924. *The Decomposition of Toluene*-p-*sulphonylhydrazones by Alkali.*

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Toluene-*p*-sulphonylhydrazones of aromatic aldehydes and ketones usually give aryldiazomethanes together with alkali toluenesulphinate. In other cases the product is an olefin, sometimes produced with rearrangement of the carbon skeleton. Some bistoluenesulphonylhydrazones of 1 : 2-diketones yield triazole derivatives.

Escales (*Ber.*, 1885, **18**, 893) showed that benzenesulphonylphenylhydrazide is decomposed by warm alkali, giving benzene, nitrogen, and benzenesulphinic acid :

$$\mathrm{Ph{\cdot}SO_2{\cdot}NH{\cdot}NHPh \longrightarrow PhH + N_2 + Ph{\cdot}SO_2H}$$

It occurred to us that the toluene-*p*-sulphonylhydrazone of an enolisable ketone might analogously yield an olefin, *e.g.* :

$$\mathrm{Ph{\cdot}SO_2{\cdot}NH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}CO_2Et \longrightarrow Ph{\cdot}SO_2{\cdot}NH{\cdot}NH{\cdot}CMe{:}CH{\cdot}CO_2Et \longrightarrow}$$
$$\mathrm{Ph{\cdot}SO_2H + N_2 + CHMe{:}CH{\cdot}CO_2H + EtOH}$$

This reaction gave in fact a little crotonic acid, and the behaviour of the hydrazones of simple, not readily enolisable ketones was next explored.

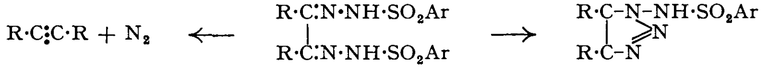
Acetone toluenesulphonylhydrazone, heated with a solution of sodium in ethylene glycol, afforded propylene; and the *cyclo*hexanone compound similarly gave *cyclo*hexene in quantitative yield. In the case of pinacolone toluenesulphonylhydrazone, the reaction was accompanied by Wagner–Meerwein rearrangement, the product being tetramethylethylene :

$$\mathrm{R{\cdot}SO_2{\cdot}NH{\cdot}N{:}CMe{\cdot}CMe_3 \longrightarrow R{\cdot}SO_2H + N_2 + Me_2C{:}CMe_2}$$

By a similar transformation camphor was converted integrally into camphene.

The hydrazones of aromatic aldehydes and ketones, on the other hand, afforded aliphatic diazo-compounds or products of their decomposition : $\mathrm{R{\cdot}SO_2{\cdot}NH{\cdot}N{:}CHPh \longrightarrow R{\cdot}SO_2H + N_2{:}CHPh}$. The derivatives of benzaldehyde, acetophenone, benzophenone, and fluorenone behaved in this way, and by working at lower temperatures substantial yields of the diazo-compounds could be attained. It is not surprising that the hydrazones of benzyl methyl ketone and of dibenzyl ketone behaved as aliphatic derivatives, giving olefins, but indan-1-one toluenesulphonylhydrazone likewise yielded substantially indene although the functional group is adjacent to the aromatic ring.

Among multifunctional derivatives, the hydrazones of α-diketones showed interesting behaviour. While from the benzil compound diphenylacetylene was obtained in good yield, others gave neither acetylenes nor diolefins but acidic compounds having the composition of sulphonamidotriazoles :



$$\mathrm{R{\cdot}C{\vdots}C{\cdot}R + N_2} \longleftarrow \begin{array}{l}\mathrm{R{\cdot}C{:}N{\cdot}NH{\cdot}SO_2Ar}\\ \quad|\\ \mathrm{R{\cdot}C{:}N{\cdot}NH{\cdot}SO_2Ar}\end{array} \longrightarrow \begin{array}{l}\mathrm{R{\cdot}C{-}N{-}NH{\cdot}SO_2Ar}\\ \quad|\quad\ \geqslant\mathrm{N}\\ \mathrm{R{\cdot}C{-}N}\end{array}$$

The results of the fission of these and other toluenesulphonylhydrazones by solutions of sodium in hot ethylene glycol are collected in the Table.

It might be supposed that the diazo-compound is always the primary product, which can yield olefin by decomposition. On this view the intermediate product in case 7 would be diazocamphane having the unaltered camphor skeleton, but Heubaum and Noyes (*J. Amer. Chem. Soc.*, 1930, **52**, 5070) have shown that the very unstable diazohydrocarbon decomposes to give tricyclene, and a subsequent isomerisation of this symmetrical hydrocarbon could not have led to the optically active camphene isolated by us. This fission, which, proceeding only under alkaline conditions, involves in cases 6 and 7 what is formally a Wagner–Meerwein change, may be formulated as follows.* The removal of a proton with formation of a negative charge on the adjacent nitrogen atom leads to a release of the sulphinate anion, and the remainder of the molecule either remains intact as a diazo-

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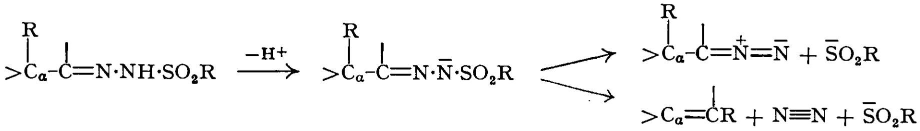
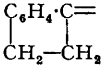
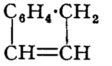
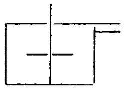
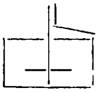
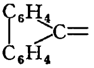
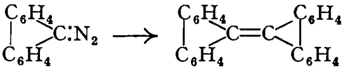
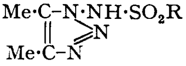
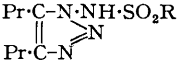
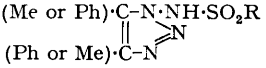
* The comments of a Referee have been helpful in the formulation of these reactions.

compound, with necessary regrouping of electrons, or undergoes fission into nitrogen and an olefin, with concomitant migration of one of the groups attached to $C_{(\alpha)}$:



$$\mathrm{>\overset{\overset{R}{|}}{C_\alpha}-\overset{|}{C}=N\cdot NH\cdot SO_2R \xrightarrow{-H^+} >\overset{\overset{R}{|}}{C_\alpha}-\overset{|}{C}=N\cdot\overset{-}{N}\cdot SO_2R \begin{array}{l} \nearrow >\overset{\overset{R}{|}}{C_\alpha}-\overset{|}{C}=\overset{+}{N}=\overset{-}{N}+\overset{-}{S}O_2R \\ \searrow >\overset{|}{C_\alpha}=CR+N\equiv N+\overset{-}{S}O_2R \end{array}}$$

When, as in most cases described, the migrating R is hydrogen, the carbon skeleton is unaltered in the olefin. The diazo-compound will be stabilised by conjugation if $C_{(\alpha)}$ is part of a benzene nucleus; it may then become the main product to the exclusion of the olefin, which is moreover structurally excluded in cases 8, 10, and 11. The triazole derivative encountered in cases 13—15 may result from ring-closure of $\overset{-}{N}=\overset{+}{N}$:CR·CR:N·$\overset{-}{N}$·SO$_2$R, but it is difficult to account for the contrasting reaction in case 16.

No.	Group X in R·SO$_2$·NH·N=X	Products	Yield (%)
1	Me$_2$C=	CH$_2$:CHMe	—
2	*cyclo*Hexylidene	*cyclo*Hexene	100
3	Ph·CH$_2$ | Me·C=	Ph·CH:CHMe	80
4	(Ph·CH$_2$)$_2$C=	Ph·CH:CH·CH$_2$Ph	95
5			92
6	Me$_3$C·CMe=	Me$_2$C:CMe$_2$	34
7		 (Camphene)	94
8	Ph·CH=	Ph·CH:N$_2$ → HO·CH$_2$·CH$_2$·O·CH$_2$Ph Ph·CH:N$_2$ → Ph·CH$_2$·SO$_2$R	54 14
9	PhMeC=	PhMeC:N$_2$ → (PhMeC:N·)$_2$	85
10	Ph$_2$C=	Ph$_2$C:N$_2$ → HO·CH$_2$·CH$_2$·O·CHPh$_2$ Ph$_2$C:N$_2$ → Ph$_2$C:CPh$_2$	14 Main product
11			95
12	Ph·CH$_2$·CPh=	[Ph·CH$_2$·CPh:N$_2$] → (Ph·CH$_2$·CPh:N-)$_2$	94
13	Me·C= | Me·C=		79
14	Pr·C= | Pr·C=		84
15	Me·C= | Ph·C=		72
16	Ph·C= | Ph·C=	Ph·C ⦀ Ph·C	73
17	HO·CHPh·CPh=	Ph·CO·CH$_2$Ph	65
18	EtO$_2$C·CH$_2$·CMe=	[HO$_2$C·CH:CHMe] → HO$_2$C·CH$_2$·CHMe·SO$_2$R	—
19	EtO$_2$C·CH$_2$·CPh=	[HO$_2$C·CH:CHPh] → HO$_2$C·CH$_2$·CHPh·SO$_2$R	—

The utility of the reaction as a preparative route to fatty diazo-compounds in favourable cases has been explored. By decomposition at moderate temperatures in ethanolic sodium ethoxide, yields of up to 60% of phenyldiazomethane and diphenyldiazomethane could be obtained; some 70% of diphenyldiazomethane was produced by stirring the hydrazone with sodium *iso*propoxide in benzene, a method less favourable in the simpler case. These and other results indicate, however, that the process is not so effective as Staudinger's method of oxidising hydrazones with mercuric oxide. A few experiments showed that *o*-nitrobenzenesulphonylhydrazones reacted appreciably faster than toluenesulphonylhydrazones but gave roughly comparable yields of diazo-compound. It is natural that the anion of the stronger nitrosulphinic acid should be split off more easily.

The observed products resulting from further change of diazo-compounds include, as well as the expected ketazine $R_2C{:}N{\cdot}N{:}CR_2$ and the olefin $R_2C{:}CR_2$ produced by its thermal decomposition, the ether formed by alkylation of ethylene glycol by the diazo-compound (cases 8 and 10), and the sulphone (case 8) similarly formed by alkylation of toluenesulphinic acid. Deoxybenzoin, the product in case 17, would result from ketonisation of the normal olefinic product, hydroxystilbene, but it is not clear why a diazo-compound is not produced.

EXPERIMENTAL

The formation of a diazo-compound by this method was first observed by Mr. A. Nisbet, working in the University of Glasgow. He also carried out various exploratory experiments, as did Miss J. I. Campbell, who contributed the work on nitrobenzenesulphonylhydrazones.

In the preparation of toluene-*p*-sulphonylhydrazide (Freudenberg and Blümmel, *Annalen*, 1924, **440**, 51), s-*ditoluene*-p-*sulphonylhydrazine*, m. p. 220—222°, was a by-product (Found: N, 8·7. $C_{14}H_{16}O_4N_2S_2$ requires N, 8·2%). It is insoluble in water and does not form a hydrazone with benzaldehyde.

Toluene-p-*sulphonylhydrazones.*

			Found (%)			Required (%)		
No.*	Form; solvent	M. p.	C	H	N	C	H	N
1	(Borsche, *Annalen*, 1926, **450**, 81)	153°	—	—	—	—	—	—
2	Prisms; EtOH	156	58·9	6·9	10·4	58·6	6·8	10·5
3	Prisms; EtOH	134—135	63·9	6·2	9·1	63·6	6·0	9·3
4	Needles; COMe$_2$–EtOH	186	69·7	5·9	7·7	69·8	5·9	7·4
5	Plates; CHCl$_3$–EtOH	192	63·7	5·2	9·5	64·0	5·4	9·3
6	Prisms; EtOH	155	58·4	7·6	10·2	58·2	7·5	10·4
7	Needles; EtOH	163—164	63·9	7·7	9·2	63·7	7·5	8·8
8	(Freudenberg and Blümmel, *loc. cit.*)...	128	—	—	—	—	—	—
9	Needles; EtOH	148	62·1	5·6	10·1	62·4	5·6	9·7
10	Prisms; COMe$_2$–EtOH	184	68·6	5·3	8·9 ‡	68·6	5·8	9·1 ‡
11	Yellow rhombohedra; COMe$_2$–EtOH	180—182 †	68·8	4·4	8·3	68·9	4·6	8·0
12	Prisms; EtOH	143	69·5	5·4	8·0	69·2	5·5	7·7
13	Plates; AcOH	204 †	51·4	5·4	13·5	51·2	5·2	13·3
14	Plates; AcOH	187 †	55·2	6·3	11·8	55·2	6·3	11·7
15	Plates; *iso*amyl alcohol	168 †	57·1	5·2	11·9	57·0	5·0	11·6
16	Prisms; *iso*amyl alcohol	184 †	61·3	4·9	9·9	61·5	4·8	10·2
17	Plates; EtOH	144—145	66·5	5·3	7·5	66·3	5·3	7·4
18	Prisms; EtOH	105	52·5	6·4	9·1	52·3	6·1	9·4
19	Rhombs; EtOH	108	60·1	5·8	8·1	60·0	5·6	8·1

* See previous Table. † With decomp. ‡ Sulphur.

The *toluenesulphonylhydrazones* (see Table) were usually prepared by refluxing equivalent quantities of the components in alcohol for 10 minutes (1 hour for the benzoin compound, case 17). In cases 1 and 13 the reaction was conducted in aqueous N-hydrochloric acid; in cases 7, 15, 16, and 19 the materials were refluxed in 1% alcoholic hydrochloric acid for ½, ½, 1, and 2 hours respectively. Butyroin (Snell and McElvain, *Org. Synth.*, 1933, **13**, 24), kept for several days with toluenesulphonylhydrazide in alcoholic hydrochloric acid, gave only octane-3 : 4-dione bistoluenesulphonylhydrazone (case 14). The acetyl derivative, prepared by boiling butyroin with acetic anhydride and sodium acetate for 2 hours, boiled at 107—108°/15 mm. (Bouveault and Locquin, *Bull. Soc. chim.*, 1906, **35**, 640, report b. p. 117—118°/21 mm.) and gave the same product with the hydrazide in warm alcoholic hydrogen chloride.

Degradation.—The " reagent " referred to below is a solution of sodium in ethylene glycol.

Case 1. The hydrazone dissolved in ether was dropped on to alcoholic sodium ethoxide solution at 60° and the distillate collected in ethereal *p*-nitrobenzoic acid. No *iso*propyl *p*-nitrobenzoate could be detected in the distillate after removal of nitrobenzoic acid. The residue from evaporation of the alkaline alcoholic solution was taken up in water, washed with benzene, and neutralised. After evaporation to dryness, sodium toluenesulphinate was shown to be present by the formation of 2 : 4-dinitrophenyl *p*-tolyl sulphone, m. p. 187°, with 1-chloro-2 : 4-dinitrobenzene (Loudon, *J.*, 1935, 537). The hydrazone, heated at 160° with excess of the reagent, gave 1·58 mols. of gas, which decolorised aqueous bromine and permanganate and afforded propylene nitrosite, m. p. 120° (Demjanow, *Chem. Zentr.*, 1901, II, 333).

2. The hydrazone (5 g.) was refluxed for 1½ hours with 1·3N-reagent (50 c.c.). Distillation afforded *cyclo*hexene (1·5 g.), which was treated with bromine in carbon tetrachloride. After evaporation the crude dibromide was heated with piperidine (3 mols.) on the water-bath for 1½ hours. The mixture was diluted with water and extracted with ligroin; the extract, washed with water, was extracted with aqueous acetic acid, and the acid solution treated with aqueous picric acid. The precipitated 3-*piperidino*cyclo*hexene picrate* crystallised from methanol in needles, m. p. 109—111°, alone or mixed with a specimen prepared from authentic *cyclo*hexene (Found : C, 52·1; H, 5·9. $C_{11}H_{19}N,C_6H_3O_7N_3$ requires C, 51·8; H, 5·6%).

3. A solution of the hydrazone (8 g.) in 1·6N-reagent (50 c.c.) was heated at 190—200°. The distillate, dissolved in ether, washed with water, dried (Na_2SO_4), and redistilled, gave β-methylstyrene (2·9 c.c.), b. p. 176—178°; the dibromide crystallised from methanol in needles, m. p. 66°.

4. The hydrazone (8·8 g.) in 50 c.c. of N-reagent decomposed vigorously when heated. The yellow oil, isolated by dilution with water and extraction with ether, gave on distillation colourless 1 : 3-diphenylpropene (4·3 g.), b. p. 70°/12 mm. [dibromide, needles (from methanol), m. p. 110°].

5. The hydrazone (7 g.) in N-reagent (50 c.c.) gave as above indene (2·5 g.), b. p. 182° (picrate, m. p. 96°).

6. The vapours produced when the hydrazone (8 g.) was heated at 160° with 1·2N-reagent (50 c.c.) were passed through a spiral immersed in ice–salt, backed by a trap containing bromine in carbon tetrachloride which was not decolorised. The distillate (0·85 g.) boiled at 70° and gave tetramethylethylene dibromide, m. p. 173° (Found : C, 29·5; H, 5·2. Calc. for $C_6H_{12}Br_2$: C, 29·5; H, 5·0%).

7. A solution of the hydrazone in 1·5N-reagent (25 c.c.) was progressively heated and 5 c.c. of distillate collected. This, taken up in ether, washed and dried, gave on redistillation 1·7 g. of camphene, b. p. 158—160°, m. p. 46°, $[\alpha]_D^{17}$ +72·4° (in Et_2O). Bromination by Pariselle's method (*Compt. rend.*, 1925, **180**, 1832) gave a mixture of camphene dibromide and ω-bromocamphene, from which the former, m. p. and mixed m. p. 90°, was isolated by fractional distillation in a vacuum.

8. The hydrazone (5 g.) was heated at 120° with 2 mols. of reagent. The material, extracted with ether after addition of water, gave on distillation : (i) 1·5 g., b. p. 128—131°/14 mm.; and (ii) 0·6 g., b. p. *ca.* 170°/14 mm. Fraction (i) was 2-benzyloxyethanol, for which Danilov *et al.* give b. p. 134—135°/13·6 mm. (*Rev. gén. Mat. Plast.*, 1934, **10**, 364); the 3 : 5-*dinitrobenzoate* formed pale yellow needles (from benzene–ligroin), m. p. 78° (Found : C, 55·5; H, 4·0; N, 8·2. $C_{16}H_{24}O_7N_2$ requires C, 55·5; H, 4·1; N, 8·1%). Fraction (ii), which crystallised from ethanol in colourless needles, was benzyl *p*-tolyl sulphone, m. p. and mixed m. p. 144° (Found : C, 68·3; H, 6·1. Calc. for $C_{14}H_{14}O_2S$: C, 68·3; H, 5·8%).

9. The hydrazone (4 g.), treated in the same way, gave acetophenone azine (1·4 g.), m. p. 124°.

10. The hydrazone (5 g.) similarly gave a fraction, b. p. 190°/15 mm., which, crystallised from *cyclo*hexane, afforded 0·45 g. of 2-*diphenylmethoxyethanol*, m. p. 63°. This was identical (mixed m. p.) with a specimen prepared by heating diphenylbromomethane (5 g.) with a solution of sodium (0·5 g.) in ethylene glycol (25 c.c.) for 3 hours at 135°. The mixture was diluted with water, and the ethereal extract dried and distilled. The product (3·6 g.) boiled at 185—190°/15 mm., and, after crystallisation from *cyclo*hexane, had m. p. 63—64°, depressed by admixture with diphenylmethanol (Found : C, 79·0; H, 7·0. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·1%). The main product in the decomposition of the hydrazone was benzophenone azine, m. p. and mixed m. p. 164°; by distillation this was changed into tetraphenylethylene.

This hydrazone was prepared by Dr. M. I. Gillibrand (personal communication) who decomposed it thus : the hydrazone (3·5 g.) was stirred with 300 c.c. of a 0·05N-solution of sodium *iso*propoxide (not quite alcohol-free) in benzene at 65—70° for 4 hours. The washed and dried solution contained 70% of diphenyldiazomethane. He observed that this and other processes gave but small yields of diazo-compound from 4 : 4′-*dimethoxybenzophenone toluene*-p-*sulphonylhydrazone*, which, prepared in dioxan, melted at 136—137° (decomp.) (Found : N, 6·4. $C_{22}H_{22}O_4N_2S$ requires N, 6·8%).

11. In the same way the hydrazone (4 g.) gave difluorenylidene (1·8 g.).

12. The hydrazone was decomposed similarly, and the solid which separated on cooling

crystallised from ethyl acetate in long yellow prisms (1 g.), m. p. 164° alone or mixed with deoxybenzoin azine.

13. The dihydrazone (11 g.) was heated with potassium hydroxide (6 g.) in ethylene glycol (50 c.c.) in a distilling flask attached to a spiral cooled in acetone–carbon dioxide. No butadiene condensed. The alkaline residue gave nothing on dilution and exhaustive extraction with ether, but when just acidified with hydrochloric acid it gave a white solid, insoluble in ether. This 4 : 5-*dimethyl*-1-*toluene*-p-*sulphonamido*-1 : 2 : 3-*triazole* (5·5 g.) crystallised from water containing a little alcohol in prisms, m. p. 139° (Found : C, 49·8; H, 5·4; N, 21·2; S, 11·9. $C_{11}H_{14}O_2N_4S$ requires C, 49·6; H, 5·3; N, 21·0; S, 12·0%). An attempt to prepare it by oxidising the dihydrazone with ferricyanide failed.

14. The hydrazone (4·8 g.) with potassium hydroxide (2·3 g.) in ethylene glycol (40 c.c.) afforded as above the ether-soluble 4 : 5-*dipropyl*-1-*toluene*-p-*sulphonamido*-1 : 2 : 3-*triazole* (2·7 g.), prisms (from aqueous alcohol), m. p. 122—123° (Found : C, 56·1; H, 7·0; N, 17·7; S, 9·7. $C_{15}H_{22}O_2N_4S$ requires C, 55·9; H, 6·9; N, 17·4; S, 9·9%).

15. As in example 14, the hydrazone (10 g.) with potassium hydroxide (2·1 g.) in ethylene glycol (40 c.c.) gave 4(or 5)-*methyl*-5(or 4)-*phenyl*-1-*toluene*-p-*sulphonamido*-1 : 2 : 3-*triazole*, prisms (from alcohol), m. p. 179—181° (Found : C, 58·4; H, 4·9; N, 17·4; S, 9·7. $C_{16}H_{16}O_2N_4S$ requires C, 58·5; H, 4·9; N, 17·1; S, 9·8%). A separate experiment showed that no nitrogen is liberated in this decomposition.

16. Decomposition of the hydrazone (4 g.) with 1·2N-reagent (25 c.c.) led to no intense colour. Ether extracted from the diluted mixture diphenylacetylene (0·95 g.), m. p. 60°, which gave the dibromide, m. p. 206—209°.

17. A solution of the hydrazone (3 g.) in 0·7N-reagent (25 c.c.) became permanently deep red when heated (this coloration was not observed when potassium hydroxide in ethylene glycol was used). The ethereal extract of the diluted mixture gave on distillation a sticky solid (1 g.) which crystallised from methanol in prisms, m. p. 55—57°. The 2 : 4-dinitrophenylhydrazone had m. p. 197—198°, alone or mixed with deoxybenzoin dinitrophenylhydrazone.

18. The hydrazone (5 g.) was heated with potassium hydroxide (5 g.) in ethylene glycol (25 c.c.), and the diluted and acidified mixture continuously extracted with ether. After evaporation of the ether, ferric chloride in hydrochloric acid precipitated ferric toluenesulphinate from the dilute aqueous solution of the residue. Continuous ether-extraction of the filtrate from the ferric salt removed β-*toluene*-p-*sulphonylbutyric acid*, which crystallised from water in prisms, m. p. 129—131° (Found : C, 54·8; H, 5·9; S, 13·4. $C_{11}H_{14}O_4S$ requires C, 54·5; H, 5·8; S, 13·2%). It was identical with a specimen prepared from toluenesulphinic acid and crotonic acid by the method used in an analogous case by Kohler and Reimer (*Amer. Chem. J.*, 1904, **31**, 163).

19. A solution of the hydrazone (0·9 g.) in ethylene glycol (10 c.c.) with potassium hydroxide (0·4 g.) became permanently deep red when heated. The mixture, diluted with water and extracted with ether, gave on acidification a precipitate of β-phenyl-β-toluene-*p*-sulphonylpropionic acid which crystallised from aqueous alcohol in needles, m. p. and mixed m. p. 198° (Found : C, 63·1; H, 5·0. Calc. for $C_{16}H_{16}O_4S$: C, 63·1; H, 5·3%). The material for comparison was prepared from cinnamic and toluene-*p*-sulphinic acids (Kohler and Reimer, *loc. cit.*).

Evaluation as a Preparative Method for Diazo-compounds.—The yield was estimated as follows. The chilled reaction mixture was diluted with ice-water and extracted with ligroin. To the washed and dried extract was added a known excess of benzoic acid in benzene, and the whole warmed if necessary until decolorised. The unused acid was then determined by shaking the mixture with a known excess of alkali and back-titration with standard acid.

Benzaldehyde *o*-nitrobenzenesulphonylhydrazone (Storrie and Cameron, *J.*, 1934, 1330) afforded the same yield of diazo-compound with sodium methoxide, ethoxide, or *iso*propoxide in 20 mins. at 60°. The nitro-compound reacted faster than the toluenesulphonylhydrazone, no doubt owing to easier elimination of the anion of a stronger sulphinic acid, but the yield of diazo-compound was not significantly altered. On the other hand acetophenone *o*-nitrobenzenesulphonylhydrazone (Storrie and Cameron, *loc. cit.*) gave better yields (44·5% in 20 mins. at 60° in sodium ethoxide) than did the toluenesulphonylhydrazone. Poor results were obtained when the hydrazone was warmed with aqueous sodium hydroxide in presence of ligroin to extract the diazo-compound as formed, or when the solid sodium salt of the hydrazone was heated in ligroin. In a preliminary experiment benzaldehyde *o*-nitrobenzenesulphonylhydrazone was heated with solid sodium ethoxide in acetonitrile at 60° for 35 mins. Dilution with water and addition of ligroin precipitated almost colourless blades, m. p. 138—139° after recrystallisation from alcohol. This appeared to be α-N′-*benzylidenehydrazinobenzyl* o-*nitrophenyl sulphone*,

$NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}CHPh{\cdot}NH{\cdot}N{:}CHPh$ (Found : C, 60·8; H, 4·5; N, 10·6. $C_{20}H_{17}O_4N_3S$ requires C, 60·8; H, 4·3; N, 10·8%), formed by addition of nitrobenzenesulphinic acid to benzaldehyde azine.

In a more detailed series of experiments the toluenesulphonylhydrazone (0·5 g.) was decomposed by sodium ethoxide (3 mols.) in ethanol (usually 25 c.c.); the use of weaker alkali gave nearly the same yields; alcoholic potash was a little inferior to sodium ethoxide. There appears to be for each set of conditions an optimal reaction time, after which more diazo-compound is decomposed than is produced; and for a given compound this optimal yield is greatest at a definite temperature. Typical results are appended.

Phenyldiazomethane (%) at end of :

Temp.	40′	50′	1	2	3	5	6	8	12	16	20	24 hr.
40—42°	—	—	—	—	—	21·6	—	—	46·8	57·6	58·8	55·7
50	—	—	14·8	29·2	44·1	—	62·3	59·0	(4·5 hr. : 61·0%)			
60	32·1	38·8	34·1	—	—	—	—	—	—	—	—	—

Diphenyldiazomethane (%) at end of :

Temp.	3	5	6	7	8	9	11	19 hr.
50°	—	—	19·2	—	24·6	—	—	49·2
60	—	46·9	—	—	—	54·9	50·5	—
65—70	55·3	58·1	—	47·7	—	38·8	—	—

Methylphenyldiazomethane (%) at end of :

Temp.	3	5	7	10 hr.
65—70°	16·3	23·4	27·0	19·2

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