40. cis-*Azo-compounds. Part IV. Some Reactions with Diphenylketen.*

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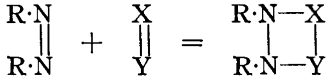
cis- and *trans*-Azo-compounds have been shown to be sharply differentiated in their behaviour towards diphenylketen. The *cis*-forms react immediately at room temperature, whereas the same adducts are obtained from *trans*-isomerides only at high temperatures. The adducts are dimethylenedi-imine derivatives. The reactions with *cis*- and *trans*-*p*-chlorobenzenediazocyanide are also described.

In Parts I—III (III, J., 1939, 1315) the preparation of hitherto unknown isomerides of numerous azo-compounds by the chromatographing of irradiated solutions of the normal forms was described. The labile isomeride of azobenzene had been shown to have the *cis*-structure and, by analogy, the other isomerides were regarded as *cis*-isomerides of the normal *trans*-compounds; their ultra-violet absorption spectra confirmed this relationship. We then sought to differentiate the isomerides chemically.

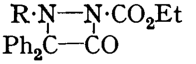
Hartley (J., 1938, 642) mentions the unexpected behaviour of *cis*-azobenzene in concentrated hydrochloric acid, but this did not provide the significant differentiation we were seeking. Oxidation of *cis*-azobenzene by the well-known method of Angeli with hydrogen peroxide in acetic acid was investigated, but reaction was slow at temperatures sufficiently low to preclude prior reversion to the *trans*-azo-compound; consequently the only product was normal and not *cis* azoxy-benzene. Again the addition of sulphite or an aromatic sulphinic acid (Hantzsch and Glogauer, *Ber.*, 1897, **30**, 2548) to the azo-group was of doubtful value, since the double linking is destroyed and the product would have afforded no clue to the configuration of the initial azo-compound. Attention was therefore turned to addition reactions of the type:



$$\begin{array}{c}R\cdot N\\ \|\\ R\cdot N\end{array} + \begin{array}{c}X\\ \|\\ Y\end{array} = \begin{array}{c}R\cdot N-X\\ \;\;|\quad\;\; |\\ R\cdot N-Y\end{array}$$

Here the *cis*-modification with a configuration approximating to that about to be assumed in the final adduct would be expected to react more rapidly than the *trans*-form.

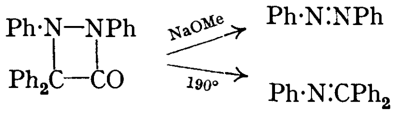
Experiments to add (*a*) maleic anhydride, (*b*) diazoacetic ester, or (*c*) *as.*-diphenylethylene to *cis*- and *trans*-azo-compounds under conditions where these configurations would be retained were without useful result. Diazoacetic ester (Müller, *Ber.*, 1914, **47**, 3001) and diphenylethylene (Ingold and Weaver, J., 1925, **127**, 378) react readily with azodicarboxylic ester to give cyclic adducts, but do not react under mild conditions with purely aromatic *cis*- or *trans*-azo-compounds. More satisfactory was the reaction with diphenylketen. Staudinger ("Die Ketene," 1912, p. 91) mentions that reaction between diphenylketen and azo-compounds had been observed when they were heated together at 150° for several hours. Neither the preparative methods nor the products are described in any detail. Ingold and Weaver (*loc. cit.*) later obtained products from diphenylketen and azodicarboxylic ester or phenylazocarboxylic ester and showed that the adducts with one molecule of each of the reactants contained four-membered rings (I). We confirmed Staudinger's brief report and obtained a small amount of an *adduct* from *trans*-azobenzene and diphenylketen only after heating at 125—130° for 24 hours. However, when *cis*-azobenzene was added to diphenylketen at room temperature, reaction was vigorous with evolution of much heat. Even in light petroleum solution at room temperature reaction was rapid and the colour of the solution faded almost instantaneously. The product was the same as that obtained from the *trans*-isomeride at a high temperature. Irradiation of a light petroleum solution of *trans*-azobenzene containing diphenylketen provided a third and more convenient route to the same compound; clearly the *cis*-isomeride reacts immediately it is formed by irradiation.



$$\begin{array}{l}R\cdot N-N\cdot CO_2Et\\ \;\;|\qquad |\\ Ph_2C-CO\end{array}$$

(I, R = CO_2Et or Ph.)

Analysis showed that this product contained one molecule of each of the reactants. The adduct was stable to cold alcoholic alkali, but on warming with a dilute solution of sodium methoxide an excellent yield of azobenzene was obtained. At temperatures below its melting point (175°) the adduct was indefinitely stable, but at a slightly higher temperature decomposition occurred and by sublimation in a vacuum azobenzene and benzophenoneanil were obtained. These facts indicated a dimethylenedi-imine structure for the adduct (II) as envisaged by Staudinger; this structure is similar to that of the compounds obtained by Ingold and Weaver. Exactly similar adducts were obtained from *m*- and



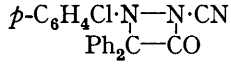
$$\begin{array}{l}Ph\cdot N-NPh\\ \quad\;\; |\qquad |\\ Ph_2C-CO\end{array} \begin{array}{l}\xrightarrow{NaOMe} Ph\cdot N{:}NPh\\ \xrightarrow[190°]{} Ph\cdot N{:}CPh_2\end{array}$$

(II.)

p-azotoluene. As before, when the *cis*-form was used, addition was rapid at room temperature, whereas when the *trans*-compound was used, high temperature was necessary; irradiation of the *trans*-form with diphenylketen again provided a convenient route to the same adducts.

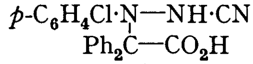
Failure to isolate some *cis*-azo-compounds must, at least in some cases, mean that reversion to the *trans*-form is so rapid as to make isolation impossible; it is not surprising, therefore, that some such compounds (*o*-azotoluene, azonaphthalenes) yielded keten adducts by irradiation of solutions of the reactants as readily as those compounds which afforded more stable *cis*-modifications. On the other hand, the remarkable reactivity of such new azo-forms as have been isolated is regarded as very strong evidence of their *cis*-structure. It is unfortunate that this differentiating addition reaction cannot be used with all azo-compounds without involving further complications. Diphenylketen reacts with the substituent group of, for example, amino- and hydroxy-azo-compounds which cannot be examined by the chromatographic method. Thus *p*-aminoazobenzene yielded p-*diphenylacetamidoazobenzene*, so that examination by this means of the ability of aminoazobenzene to assume a *cis*-configuration is impossible.

This very great difference in reactivity suggested that other pairs of compounds containing *cis*- and *trans*-N : N linkages might show similar differences. *cis*- and *trans*-*p*-Chlorobenzenediazocyanide (Le Fèvre and Vine, J., 1938, 436) both reacted readily with diphenylketen in light petroleum; the same colourless *adduct*, m. p. 121°, was obtained from both compounds, although on one occasion the *cis*-cyanide afforded an isomeric adduct, m. p. 266°. These are provisionally regarded as the dimethylenedi-imine compounds formed by addition across the azo-linkage. The "normal" compound, m. p. 121°, is, in conformity with Ingold and Weaver's compounds, formulated as (III). Mild treatment with caustic alkali converted it into the *acid* (IV) (cf. Ingold and Weaver, *loc. cit.*); the latter was, however, unlike Ingold and Weaver's compound, not recyclised by treatment with acetyl chloride but was converted into another compound the nature of which was not fully investigated; it was not the acid chloride of (IV) or its *N*-acetyl derivative. The similar behaviour of the *cis*- and *trans*-cyanides indicates that the present differentiation between *cis*- and *trans*-azo-isomerides is to be expected only among otherwise unreactive aromatic azo-compounds.



$$\begin{array}{c} p\text{-}C_6H_4Cl\cdot N—N\cdot CN \\ Ph_2C—CO \end{array}$$

(III.)



$$\begin{array}{c} p\text{-}C_6H_4Cl\cdot N—NH\cdot CN \\ Ph_2C—CO_2H \end{array}$$

(IV.)

EXPERIMENTAL.

4-*Keto*-1 : 2 : 3 : 3-*tetraphenyldimethylene*-1 : 2-*di-imine*.—(*a*) *trans*-Azobenzene (4 g.) was heated with diphenylketen (5 g.) in an atmosphere of carbon dioxide at 125—130° for 42 hours. The dark melt was digested with light petroleum, and the residual orange oil stirred with methanol. The pale yellow *adduct*, recrystallised from ethyl acetate, formed white needles (1·4 g.), m. p. 175° (Found : N, 7·6. $C_{26}H_{20}ON_2$ requires N, 7·5%). (*b*) *cis*-Azobenzene (0·5 g.) was treated with diphenylketen (0·6 g.) in light petroleum. The mixture reacted rapidly, but was kept overnight; the product, identical with that obtained in (*a*), was then filtered off and crystallised from ethyl acetate (0·4 g.). (*c*) Equimolecular quantities of diphenylketen and *trans*-azobenzene in light petroleum were irradiated before a mercury vapour lamp until the solution was bleached to pale yellow, The yellow oil which had separated was stirred with methanol; the adduct, identical with that obtained in (*a*) and (*b*), then solidified.

(i) The adduct (1 g.) was refluxed with 10% sodium methoxide in methanol (90 c.c.). After 30 minutes the solution was diluted with water and extracted with ether to give *trans*-azobenzene (0·32 g.). (ii) The adduct (0·3 g.) was heated at 190° for 1 hour. When the residual oil was heated at 60°/0·002 mm., large crystals of *trans*-azobenzene sublimed. At 100°/0·002 mm. benzophenoneanil, m. p. 112°, sublimed and was identified by mixed melting point.

4-*Keto*-3 : 3-*diphenyl*-1 : 2-*di*-o-*tolyldimethylene*-1 : 2-*di-imine*.—*o*-Azotoluene (1 g.) and diphenylketen (1·1 g.) in pure light petroleum were irradiated overnight before a mercury vapour lamp in an atmosphere of carbon dioxide. The white crystalline precipitate was recrystallised from ethyl acetate to give soft white needles (0·8 g.), m. p. 162° (Found : N, 7·2. $C_{28}H_{24}ON_2$ requires N, 7·0%).

4-*Keto*-3 : 3-*diphenyl*-1 : 2-*di*-m-*tolyldimethylene*-1 : 2-*di-imine*.—*cis*-*m*-Azotoluene (0·4 g.) and diphenylketen (0·6 g.) were mixed in light petroleum solution : the colour faded almost immediately. The petroleum was evaporated, and the residual oil dissolved in the minimum quantity of methanol. On standing, the *di-imine* was deposited; it was recrystallised from ethyl acetate (0·15 g.), m. p. 118° (Found : N, 7·1. $C_{28}H_{24}ON_2$ requires N, 7·0%). The same compound (0·75 g.) was obtained by irradiating *trans*-*m*-azotoluene (0·5 g.) with diphenylketen (0·6 g.) in light petroleum or, in very small yield, by heating the reactants in absence of solvent.

4-*Keto*-3 : 3-*diphenyl*-1 : 2-*di*-p-*tolyldimethylene*-1 : 2-*di-imine*.—*cis*-*p*-Azotoluene (0·3 g.) and diphenylketen (0·4 g.) were mixed in light petroleum. Reaction was rapid and a part (50 mg.) of the product separated at once. A further 0·5 g. was obtained by evaporating the mother-liquor and cooling the residue. The *di-imine* crystallised from ethyl acetate in white needles, m. p. 172° (Found : N, 7·1. $C_{28}H_{24}ON_2$ requires N, 7·0%). The same compound (0·1 g.) was obtained by irradiating *trans*-azotoluene (0·5 g.) and diphenylketen in light petroleum.

4-*Keto*-3 : 3-*diphenyl*-1 : 2-*di*-β-*naphthyldimethylene*-1 : 2-*di-imine*.—β-Azonaphthalene (0·5 g.) in 20 c.c. of benzene–light petroleum was treated with diphenylketen (0·4 g.), and the solution irradiated overnight. More petroleum was then added, precipitating a light yellow granular solid. The *di-imine* recrystallised from ethyl acetate in small colourless cubes (75 mg.), m. p. 222° (Found : N, 5·7. $C_{34}H_{24}ON_2$ requires N, 5·9%).

p-*Diphenylacetamidoazobenzene*.—*p*-Aminoazobenzene was treated with an equal weight of diphenylketen in benzene. After 12 hours, the solid was filtered off and recrystallised from benzene, forming light yellow-brown plates, m. p. 194° (Found : N, 10·4. $C_{26}H_{21}ON_3$ requires N, 10·6%). The same compound was obtained from *p*-aminoazobenzene and diphenylacetyl chloride.

4-*Keto*-1-*cyano*-2-p-*chlorophenyl*-3 : 3-*diphenyldimethylene*-1 : 2-*di-imine*. — *cis*-*p*-Chlorobenzenediazocyanide (1 g.) in light petroleum (15 c.c.) was added to diphenylketen (1 g.), also in light petroleum. Most of the colour was discharged at once and scratching caused the *di-imine* to separate (1·5 g.). Recrystallised from ethanol, it formed needles, m. p. 121° (Found : N, 11·4. $C_{21}H_{14}ON_3Cl$ requires N, 11·7%). When *trans*-*p*-chlorobenzenediazocyanide and diphenylketen were treated in the same manner, reaction was slower; small white needles began to separate after 30 minutes and the colour was practically discharged after 2 days. The product was identical with that obtained from the *cis*-cyanide. On one occasion the *cis*-cyanide afforded a product (Found : N, 11·8%), which crystallised from ethanol in white needles, m. p. 266°, but this preparation could not be repeated. The di-imine (1 g.), m. p. 121°, was refluxed for 1 hour with ethanol (20 c.c.) and 10% aqueous sodium hydroxide (5 c.c.). The solution was acidified, and the oil so obtained extracted with chloroform. The extract was dried and on evaporation deposited white cubes of α-β′-*cyano*-α′-p-*chlorophenylhydrazinodiphenylacetic acid*; this crystallised from ethanol in small white prisms, m. p. 288° (decomp.) (Found : N, 11·5. $C_{21}H_{16}O_2N_3Cl$ requires N, 11·5%). The compound was soluble in cold alkali, but no ammonia was evolved on short boiling.

We thank Prof. I. M. Heilbron for advice and encouragement and the Chemical Society for a grant.

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[*Received, January 1st*, 1941.]