

### 195. *The Mechanism of Some Addition Reactions of Nitroethylenes.*

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IN the course of work carried out at Knoevenagel's suggestion, one of us (*J. pr. Chem.*, 1902, **66**, 16) found that 2-bromo-2-nitro-1-*p*-nitrophenylethylene,  $\text{O}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CBr}\cdot\text{NO}_2$ , undergoes partial addition, at its double bond, of a molecule of alcohol on mere recrystallisation from this solvent. The corresponding *o*-nitro-compound reacted similarly, though less readily, whereas 2-nitro-1-*p*-nitrophenylethylene, 2-nitro-1-phenylethylene, and 2-bromo-1-phenylethylene showed no addition even on prolonged boiling with alcohol. The reaction therefore appeared to require the presence of a tertiary nitro-group which, through its oxygen, would initiate a Thiele 1 : 4-addition:  $\text{R}\cdot\text{CH}:\text{CX}\cdot\text{NO}_2 \rightarrow \text{R}\cdot\text{CH}(\text{Oalk})\cdot\text{CX}\cdot\text{NO}\cdot\text{OH} \rightarrow \text{R}\cdot\text{CH}(\text{Oalk})\cdot\text{CHX}\cdot\text{NO}_2$  (compare the addition of hydrogen to  $:\text{CH}\cdot\text{CO}\cdot$ ; Thiele, *Annalen*, 1899, **306**, 87), and it was suggested that the failure of a secondary nitro-group to react similarly might

be explained by attributing to it the bridged formula  $\begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{N} \cdot \text{OH} \end{array}$ . More recent observations (J., 1928, 453 \* and unpublished work) appear to support the assumption of the presence of a bridged form of "true" primary and secondary nitro-compounds, at any rate in solution, but only in equilibrium with their  $\text{NO}_2$ -form. It follows that the complete refusal of secondary nitroethylenes to add alcohol can no longer be ascribed to a different formulation.

It seemed therefore desirable to obtain more extended and more quantitative information concerning this reaction, and to correlate it on a more general basis. Since 1905, one of us has attempted to interpret reactivity as a function of three constitutional factors, *viz.*, an "electropolar" and a "steric" factor, and a "quantitative" factor causing an alternating distribution of chemical force within the molecule; and this view appears to have been accepted fairly generally—often with an electronic interpretation of the factors. A similar treatment of the varying reactivity of nitroethylenes presents no difficulty. Our experimental results (see table) show that, out of fourteen nitroethylenes, only three have a pronounced tendency to add alcohol; and that the eleven which—whether in the dark or in diffuse daylight—show little or no additivity include nitroethylenes with tertiary as well as secondary nitro-groups, and *cis*- as well as the corresponding *trans*-forms. Obviously, therefore, the different behaviour of these sets of compounds cannot be attributed either to the constitution of the nitro-groups or to the configuration of the ethylenic groups. It appears, however, that the following mechanism, in conjunction with the three above-mentioned factors, can account for all the facts.

(1) *The Mechanism of the Reaction.*—This consists, we suggest, of a slow initial 1 : 4-addition of alcohol to yield an *isonitro*-compound, followed by two competing rapid reactions, *viz.*, reversal of the addition, whereby the nitroethylene is regenerated, and stabilisation of the addition product by rearrangement of its *isonitro*-form to

\* The paper cited above dealt with the nitration of phenylbromocyanonitromethane. Some of the theoretical conclusions therein have been subjected to criticism by Baker and Ingold (J., 1929, 423), to which we have not yet replied because one of us (E. L. H.) had to take up other work early in 1929 and no other co-worker has been available. But since in their contribution—which is largely a repetition of ours as regards both the use of our methods and the restatement of our quantitative results—these authors lay great stress on the only two discrepancies from our experimental data which they claim to have observed, we take this first opportunity to state that we have repeated these two experiments and fully confirmed our own results. That Baker and Ingold's earlier similar allegation (J., 1926, 2465) was also incorrect, has been proved by us (*loc. cit.*) and tacitly admitted in their later paper.

the "true" nitroethoxyethane derivative. The following observations may be cited in support :

(a) 2-Nitro-2-phenyl-1-*p*-methoxyphenylethylene, on prolonged boiling with alcohol, reacts only to a very slight extent; its alcohol addition product, on similar treatment with alcohol, shows no detectable change. The reaction is therefore virtually irreversible as between the initial and the final products.

(b) An aqueous alkaline solution of the *iso*-form of the above alcohol addition product, on treatment with an excess of hydrochloric acid, deposits chiefly the corresponding nitroethylene. This *iso*-form is therefore capable of a very rapid separation of alcohol.

(c) This is caused neither by ionisation of the *iso*-form, since its ion, *e.g.*, in an aqueous alkaline solution, is stable, nor by rearrangement to the "true" form and action thereon of hydrogen ions, since the "true" form, dissolved in alcoholic hydrogen chloride, is also stable. It is therefore the un-ionised *iso*-compound which is responsible for the rapid loss of alcohol. This is confirmed by the fact that precipitation by carbon dioxide instead of hydrochloric acid largely prevents this separation of alcohol (compare analogous observations by Meisenheimer, *Annalen*, 1907, **355**, 249; Rosenmund, *Ber.*, 1913, **46**, 1034; Heim, *Ber.*, 1911, **44**, 2013). For it is known that solutions of the salts of isonitroparaffins tend to separate the *iso*-form in the presence of a strong acid, and the "true" form on addition of a weak acid, obviously because a lower concentration of hydrogen ions allows more time for a direct rearrangement of the anion (compare Knorr, *Ber.*, 1895, **28**, 706; *Annalen*, 1896, **293**, 1; Wislicenus, *Ahrens Sammlung*, 1897, II, 187; Lapworth, J., 1898, **73**, 445; J., 1901, **79**, 1265, for tautomeric anions = "prototropy"; and Flürscheim, J., 1910, **97**, 84, for tautomeric kations = "anionotropy") from its *iso*- to its "true" form before the un-ionised form can accumulate. In other words, the conditions which tend to produce the un-ionised *iso*-form and those which tend to cause separation of alcohol are identical. Further confirmation is supplied by our observation that 2-bromo-2-nitro-1-*p*-nitrophenylethylene forms an alcohol addition product which can be precipitated from its alkaline solution by means of hydrochloric acid without separating alcohol, whereas this is not the case when *p*-nitrophenyl has taken the place of bromine. The bromo-compound having a relatively acidic nitro-group, its *iso*-form must exhibit a higher degree of electrolytic dissociation.

That the "true" alcohol addition product is stable in alcohol, though it might be expected to be in equilibrium with its *iso*-form, is not really surprising. A rough computation, based on all relevant

kinetic and conductivity data on nitro- and *isonitro*-compounds and their mutual transitions, shows that in experiment No. 22 (see table) the amount of nitroethylene produced by rearrangement to the un-ionised *iso*-form and separation of alcohol therefrom should theoretically be of the order of only a fraction of 1%. This implies, incidentally, that in the absence of any obvious change in analogous cases it must not necessarily be assumed, with Kohler and Stone (*J. Amer. Chem. Soc.*, 1930, **52**, 761), that solutions of "true" nitro-compounds do not contain any *iso*-form whatsoever produced by spontaneous isomerisation.

(2) *The Effect of the Three Factors.*—(a) *The quantitative (alternating) factor* affects the rates of addition and separation of alcohol in the same direction. Thus a 1-*p*-methoxy-group (No. 15), through an alternating transmission of the quantitative effect, lowers the amount of available affinity at the  $\alpha$ -carbon (whereby the mobility of the alkoxy-radical, leading to separation of alcohol, is enhanced), but increases it at the oxygen of the  $\beta$ -nitro-group (whereby addition of hydrogen, resulting in addition of alcohol, is facilitated); and a 1-*p*-nitro-group does the reverse. Actually, the resulting rates of addition are found for Nos. 15 and 7 to be of the same order (slight addition).

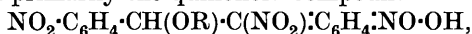
(b) *The steric effect* of a *cis*- or *o*-group in retarding addition is, similarly, partly counteracted, since it also inhibits the reverse reaction by enhancing the degree of ionisation of the *iso*-form. The resulting change of 2-bromo-2-nitro-1-*o*-nitrophenylethylene (*loc. cit.*), though slower than for the *p*-isomeride, is still of the same order (pronounced addition), and the changes of *cis-trans*-isomerides (Nos. 9 and 10; 12 and 16) are also of the same order (slight addition).

(c) *The electropolar factor*, on the other hand, is decisive in this reaction. An acidic substituent near the nitro-group (the reverse applies to a basic group) not only facilitates addition by enhancing the degree of polar affinity of the nitro-oxygen\* for the alcohol-hydrogen, but also inhibits separation of alcohol by increasing the degree of ionisation of the *iso*-form. The observed rate of addition follows, indeed, the order of electropolarities of the substituents

\* It has of course long been recognised (compare especially Michael, *J. pr. Chem.*, 1888, **37**, 473; 1899, **60**, 286; also Flürscheim, *Ber.*, 1906, **39**, 2015; Loevenich and Gerber, *Ber.*, 1930, **63**, 636) that "negative" substituents inhibit the addition of a "negative" reagent, and vice versa. It must be pointed out, however, that in any particular phase of an addition this electropolar effect of a given substituent depends on its relative electrochemical nature and position with regard to the individual atoms which actually interact in such phase, *e.g.*, oxygen and hydrogen in our initial addition phase.

immediately adjacent to the nitro-group : \* Br (pronounced addition) > *m*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub> (slight addition) > H, CH<sub>3</sub> (no addition).

(3) *The Reactivity of 2-Nitro-1 : 2-di-p-nitrophenylethylene*.—This reactivity, which is pronounced, though the three factors should cause it to rank with the slight additive capacity of the *m*-nitro-compounds Nos. 5 and 6, is explained by our mechanism. This substance alone can add alcohol in another way, *viz.*, in positions 1 : 8, to yield primarily the quinonoid compound



from which alcohol should not separate readily, if at all. A much faster initial addition in positions 1 : 8 than 1 : 4 seems less likely, since, contrary to the rapid isomerisation of phenylnitromethane by strong alkaline agents, *p*-nitrotriphenylmethane (Hantzsch and Hein, *Ber.*, 1919, 52, 493) is only slowly transformed into its (quinonoid) salt.

(4) *Addition Reactions of Nitroethylenes with Other Compounds containing Mobile Hydrogen (or Metal)*.—Such additions, *e.g.*, with alkali alkoxides or with ammonia and amines (see Loevenich and Gerber, *loc. cit.*), may also be interpreted by the above mechanism. In the latter cases the addition compound is formed much more rapidly, not merely because the initial addition occurs more readily (some amines, unlike alcohol, combine even with 1-bromo-2-phenylethylene, though much more slowly than with 1-bromo-1-nitro-2-phenylethylene), but also because the inverse reaction is inhibited through stabilisation of the undissociated *isonitro*-form by salt formation.

The preparation of some new nitroethylenes, and observations on *cis-trans*-rearrangements, including the formation of the hitherto unknown stereoisomeride of *p*-methoxynitrostilbene, are described below.

#### EXPERIMENTAL.

*2-Nitro-1-phenyl-2-m-nitrophenylethylene*.—0.9 G. of *m*-nitrophenylnitromethane, 0.53 g. of benzaldehyde, and 0.3 c.c. of a 33.33% solution of methylamine in alcohol (general method of Knoevenagel and Walter, *Ber.*, 1904, 37, 4502) were left for 24 hours. The product solidified when rubbed with alcohol and a

\* The ready addition of alcohol to *m*- and *p*-nitro- $\alpha$ -nitrocinnamic esters (Friedländer and Mähly, *Annalen*, 1885, 229, 210) appears to be the only other recorded case of an alcohol addition to nitroethylenes in the absence of alkali, and agrees with the above sequence. Remembering, however, the ready addition of alcohol to acraldehyde in the absence of alkali (Newbury and Chamot, *Amer. Chem. J.*, 1890, 12, 521), the possibility is not excluded that in the nitrocinnamic esters hydrogen may primarily attach itself, not to a nitro-group activated by carbonyl, but to carbonyl activated by a nitro-group.

little sulphuric acid, and separated from benzene-petrol in almost colourless crystals (0.263 g.), m. p. 179—180° (Found: N, 10.6.  $C_{14}H_{10}O_4N_2$  requires N, 10.4%).

*2-Nitro-1-p-nitrophenyl-2-m-nitrophenylethylene.*—1.82 G. of *m*-nitrophenylnitromethane, 1.51 g. of *p*-nitrobenzaldehyde, and 0.3 c.c. of a 33.33% solution of methylamine in alcohol were heated on a water-bath to complete solution, then left for 24 hours at room temperature. The product was washed with alcohol and repeatedly crystallised from toluene, forming chamois-coloured crystals, m. p. 236—237° (Found: N, 13.6.  $C_{14}H_9O_6N_3$  requires N, 13.3%).

*2-Nitro-1:2-di-p-nitrophenylethylene.*—From a mixture of the dinitro-compounds obtained by nitration of 2-nitro-2-phenyl-1-*p*-nitrophenylethylene essentially according to Baker and Wilson (J., 1927, 842), the *pp'*-dinitro-compound was obtained by repeated crystallisation from ethyl acetate. It formed pale greenish-yellow crystals, m. p. 210.5—211°, and its constitution was proved by oxidising 0.400 g. with permanganate, whereby 0.359 g. of *p*-nitrobenzoic acid, m. p. 233—235°, was obtained (Found: N, 13.5.  $C_{14}H_9O_6N_3$  requires N, 13.3%).

*Stereoisomeric 2-Nitro-2-phenyl-1-p-methoxyphenylethylene.*—A solution of 0.5 g. of the known greenish form (m. p. 151.5—152°) in 500 c.c. of alcohol was allowed to evaporate spontaneously in direct sunlight. The residue of brown crystals, m. p. 105—108°, which were much more soluble in organic solvents than the initial material, separated from petroleum (b. p. 60—80°) in fine brownish-orange needles, m. p. 112—113°. A slight admixture of the greenish form depressed the melting point (Found: N, 5.4, 5.7.  $C_{15}H_{13}O_3N$  requires N, 5.5%).

*2-Nitro-1-ethoxy-2-phenyl-1-p-methoxyphenylethane.*—The above *p*-methoxy-derivative, m. p. 151.5—152°, was dissolved in warm absolute alcohol (30 parts), potassium hydroxide (slight excess of 1 mol.) added, and the solution immediately and rapidly cooled; it was then diluted with much water (it should remain clear) and treated in an open vessel with a rapid current of carbon dioxide until no further precipitation occurred (3—4 hours). The pale yellow deposit (yield, about 80%; m. p. about 93—100° after drying at 70—75°) contained about 25% of regenerated initial material, which was eliminated by fractional crystallisation from petroleum (b. p. 60—80°). The alcohol addition compound was thus obtained entirely colourless and with the constant m. p. 107.5—108° (Found: N, 4.8.  $C_{17}H_{19}O_4N$  requires N, 4.65%).

Samples of 2-nitro-2-phenyl-1-(3':4'-methylenedioxyphenyl)-ethylene (piperonylidenephenylnitromethane), 2-nitro-1-(3':4'-methylenedioxyphenyl)-2-methylethylene (piperonylidene-nitro-

ethane), and 2-nitro-1-phenyl-2-methylethylene (benzylidenenitroethane) had been kindly given to one of us in 1902 by Prof. Knoevenagel and Dr. Walter; the remaining compounds were prepared according to the literature.

*Alcohol Additions.*—These are tabulated below. Several additions, corresponding to Nos. 4, 10, and 13 and not included in the table, were performed with commercial absolute alcohol, but resulted in appreciable hydrolysis at the ethylenic bond; from the *p*-methoxy-derivative, for instance, some anisaldehyde was thus produced. With alcohol dried by magnesium amalgam, used in Nos. 9, 10, and 13, hydrolysis still occurred in traces, so that the relative weights of (alkali-soluble) addition product obtained are in these cases too high by a fraction of 1% (admixture of phenylnitromethane). In all the remaining additions, calcium-dried alcohol was used. The solutions were 0.1*N*, excepting with the most rapidly reacting compounds (Nos. 2 and 3; 0.05*N*) and with the less soluble substances (Nos. 4, 5, and 6; 70, 60, and 70 c.c. of alcohol, respectively). They were boiled with careful exclusion of moisture—Nos. 16 and 9 to 13 in the dark, the remainder in diffuse daylight—and the alcohol was then evaporated in a vacuum. The addition product was separated from unchanged material by exhaustive extraction of the solid with cold 10% aqueous potassium hydroxide, blank tests having shown that the tertiary nitroethylenes were insoluble therein. This was then filtered, whereafter the clear alkaline solution was acidified with hydrochloric acid and extracted with ether. For calculating the percentage of addition compound formed, there were available the constant weights (obtained by drying at 80°) of the portions soluble and insoluble in alkali and also, as an approximate control only, of the material before treatment with alkali (giving the weight of added alcohol, calculation from which of the molecular percentage involved multiplying the experimental error up to seven times). The fact that the alkali-soluble portions actually consisted of the alcohol-addition compounds also where any increase in weight was too small to be reliably detected, was conclusively proved for Nos. 11, 12, and 16 where the nitroethylenes regenerated from the alkaline solutions of the addition compounds by precipitation with mineral acid were identified (see below). The purity of the alkali-insoluble portions and their identity with unchanged initial material were always checked by m. p. and mixed m. p. determinations. The great tendency of the *pp'*-dinitro-derivative (No. 4) to add alcohol was confirmed by three further, but only approximate, determinations; thus, at about 78° in a stoppered bottle, over 70% was added in 22½ hours. In the tables, the compounds are given in the order of

decreasing reactivity, those being bracketed together which belong to one of the three groups: I = 40 to 100% mol. addition in 7 hours; II = >0, <6%; III = 0%. In No. 6 the experimental error was large owing to the small amount available; it should add alcohol a little more readily than No. 5.

No.	Compound used.	Wt., g.	Hours boiling.	Increase in wt., g.	KOH-soluble, g.	KOH-insoluble, g.	Addition, mol. %.
1	$p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CH:CH:Br}\cdot\text{NO}_2$	0.273	7	—	all	0	100
2		0.100	0.66	0.009	0.070	0.040	60
3	$\text{C}_6\text{H}_5\text{-CH:CH:Br}\cdot\text{NO}_2$	0.458	0.66	0.015	0.080	0.394	14
4	$p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CH:CH:C(NO}_2\text{)-C}_6\text{H}_4\text{-NO}_2(p)$	0.202	7	0.012	0.08	0.120	40
5	$\text{C}_6\text{H}_5\text{-CH:CH:C(NO}_2\text{)-C}_6\text{H}_4\text{-NO}_2(m)$	0.204	7	0.002	0.011	0.195	~5
6	$p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CH:CH:C(NO}_2\text{)-C}_6\text{H}_4\text{-NO}_2(m)$	0.062	7	—	0.001	0.060	>2 <6
7	$p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CH:C(NO}_2\text{)-C}_6\text{H}_5$	0.270	7	—	0.004	—	~2
8		0.540	8	—	—	0.527	~2
9	$\text{C}_6\text{H}_5\text{-CH:CH:C(NO}_2\text{)-C}_6\text{H}_5$ m. p. 126.5—127.5°	0.1562	5.25	—	0.0019	—	~1
10	$\text{C}_6\text{H}_5\text{-CH:CH:C(NO}_2\text{)-C}_6\text{H}_5$ m. p. 73.5—74°	0.1480	5.83	—	0.0011	—	~1
11		0.900	50	—	0.040	0.856	4.5
12	$p\text{-OMe-C}_6\text{H}_4\text{-CH:CH:C(NO}_2\text{)-C}_6\text{H}_5$ m. p. 112—113°	0.500	50	—	0.017	0.472	4.5
13	$p\text{-OMe-C}_6\text{H}_4\text{-CH:CH:C(NO}_2\text{)-C}_6\text{H}_5$ m. p. 151.5—152°	0.4478	6	—	0.0061	—	~1
14	"	0.510	8	—	—	0.504	~1
15	"	0.510	7	—	0.003	0.506	~1
16	"	0.510	50	—	0.015	0.489	3.5
17	$(mp)\text{-H}_2\text{C(O)}\text{C}_6\text{H}_5\text{-CH:CH:C(NO}_2\text{)-C}_6\text{H}_5$	0.214	7	—	pptd. with bromine	0.211	~1
18	$\text{C}_6\text{H}_5\text{-CH:CH:C(NO}_2\text{)-CH}_3$	0.213	7	—	0	—	0
19	$(mp)\text{-H}_2\text{C(O)}\text{C}_6\text{H}_5\text{-CH:CH:C(NO}_2\text{)-CH}_3$	0.163	7	—	0	—	0
20	$\text{C}_6\text{H}_5\text{-CH:CH-NO}_2$	0.300	7	unchanged	(m. p., mixed m. p.)	0	0
21	$p\text{-OMe-C}_6\text{H}_4\text{-CH(OMe)-CH(NO}_2\text{)-C}_6\text{H}_5$	0.0197	3.66	"	"	"	"
22	$p\text{-OMe-C}_6\text{H}_4\text{-CH(OEt)-CH(NO}_2\text{)-C}_6\text{H}_5$	0.0433	7	"	"	"	"

Alcohol Separations.—(a) Stability of alcohol addition products in boiling alcohol. See table, Nos. 21 and 22, wherein 4.8 and 2.5 g., respectively, of alcohol (dried by magnesium amalgam) were used.

(b) Stability of alcohol addition products on dry heating. The compound No. 21 in the table, obtained according to Meisenheimer (*loc. cit.*) by treatment of No. 13 with potassium hydroxide in methyl alcohol, was heated to its melting point (138.5—139°), then allowed to solidify, and heated again. The melting point remained unchanged. Our corresponding ethyl alcohol derivative (No. 22) also showed no change in its melting point when heated at 78° for 2½ hours.

(c) Stability of alcohol addition products towards hydrogen ions. 0.01 G. of compound No. 22, dissolved in 0.88 g. of alcohol and 0.06 g. of concentrated hydrochloric acid, was kept at about 12° for 4 days and, after evaporation of the alcohol at room temperature, was washed with a little water. The melting point was unchanged.

(d) Varying instability of the iso-forms of alcohol addition products when liberated from their salts. Aqueous alkaline solutions remained clear, showing that no alcohol had separated. On introducing acids, the following observations were made: (1) A solution of the



methyl alcohol addition compound (No. 21) in aqueous potassium hydroxide was treated with an excess of hydrochloric acid. The precipitate was the corresponding nitroethylene, almost pure (m. p. 143—150° instead of 151.5—152°). (2) 0.5 G. of the same nitroethylene was shaken with 3 c.c. of ethyl alcohol and 3 c.c. of 10% aqueous potassium hydroxide until all was dissolved. To one-half of this solution was added 1 c.c. of concentrated hydrochloric acid in 6 c.c. of water, whereby the initial material (m. p. 149—151°) was precipitated; the other half was diluted with 10 c.c. of water and treated with a current of carbon dioxide for  $\frac{1}{2}$  hour, giving a precipitate, m. p. 92—98°, which consisted essentially of the ethyl alcohol addition compound, m. p. 107.5—108° (compare its preparation). (3) After the prolonged action of alcohol (No. 16) on the same nitroethylene, precipitation of the alkali-soluble addition compound by hydrochloric acid again yielded the initial material (m. p. 145—150°, after pressing on a porous plate; mixed m. p.). (4) Similarly, precipitation by hydrochloric acid of the alkaline solution of the addition compound from the prolonged action of alcohol on  $\alpha$ -nitrostilbene (No. 11) gave the initial material (m. p. 68—71°, after pressing on a porous plate; mixed m. p.). (5) On the other hand, the alcohol addition compound from 2-bromo-2-nitro-1-*p*-nitrophenylethylene (No. 1) (compare 1902 paper), when dissolved in cold 10% aqueous potassium hydroxide and precipitated by hydrochloric acid, was recovered as such, no nitroethylene being regenerated. (6) An intermediate position between compounds Nos. 16 and 11 on the one hand, and No. 1 on the other, is occupied by the *pp'* $\alpha$ -trinitro-derivative (No. 4), since both the alcohol addition compound and the regenerated nitroethylene were obtained in substantial proportions when alkaline solutions of the former were precipitated by hydrochloric acid; these proportions varied, of course, with varying concentrations of the ingredients.

*cis-trans-Rearrangements.*—(a) *2-Nitro-2-phenyl-1-p-methoxyphenylethylenes.* The change of the higher- into the lower-melting form has been described above. The reverse transition occurs when the lower-melting form is subjected to prolonged boiling in alcohol in the dark, since in No. 12 the alkali-insoluble portion had m. p. 119—134° (mixed m. p. with lower-melting form 105—117°, with higher 130—144°). This change was also observed when the nitroethylene was regenerated from the alcohol addition product of the form of m. p. 112—113° by means of hydrochloric acid, whereupon it melted, after recrystallisation from petroleum (b. p. 120—140°), at 150—152° (mixed m. p.). When precipitated from the alkali-soluble portion in No. 12, it melted at 143—148° (mixed m. p.). Similarly, on dissolving 0.50 g. of the isomeride, m. p. 112—113°,

in 5 c.c. of a 4% solution of potassium hydroxide in methyl alcohol at 22°, removing the alcohol in a vacuum, adding water (whereupon the solution remained clear), and passing in a current of carbon dioxide for 3 hours, then repeatedly extracting the filtered precipitate with cold 10% aqueous potassium hydroxide, there remained undissolved 0.056 g. of the higher-melting form (m. p. 148—151°; mixed m. p.). The alkaline extract, on renewed treatment with carbon dioxide, gave 0.430 g. of a precipitate, m. p. 123—127°, which after recrystallisation from little methyl alcohol had the constant m. p. 138.5—139° and was identical (mixed m. p.) with the methyl alcohol addition product from the higher-melting form. The latter, on exactly similar treatment, gave products with virtually identical melting points and weights (0.054 and 0.440 g.). This form, m. p. 151.5—152°, showed no sign of isomerisation when a solution of 0.1 g. in 60 c.c. of alcohol was kept in the dark at room temperature (m. p. unaltered) or was boiled for a long time in the dark (m. p. of alkali-insoluble portion in No. 16 unaltered). The form, m. p. 112—113°, after being left in benzene with a trace of iodine in the dark for 48 hours, had m. p. 144—146° (mixed m. p. with form of m. p. 151.5—152°). (Concerning the effect of iodine in benzene, in certain other cases, compare Rice, *J. Amer. Chem. Soc.*, 1926, **48**, 269.) The isomeride, m. p. 151.5—152°, remained unchanged in diffuse light with a trace of iodine in benzene during 4½ hours, but in direct sunlight two samples, simultaneously exposed for 2½ hours in benzene, with and without iodine, both had their melting points lowered to 146—149° (drops visible from about 100°). Obviously the higher-melting, less coloured form is in this case by far the more stable.

(b) *2-Nitro-1:2-diphenylethylenes*. Here it is the *lower-melting* form which is less coloured and produced in much the greater proportion by synthetical methods, though neither isomeride exhibits any pronounced tendency to pass into the other. Thus after boiling with alcohol in the dark (Nos. 10 and 11), and in a further experiment in which boiling was performed for 7 hours in diffuse daylight, the alkali-insoluble portion consisted of the unaltered lower-melting form; and after boiling in the dark (No. 9), the higher-melting isomeride was similarly recovered as such. When solutions of each compound in ether had been simultaneously exposed to direct sunlight for 1½ hours, the melting points had fallen to 120—125° (drops visible from 105°) and to 65—71° (drops from 62°), and in each case, after recrystallisation from petroleum (b. p. <60°), crystals of the other isomeride could be detected. Similar slight isomerisations of *both* forms also occur at elevated temperatures (see Heim, *Ber.*, 1911, **44**, 2016). In the experiments

with the other nitroethylenes, the melting points of the alkali-insoluble portions showed that no isomerisations had occurred.

This work was mainly carried out in 1926 and 1927 at the Davy Faraday Laboratory of the Royal Institution. We desire to express our obligation to Sir W. H. Bragg and the Royal Institution, who have placed the facilities of the laboratory at our disposal; also to the Advisory Council of the Department of Scientific and Industrial Research and to the Government Grants Committee of the Royal Society for grants to one of us (E. L. H.).

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