31. *The Action of Cuprous Oxide on Diazotised Amines. Part II. Reactions in Solutions of Various Alcohols and Organic Solvents. Preparation of* 1 : 6-*Dinitronaphthalene.*

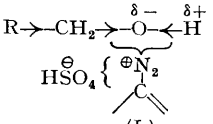
By Herbert H. Hodgson and Harold S. Turner.

1 : 6-Dinitro-2-naphthylamine has been diazotised by an inverted Hodgson–Walker procedure, and the diazo-solution decomposed by a suspension of cuprous oxide in a series of alcohols and other organic solvents, whereby the deamination utility of the combination, which is greatly superior to that of either component separately, has been determined. The efficiency of deamination is found to be quite regular from the standpoint of electronic theory, but in a large number of cases, particularly for the more anionoid alcohols, an appreciable induction period occurs before a rapid decomposition, which suggests a two-stage reaction, *viz.*, initial formation of a complex between organic solvent and diazonium salt, followed by decomposition facilitated by the cuprous oxide. An improved method is described for the preparation of 1 : 6-dinitronaphthalene.

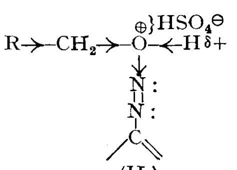
Previous work by the authors (J., **1942**, 748) on the action of cuprous oxide on diazotised amines in ethyl-alcoholic solution has been extended to an examination of the utility of a series of alcohols and other solvents in deamination. As it was necessary to use one amine with a number of solvents, choice was made of 1 : 6-dinitro-2-naphthylamine because the 1 : 6-dinitronaphthalene formed in the reaction was a high-melting solid which could be isolated without loss owing to secondary reactions in the deamination medium, and, moreover, large amounts of it were required for another investigation. For this purpose 1 : 6-dinitro-*p*-toluenesulphon-2-naphthalide was hydrolysed by concentrated sulphuric acid (cf. Bell, J., **1929**, 2784) and the amine diazotised by an inverted Hodgson and Walker procedure (J., **1933**, 1620), the diazo-solution being then poured into a suspension of cuprous oxide in the organic solvent (cf. Hodgson and H. S. Turner, *loc. cit.*).

It has long been known that the facility or otherwise of deamination is related to the electronic character of the nuclear substituents of the diazotised amines, and now the present experiments with alcohols and other solvents have revealed an additional powerful effect which is dependent on the nature of the groups attached to the α-carbon atom of the alcohol employed. The percentage yields of 1 : 6-dinitronaphthalene are here shown in parentheses after the relevant alcohol: β-chloroethyl (69·5), methyl (60·2), *iso*propyl (59·7), ethyl (57·6), *iso*butyl (51·2), ethylene glycol (48·3), *n*-propyl (40·6), *n*-butyl (30·0). This order differs from the more limited one given by Hodgson and Kershaw (J., **1930**, 2784) for the decomposition of benzenediazonium sulphate by aliphatic alcohols, when the sequence (based on formation of aldehyde) was ethyl > *iso*propyl > *n*-propyl > *iso*butyl > *n*-butyl > methyl (from which no formaldehyde was produced), by the fact that methyl alcohol now takes its correct place, *iso*propyl alcohol exchanges places with ethyl alcohol, and the positions of *iso*butyl and *n*-propyl alcohol are reversed.

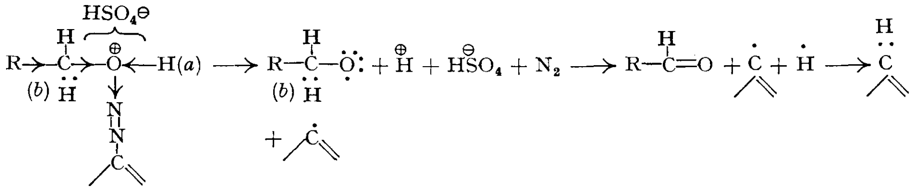
The mechanism of the reaction described for the simpler reaction of alcohols with a diazonium salt (cf. Hodgson, *J. Soc. Dyers Col.*, **1931**, **47**, 93) has now to be modified slightly to account for the combined reactivity of alcohol and cuprous oxide. It is assumed that there is initially complex formation between the alcohol and the diazonium salt, in which the union may be purely electrostatic (I) or dative (II). That such union occurs, follows from a noteworthy feature of the present series of experiments in which a period of induction precedes evolution of nitrogen. This period of induction is appreciable for all the alcohols except β-chloroethyl, methyl, and ethyl, and for ethylene glycol, as well as for the other ketonic and ester media in which decompositions have been investigated. In these cases, the addition of the diazo-solution to the medium in which the cuprous oxide is suspended, is not attended by an immediate evolution of nitrogen, but by the formation of a deep brownish-red solution (*i.e.*, an indication that the complex has a dative union with an ephemeral diazo-oxide structure) and only a very gradual rise of temperature. After induction periods which increase from *iso*propyl to *n*-butyl alcohol, the colour of the solution changes to yellow (diazonium-salt formation) and a rapid reaction commences quite suddenly with rise of temperature. Consideration of the following scheme indicates that the next stage of the reaction is the ionisation of hydrogen (*a*), which will depend upon the inductive effect of the alkyl group. In the case of β-chloroethyl alcohol, the chlorine with its $-I$ inductive effect will assist in the ionisation of hydrogen (*a*), whereas the alkyl groups with their $+I$ effects will tend to prevent it.



(I.)



(II.)



The experimental order found above for the effects of the alkyl groups in the alcohols is more regular than the order showing group influence upon the strengths of the corresponding aliphatic acids (cf. Dippy, *Chem. Rev.*, **1939**, **25**, 188 *et seq.*) which is methyl > *iso*butyl > *iso*propyl > *n*-butyl > ethyl, although here also, methyl > *iso*propyl > ethyl. After the ionisation of hydrogen (*a*), with release of electron to the oxygen, follows the rupture of the diazo-radical with evolution of nitrogen, and simultaneous formation of the aryl radical ⪢C· and separation of atomic hydrogen ·H at (*b*), which then unite to form ⪢C:H. The decomposition of the diazo-group will be facilitated by the cuprous oxide, which itself may contribute directly to the reduction of the diazonium salt, thereby enhancing the yield of deaminated product (cf. Hodgson, Leigh, and G. Turner, J., **1942**, 744). This facilitation of decomposition by cuprous oxide is shown when methyl alcohol is used, since in the simpler case of the decomposition of benzenediazonium sulphate, the hydrogen (*b*) of the methyl alcohol is not detached, and the $\cdot OCH_3$ and aryl radicals then unite. In the present series of experiments, therefore, methyl alcohol is in its proper place.

The period of induction thus represents the time necessary for the complex to form and rearrange before decomposition, and this period increases with enhancement of anionoid character of the alcoholic oxygen, as theory foretells. The inferior position of ethylene glycol compared with ethyl alcohol is anomalous, since glycollic acid has a dissociation constant much greater than that of acetic acid, so on this account, ethylene glycol should deaminate much more readily than methyl alcohol. Perhaps the inferiority is due to hydroxyl bonds (cf. Bernal and Megaw, *Proc. Roy. Soc.*, **1935**, **151**, *A*, 384) in the ethylene glycol, which would retard formation of the initial complex with consequent retardation of deamination, so that other decompositions of the diazonium salt would proceed (cf. Hodgson, Leigh, and G. Turner, *loc. cit.*). This explanation is supported by the fact that there is no induction period prior to decomposition, which in this case would be initiated by the action of cuprous oxide on the diazonium salt. The glycol appears to react at both the $CH_2\cdot OH$ groups simultaneously, since glyoxal predominates as the oxidation product.

With *tert.*-butyl alcohol, where the α-carbon atom lacks a hydrogen atom, deamination was very poor, and probably due to the reducing action of cuprous oxide alone, which, in absence of an alcohol or other organic solvent, affords a yield of only 18% of deaminated product.

Acetone and ethyl acetate both give induction periods before decomposition, and their reactivity is probably due to their tautomeric enolic forms, whereas with *cyclo*hexanone, where the enolic form is more difficult to attain, and in these experiments probably impossible, the results were similar to those with *tert.*-butyl alcohol. With benzyl alcohol there was a short induction period, but no benzaldehyde was formed and no deamination product could be isolated.

The superiority of the cuprous oxide–alcohol procedure is indicated by the fact that with ethyl alcohol alone the yield of 1 : 6-dinitronaphthalene is 21%, with cuprous oxide alone 18%, and with the combination 57·6%. The comparatively high yield (69·5%) obtained by the use of ethylene chlorohydrin indicates that this alcohol should be extremely useful as a general deaminating agent; *e.g.*, a 75% yield of 1 : 3-dinitronaphthalene has been obtained from 2 : 4-dinitro-*p*-toluenesulphon-1-naphthalide.

The method now described is the only good one available for the preparation of 1 : 6-dinitronaphthalene (cf. Graebe and Drews, *Ber.*, 1884, **17**, 1172; Graebe, *Annalen*, 1904, **335**, 143; Gaess, *J. pr. Chem.*, 1891, **43**, 32; Veselý and Dvorăk, *Bull. Soc. chim.*, 1923, **33**, 319). These authors obtained 1 : 6-dinitronaphthalene *via* a long sequence of operations starting from β-naphthol or β-naphthylamine, and in yields not exceeding 15%.

The yields quoted in the table are comparative for an identical procedure with each alcohol, but by individual modifications the yields might be substantially increased; *e.g.*, a 65·5% yield has been obtained with ethyl alcohol by a slight variation of details. An improved procedure is also given for the nitration of *p*-toluenesulphon-2-naphthalide (cf. Morgan and Micklethwait, J., 1912, **101**, 148; Bell, *loc. cit.*).

EXPERIMENTAL.

1 : 6-Dinitro-*p*-toluenesulphon-2-naphthalide was prepared by dissolution of *p*-toluenesulphon-2-naphthalide (50 g.) (Hodgson and Smith, J., 1935, 1854) in hot glacial acetic acid (150 c.c.) and gradual addition, at 55° initially, of nitric acid (35 c.c., *d* 1·42), the temperature being kept below 85°. If no rise of temperature occurred with the first few drops of acid, sodium nitrite (*ca.* 0·01 g.) was added, since this prevented a delayed but subsequently violent reaction. When 20—25 c.c. of acid had been added, the reaction mixture suddenly set to a solid crystalline mass; this was broken up so as to permit resumption of stirring, which was continued until the mixture had attained room temperature. The crude, solid 1 : 6-dinitro-*p*-toluenesulphon-2-naphthalide was removed, washed with glacial acetic acid (30 c.c.), followed by 50% aqueous acetic acid, until the filtrate was colourless, the acid expressed as far as possible by suction, and the solid dried at 70°, being thus obtained in pale creamy-yellow needles, m. p. 197° unchanged by one crystallisation from ethyl alcohol (Morgan and Micklethwait, *loc. cit.*, give m. p. 194°); yield, 54 g. (83%).

1 : 6-Dinitro-2-naphthylamine was obtained from the *p*-toluenesulphonamide by means of concentrated sulphuric acid (Bell, *loc. cit.*). For subsequent deamination experiments, the amine was not isolated but diazotised directly in the sulphuric acid solution.

Combined Hydrolysis and Diazotisation of 1 : 6-*Dinitro*-p-*toluenesulphon*-2-*naphthalide. General Method.*—The sulphonamide (*x* g.) was stirred into sulphuric acid (2*x* c.c., *d* 1·84) at room temperature; the mixture warmed to 30—35° during addition, and this was raised to 40° for completion of the hydrolysis. The mixture was then treated below 20° with a solution of sodium nitrite (0·24*x* g.) in sulphuric acid (1·1*x* c.c.), and stirred gradually into glacial acetic acid (4*x* c.c.) below 20° and kept during 20 mins. to complete the diazotisation.

Replacement of the Diazonium Group by Hydrogen, and Preparation of 1 : 6-*Dinitronaphthalene.*—(1) *By ethyl alcohol alone.* The diazo-solution above (from 50 g. of sulphonamide) was stirred into ethyl alcohol (600 c.c.), the mixture heated on the water-bath for 4 hours, and poured on ice (2000 g.). The crude, dark brown solid which was precipitated (26 g.) was filtered off, washed, and the dried cake extracted twice with ethylene dichloride (200 c.c. for 4 hours, followed by 150 c.c. for 2 hours). The combined filtered extracts were refluxed with animal charcoal (5 g.) for 2 hours, and then the 1 : 6-dinitronaphthalene (6 g., 21% yield) obtained by alternate removal by distillation of excess solvent and crystallisation, separated in light brown needles, m. p. 155°.

(2) *By cuprous oxide alone.* The stirred diazo-solution from the sulphonamide (20 g.) was treated gradually during 20 mins. with cuprous oxide (28 g.), and then stirred for 2 hours while the reaction subsided. The mixture was poured into water (1000 c.c.), and the solid precipitate (17 g.) filtered off and extracted with ethylene dichloride (300 c.c.) as in (1); the filtered extract, after refluxing with animal charcoal, was reduced in volume to 20 c.c., whereupon impure 1 : 6-dinitronaphthalene (2 g., 18% yield) was obtained.

(3) *By cuprous oxide in various alcohols, ketones, and esters.* The diazo-solution from the sulphonamide (15—20 g.) was poured into a suspension of cuprous oxide (12—20 g.) in the medium (130—200 c.c.). With methyl, ethyl, and β-chloroethyl alcohols and with ethylene glycol, the reaction commenced immediately with rapid rise of temperature and formation of a clean deaminated product. With the higher alcohols, ketones, and esters, there was an induction period during which no nitrogen was evolved, and within which the temperature increased very slowly, the reaction mixtures in these cases all becoming deep reddish-brown; a vigorous evolution of nitrogen was accompanied by a rapid rise of temperature. The solution was then poured into excess of water, and in some cases the reaction product was treated with steam to remove by-products insoluble in water. In every case where an alcohol was used, a large amount of its acetate was formed; also the higher alcohols which were insoluble in the quantity of water used had to be removed before filtration. The precipitate was then filtered off, washed, dried (at *ca.* 70°), and extracted with ethylene dichloride (300 c.c.), the filtered extract being refluxed with animal charcoal (2·5 g.) for an hour. Excess solvent was then removed by distillation until 35 c.c. remained, from which the 1 : 6-dinitronaphthalene crystallised out on cooling, the mother-liquor being further concentrated to yield two more crops. The data for the various organic compounds used are assembled in the table.

An Improved Procedure for the Preparation of 1 : 6-*Dinitronaphthalene.*—1 : 6-Dinitro-*p*-toluenesulphon-2-naphthalide (50 g.) was hydrolysed and diazotised as above. The diazo-solution was then run at such a rate into a vigorously stirred suspension of finely ground cuprous oxide (35 g.) in ethyl alcohol (450 c.c.) that the maximum temperature attained was 70°. The reaction was rapid, but stirring was continued for an hour for the mixture to acquire room temperature, whereupon it was poured into water (3000 c.c.), a fawn-coloured precipitate (25·2 g.) being obtained. This crude 1 : 6-dinitronaphthalene was removed and extracted with ethylene dichloride (450 c.c.), the extract boiled with charcoal (2 g.), filtered, and cooled; the almost pure 1 : 6-dinitronaphthalene (18·4 g., 65·5% yield; *i.e.*, 54·4% from β-naphthylamine) (cf. Veselý and Dvorăk's yield of 10—15%) was obtained in pale yellow needles, m. p. 165·5°. 1 : 6-Dinitronaphthalene can be distilled in air with only slight decomposition, b. p. *ca.* 360°, but without decomposition at 10 mm., b. p. *ca.* 235°; when crystallised from ethylene dichloride (3 times) and then from glacial acetic acid (3 times), it is obtained in creamy white needles, m. p. 166·5° (Veselý and Dvorăk, *loc. cit.*, give m. p. 161°; Gaess, *loc. cit.*, gives m. p. 166—167°) (Found : N, 12·84. Calc. : N, 12·85%).

Medium.	Vol., c.c.	Naphthalide, g.	Cu_2O, g.	Final temp.	Yield of dinitro-compound.		Description of product (needles in all cases).	Remarks.
					G.	%.		
Methyl alcohol	200	17·1	14·0	57°	5·8	60·2	Light golden-yellow; m. p. 165·5—166·5°	No H·CHO formed *
Ethyl alcohol	250	20·0	14·0	50	6·5	57·6	Golden-yellow; m. p. 165·5°	Much CH_3·CHO formed *
n-Propyl alcohol	150	15·0	12·0	50	3·45	40·6	Light brown; m. p. 163·5—165·5°	Much CH_3·CHO formed †
*iso*Propyl alcohol	200	20·0	15·0	55	6·75	59·7	Yellow; m. p. 165·5—166·5°	Some CH_3·CHO formed †
n-Butyl alcohol	130	15·0	12·0	60	2·55	30·0	Fawn; m. p. 163·5—165·5°	Much aldehyde formed †
tert.-Butyl alcohol	200	20·0	20·0	60	—	—	—	After steaming off the alcohol and ester, an intractable tar remained †
*iso*Butyl alcohol	150	15·0	12·0	60	4·35	51·2	Ochre-yellow; m. p. 163·5—165·5°	Much aldehyde formed †
Ethylene glycol	200	20·0	15·0	—	4·1	48·3	Light golden-yellow; m. p. 164·5—166·5°	Glyoxal evolved, and a small quantity of glycollaldehyde appeared to be formed *§
Ethylene chlorohydrin	200	20·0	15·0	45	7·85	69·5	Fawnish-yellow; m. p. 162·5—164·5°	Much CH_2Cl·CHO formed *‡
Benzyl alcohol	200	20·0	15·0	50	—	—	—	No Ph·CHO detected. After steaming, an intractable tar remained †
Acetone	200	20·0	15·0	55	4·0	35·5	Brown; m. p. 160·5—162·5°	
*cyclo*Hexanone	200	20·0	15·0	—	—	—	—	After steaming, an intractable tar remained †
Ethyl acetate	200	20·0	15·0	50	4·5	39·8	Deep brown; m. p. 162·5—164·5°	— †

* No appreciable period of induction.

† The reaction mixture was steamed to remove the excess of alcohol and ester.

‡ Identified as the 2 : 4-dinitrophenylhydrazone.

§ Glyoxal was identified thus: (*a*) the evolved vapours when aspirated through a cooled U-tube gave a green liquid showing Tollens's test and Schiff's test, but not reducing Fehling's solution; (*b*) by its 2 : 4-dinitrophenylhydrazone.

Combined Hydrolysis and Deamination of 2 : 4-*Dinitro*-p-*toluenesulphon*-1-*naphthalide by Cuprous Oxide in Ethylene Chlorohydrin.*—The naphthalide (50 g.) was converted into the diazo-solution as described by Hodgson and Birtwell (work about to be published), and this was run into a suspension of cuprous oxide (40 g.) in ethylene chlorohydrin (450 c.c.). The temperature rose to 62°, nitrogen was vigorously evolved, and after an hour the mixture was poured into water (2 l.). After extraction as above with ethylene dichloride, the 1 : 3-dinitronaphthalene (21·2 g., 75·2% yield) was obtained in yellow needles, m. p. 145°.

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TECHNICAL COLLEGE, HUDDERSFIELD.

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