isomerisation. It is now found that when an irradiated solution of bisbenzeneazobenzene (which gives only one adsorption band on alumina before irradiation) is filtered through alumina the primary result is the rapid elimination of unchanged *trans-trans-compound* from the chromatogram, after which the strongly adsorbed fraction develops two adsorption zones. The uppermost of these yields upon elution a product which melts at 136°, thereby reverting to the normal form, m. p. 166°, as does also the product from the intermediate band, but the individuality of these isomerides is shown, not only by their chromatographic behaviour, but also by their absorption spectra (in light petroleum). The uppermost compound was allowed to revert spontaneously into the *trans-trans*-modification, and repeated chromatographic analyses of the product failed to reveal the spontaneous production of the third isomeride. On the other hand, the original intermediate band was eluted and kept overnight in benzene-petroleum solution in the dark. The greater part of the isomeride under these conditions undergoes conversion into normal bisbenzeneazobenzene but on being again passed through the alumina, the solution afforded three adsorption zones clearly separated on a chromatogram exactly like that obtained by chromatographing a freshly irradiated solution of bisbenzeneazobenzene. The intermediate production of the most firmly adsorbed isomeride by the partial reversion of that initially adsorbed in the intermediate band is very strong evidence that the intermediate band corresponds to *cis-cis-* and the topmost band to *cis-trans*bisbenzeneazobenzene.

When irradiated in petroleum solution and then analysed chromatographically, 4:4'bisbenzeneazodiphenyl behaved in a manner exactly simulating bisbenzeneazobenzene to give two labile isomerides again distinguished by their absorption spectra. The normal compound is produced from these isomerides when attempts are made to determine characteristic m. p.'s. Exactly analogous observations to those made on bisbenzeneazobenzene indicate the *cis-trans*-orientation for the topmost adsorption band and the cis-cis- for the intermediate one.

4:4'-Bis(benzeneazo)azobenzene (III) when similarly treated gave indication of the

formation of at least one isomeride in chloroform soluh tion, less readily in benzene-petroleum, but these experiments were not pursued further because of the increasing number of stereochemical possibilities (five forms are

theoretically possible).

Although analogous independence of the double bonds in $\alpha\omega$ -diphenylpolyenes has not been confirmed by isolation of stereoisomerides ("Stereochemie," Freudenberg, 1933, 915; cf. Kuhn, Ber., 1938, 71, 1889) the behaviour of diphenyl-hexatriene and -octatetraene on a chromatographic column after irradiation in benzene-petroleum solution (less satisfactory in carbon disulphide) indicates the formation of labile (cis-) isomerides.

EXPERIMENTAL.

Except where otherwise stated, all the separations were effected by irradiating a solution of the trans-compound (which had been chromatographically purified) in Pyrex glassware at ca. 12" from a mercury vapour lamp and then again passing it through a column of active alumina (usually 15–20 cm. \times 1 cm. diameter). In every case in which a *cis*-isomeride has been obtained there is a noticeable deepening in colour after irradiation, and this form is very much more firmly adsorbed than the trans-, which can usually be readily washed out of the column, thus effecting complete separation of the isomerides. In most cases it was preferable to separate the cis-isomeride at intervals of 30-45 mins. rather than continue the irradiation, as the conversion trans \rightarrow cis seldom exceeds 10% even after prolonged periods. Elution was effected by adding a little alcohol to a suspension of the isolated alumina band in the same solvent as that in which the original adsorption was effected, and the filtered solution was freed from alcohol as quickly as possible by washing with water. The dried solution was then concentrated in a vacuum at 20-25°, and the cis-compound purified by crystallisation, usually from petroleum or petroleum-benzene, at a low temperature. All operations subsequent to the adsorption were performed as far as possible in absence of light. The cis-compounds, when they differed in appearance from their trans-isomerides were darker in colour, but pairs of isomerides always gave identical colours when dissolved in concentrated sulphuric acid.

cis-m-Methylazobenzene.—2 G. of the oily trans-isomeride (Jacobsen, Ber., 1895, 28, 2544) in petroleum solution were irradiated (45 mins.) and chromatographed. The chromatogram, after being washed with 50 c.c. of petroleum, contained material firmly adsorbed as a light orange band. Elution afforded cis-m-methylazobenzene as a red oil (Found : N, 14.3. $C_{13}H_{12}N_2$ requires N, 14.3%).

o-Methylazobenzene failed to isomerise under similar conditions even after $2\frac{1}{2}$ hrs.' irradiation.

cis-m-Azotoluene, prepared from the *trans*-isomeride (Buchka and Schachtebeck, Ber., 1889, **22**, 835) (1 g. in 50 c.c. of light petroleum ether), was obtained as a red oil (Found : N, 13·3. $C_{14}H_{14}N_2$ requires N, 13·3%).

cis-m-Nitroazobenzene.—0.2 G. of a fresh sample of the trans-isomeride (Bamberger and Hübner, Ber., 1903, 36, 3818), dissolved in 150 c.c. of light petroleum, was filtered through a column of alumina, and the chromatogram washed with petroleum. The firmly adsorbed material on elution gave red crystals which had m. p. 72°, 82°, 85° in successive determinations and were identical with the *cis*-form isolated by repeatedly irradiating the original filtrate, adsorbing the *cis*-compound at intervals by chromatographic filtration, and working up the united products of several irradiations. The cis-compound separated from a concentrated petroleum solution in red crystals (Found : N, 18·3. $C_{12}H_9O_2N_3$ requires N, 18·5%), m. p. 70° rising to 94—95° after melting several times (mixed m. p. with the original *trans*-compound : before reversion, 89—91°; after reversion, 96°). The *cis*-compound is considerably darker in colour in petroleum than the *trans*-modification, and the latter, when chromatographically pure, is lighter than the normal preparation. The *cis*-compound remained substantially unchanged after standing in the light in petroleum solution for 3 days.

cis-mm'-Dinitroazobenzene.—The trans-variety was best prepared by adding a concentrated solution of *m*-nitronitrosobenzene in glacial acetic acid to an equivalent amount of *m*-nitroaniline in the same solvent; the azo-compound separates after 2 hrs. at room temperature, m. p. 150°, and is free from the *cis*-form. 0.2 G. in 45 c.c. of benzene-petroleum (2:1) was repeatedly irradiated (30 mins.) to give the cis-isomeride in the usual way, m. p. 144° (Found : N, 20.3. $C_{12}H_8O_4N_4$ requires N, 20.6%). The compound reverted to the stable form on standing overnight.

cis-p-Nitroazobenzene.—0.2 G. of the trans-compound (Bamberger and Hübner, loc. cit.) in 150 c.c. of light petroleum was repeatedly irradiated, giving dark orange crystals of the ciscompound, m. p. 128° (Found : N, 18.5. $C_{12}H_9O_2N_3$ requires N, 18.5%).

Oxidation of p-Nitroaniline with Sodium Hypochlorite (cf. Meigen and Normann, Ber., 1900, 33, 2716).—13 G. of p-nitroaniline in 700 c.c. of benzene were stirred for 2.5 hrs. with 500 c.c. of sodium hypochlorite solution (100 g. of sodium hydroxide, 71 g. of chlorine, 1000 c.c. of water). The red crystalline mass obtained on evaporating the benzene layer was extracted with a little boiling acetic acid, leaving a residue, m. p. 263°; m. p. after crystallisation from benzene, 222°. The filtrate deposited small red plates, m. p. 223°, which after two filtrations through alumina had m. p. 165°; the m. p. rose on repeated crystallisation from benzene to 267° (Found : Cl, 33·1; M, cryoscopic in camphor, 383. $C_{12}H_4O_5N_4Cl_4$, tetrachloro-4 : 4'-dinitroazoxybenzene, requires Cl, 33·3%; M, 426). The acetic acid mother-liquor from the crystallisation of the

1314 Cook and Jones: cis-Azo-compounds. Part II.

substance, m. p. 223°, on dilution with water yielded 2:6-dichloro-4-nitroaniline, m. p. 191° (Found : Cl, 33.9. Calc. for $C_6H_4O_2N_2Cl_2$: Cl, 34.3%). If the solution was stirred for a shorter time, the benzene solution on evaporating and cooling deposited red-brown plates of 2:2'dichloro-4: 4'-dinitroazobenzene, m. p. 265° (Green and Rowe, J., 1907, 101, 2451); the motherliquor on further evaporation gave brown crystals, m. p. 140° rising to 144° after crystallisation from benzene (Found : Cl, 19.92; M, cryoscopic in camphor, 340. Calc. for $C_{12}H_6O_5N_4Cl_2$, dichloro-4: 4'-dinitroazoxybenzene: Cl, 19.94%; M, 356). trans-pp'-Dinitroazobenzene was prepared (cf. Witt and Kopetschni, Ber., 1912, 45, 1134) by dissolving 5 g. of p-nitroaniline in 12.5 c.c. of concentrated sulphuric acid, diluting to 55 c.c. with water and adding 20 g. of potassium persulphate in small portions at 60–70°. After 1 hr., the brown precipitate was collected, recrystallised from glacial acetic acid (yield 3 g.), and then several times from toluene or xylene; m. p. 214-216°. There was no detectable difference between the chromatograms of irradiated and unirradiated solutions in benzene or chloroform.

 α - and β -p-Azophenol hydrates (Willstätter and Benz, loc. cit.) yielded the α -compound on fusion and gave the same picrate (brown plates from methanol, m. p. 183°) (Found : C, 47.06; H, 3.43. C₁₂H₁₀O₂N₂,C₆H₃O₇N₃,H₂O requires C, 46.9; H, 3.25%). Distillation of both compounds at $170^{\circ}/0.002$ mm. yielded a mixture of green and orange forms of the anhydrous α -azophenol which were separated mechanically and showed identical absorption spectra. Both azophenols were acetylated to substantially the same diacetyl compound (" cis ", crude m. p. 187-190°, once recrystallised, 194°; "trans", m. p. 196°).

trans-p-Azoanisole was produced by methylating α - or β -azophenol with methyl sulphate or diazomethane; it formed yellow needles from alcohol, m. p. 158°. Reaction in dry ether free from alcohol was slow (e.g., the phenol was recovered unchanged after standing with diazomethane for 16 hrs.) but methylation was complete after 4 days.

cis-p-Azoanisole.—500 Mg. of the trans-ether in 300 c.c. of light petroleum were irradiated (30 mins.), chromatographed, the chromatogram developed with petroleum--benzene (4:1), and the cis-isomeride eluted with benzene (38 mg. from two irradiations). The compound reverts to the *trans*-variety on heating and has no characteristic m. p. (Found : N, 11.45. $C_{14}H_{14}O_2N_2$ requires N, 11.6%).

o-Azophenol (Willstätter and Benz, loc. cit.) was unchanged after distillation (140°/0.001 mm.). 2 G. of it in 9 c.c. of 10% sodium hydroxide, treated with 5 c.c. of methyl sulphate, gave orange-red needles, m. p. 110°, from methanol, of o-azophenol monomethyl ether (Found : C, 68.3; H, 5.7. $C_{13}H_{12}O_2N_2$ requires C, 68.3; H, 5.7%), and a suspension of this in alkali, on treatment with excess of methyl sulphate and warming, afforded the dimethyl ether, m. p. 153°. This was unaffected by irradiation.

4-Hydroxybenzeneazophloroglucinol (Weselsky and Benedikt, Ber., 1879, 12, 227) was obtained in a red form when precipitated rapidly from methanol-water, and in a green-black form with a greenish lustre when it separated slowly from methanol. Both forms gave the same tetramethyl ether with diazomethane; m. p. 118° from methanol (Found : N, 9.4. $C_{16}H_{18}O_4N_2$ requires N, 9.3%).

cis-2: 4-Dimethoxyazobenzene.—The diphenolic compound yielded with diazomethane only the 2-hydroxy-4-methoxy-compound, m. p. 115°, which was unsuitable for chromatographic examination; the dimethyl ether was only obtained by using excess of methyl sulphate, m. p. 91°. The cis-dimethoxy-compound was obtained from benzene-petroleum (1:1) in the usual way (Found : N, 11.7. C₁₄H₁₄O₂N₂ requires N, 11.6%).

The 2:6-dimethoxy-compound was obtained similarly (Found: N, 11.67%). Both these cis-compounds were obtained as red oils solidifying after 2 days to the trans-isomeride.

cis-Benzeneazo- α -naphthyl Methyl Ether.—0.3 G. of the trans-compound was irradiated, and the cis-modification isolated in the usual way, m. p. 70° (Found: N, 10.5. C17H14ON2 requires N, 10.7%). No isomerisation of trans-benzeneazo- β -naphthyl methyl ether was detected. The following two substituted benzeneazo- β -naphthyl methyl ethers gave labile isomerides. (i) o-Iodoaniline (3 g.) was diazotised, and coupled with β -naphthol in alkaline solution. The free o-iodobenzeneazo- β -naphthol crystallised from 100–120 c.c. of glacial acetic acid in small red needles, m. p. 176° (Found : I, 34·1. C₁₆H₁₁ON₂I requires I, 33·9%). 2 G. of the hydroxycompound were shaken with 30 g. of methyl sulphate and 100 c.c. of 30% sodium hydroxide to give a red-brown oil which soon solidified to bright red needles, m. p. 94° after crystallising from methanol, of trans-0-iodobenzeneazo- β -naphthyl methyl ether (Found : I, 32.8. $C_{17}H_{13}ON_2I$ requires I, 32.7%). (ii) 1-Nitroso-2-methylnaphthalene was reduced to 1-amino-2-methylnaphthalene, diazotised, and coupled with β -naphthol (cf. Lesser, Annalen, 1913, 402, 41). 2 G. of the azo-compound were dissolved in a little acetone and methylated as in (i). The red-

[1939] cis-Azo-compounds. Part III. Absorption Spectra. 1315

brown oil was extracted with petroleum, the extract filtered through alumina, and then evaporated to yield 2-methoxy-2'-methyl- α -azonaphthalene, m. p. 72° (from petroleum) (Found : N, 8.8. $C_{22}H_{18}ON_2$ requires N, 8.6%).

cis-p-Chloroazobenzene, previously obtained as an oil (J., 1938, 876), has now been obtained in crystalline form, m. p. 32°. trans-p-Bromoazobenzene, m. p. 82° (Noelting and Werner, Ber., 1890, 23, 3254), was converted in the usual way in petroleum solution into cis-p-bromoazobenzene, a dark red oil solidifying after 2 hrs., m. p. 39° (Found : N, 10.96. $C_{12}H_9N_2Br$ requires N, 10.75%). cis-p-Iodoazobenzene, m. p. 62°, was obtained in exactly the same manner from the trans-compound (Willgerodt and Smith, Ber., 1904, 37, 1311), and reverted to this on melting 2 or 3 times (Found : N, 8.9. $C_{12}H_9N_2I$ requires N, 9.1%). The last two cis-compounds are unusually firmly adsorbed on alumina relative to the trans-forms, and both are abnormally stable under ordinary conditions. cis-p-Iodoazobenzene contained no chromatographically detectable amount of the trans-variety after the solid had stood for 2 weeks in absence of light.

oo'-Di-iodoazozybenzene.—5 G. of o-iodonitrobenzene, dissolved in 50 c.c. of acetone, were quickly treated with an aqueous solution of sodium stannite (prepared from 6.2 g. of stannous chloride and 3.2 g. of sodium hydroxide), and the solution, which quickly became violet, was refluxed for 45 mins. The crystalline precipitate was filtered off, washed successively with sodium hydroxide, dilute hydrochloric acid, and water, and recrystallised from acetone, forming small, light orange cubes, m. p. 148° (1.2 g.) (Found: I, 56.4. $C_{12}H_8ON_2I_2$ requires I, 56.4%); the same *product* was obtained with larger amounts of stannite. 200 Mg. in a little acetone diluted with 30 c.c. of alcohol were reduced with 6 g. of 4% sodium amalgam. After 1 hr. the solution was decanted, any hydrazo-compound oxidised with a few drops of hydrogen peroxide, and the solution diluted with water and extracted with 50 c.c. of petroleum. Evaporation yielded orange crystals which, recrystallised from methanol-water, proved to be azobenzene (m. p. and mixed m. p., 67°).

cis-cis- and cis-trans-Bisbenzeneazobenzenes.—0.5 G. of normal bisbenzeneazobenzene in 100 c.c. of petroleum-benzene (4:1) was irradiated for 45 mins., adsorbed on alumina, the column repeatedly washed with 200 c.c. of the same solvent, and then with 75 c.c. of petroleumbenzene (1:1). The chromatogram then had a topmost band (2 cm., deep orange), an intermediate zone (1 cm., light orange), and a third zone of unchanged material. Normal working-up yielded from the topmost zone cis-trans-bisbenzeneazobenzene (orientation, see p. 1312), m. p. 136° (Found : N, 19.4. $C_{18}H_{14}N_4$ requires N, 19.6%). The intermediate zone contained the *ciscis*-isomeride.

Irradiated 4:4'-bis(benzeneazo)azobenzene [0·1 g. in 25 c.c. of chloroform or benzenepetroleum (1:1)] likewise gave a band of very strongly adsorbed material, but no further separation was observed. Material recovered from this zone had a m. p. identical with that of the starting material.

4: 4'-Bisbenzeneazodiphenyl was conveniently prepared (cf. *Ber.*, 1896, 29, 103; J., 1895, 67, 925) by adding 5 g. of benzidine in 40 c.c. of acetic acid to 8.5 g. of nitrosobenzene in 25 c.c. of acetic acid. The pure compound was filtered off after 1 hr. (yield, 8 g., m. p. 224°). cis-cisand cis-trans-*Bisbenzeneazodiphenyls* (Found : N, 15.3. $C_{24}H_{18}N_4$ requires N, 15.5%), which revert to the *trans-trans*-variety on melting, were obtained in the same way as the corresponding bisbenzeneazobenzenes.

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