Reaction of Sulphonyl Azides with Unstrained Olefins

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Aromatic sulphonyl azides react readily with unstrained olefins to give imines ⇌ enamines which, on hydrolysis, give the corresponding sulphonamide and ketone. In some cases, rearrangement occurs during the nitrogen elimination step. Reduction of the imines *in situ* with sodium borohydride leads to the arenesulphonamides in good yield.

THE formation of ferrocenesulphonamide in high yield from the reaction of ferrocenesulphonyl azide in cyclohexene at 120°,[1] and of some unusual compounds from benzene-*o*-disulphonyl diazide and cyclohexene which, on hydrolysis, gave cyclohexanone as one of the products [2] led us to study the reaction of aromatic sulphonyl azides with unstrained olefins and examine its scope in the conversion of olefins into ketones. The recent report on the reaction of *o*-nitrobenzenesulphonyl azide with methylenecycloalkanes and with cyclohexene as a route to ketones [3] prompts us to report our results.

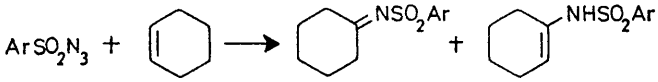
The reaction of sulphonyl azides with strained olefins,[4] enamines,[5] and vinyl ethers [6] has been studied previously, but little is known, if anything, about their reaction with unstrained olefins not bearing an oxygen or nitrogen substituent. On the other hand, aryl [7] and cyanogen azides [8] do react with unstrained olefins to give products arising from the 1,3-dipolar addition of the azide function to the olefin.

In agreement with Wohl's findings [3] we have observed that sulphonyl azides react cleanly with unstrained olefins under mild conditions to give high yields of products. The reaction of cyclohexene with various arenesulphonyl azides was examined in detail.

Decomposition of *o*-nitrobenzenesulphonyl azide in an excess of a boiling equimolar mixture of cyclohexene and benzene gave a quantitative yield of a mixture of the imine (1) and the enamine (2). Comparison of the area of the vinyl proton peak in (2) with that of the aromatic proton peaks indicated that (1) was the major product [(1) : (2) 77 : 23], in agreement with Wohl [3] who found that (1) was the main product when the azide was decomposed in neat cyclohexene. When *p*-nitrobenzenesulphonyl azide was boiled with an equimolar mixture of cyclohexene and cyclohexane for 46 h a quantitative yield of *N*-cyclohexylidene-*p*-nitrobenzenesulphonamide (3) was obtained, free (within the limits of experimental detection) of the enamine (4) (no NH in the n.m.r. or i.r. spectra, and no vinylic proton in the n.m.r. spectrum). If, on the other hand, the reaction time was extended to 100 h an almost equimolar mixture of (3) and (4) (57 : 43) was obtained.

The products (1)—(4) could be isolated and analysed, but were very susceptible to hydrolysis, and gave a quantitative yield of the sulphonamide together with a low yield of cyclohexanone.

The reaction of benzenesulphonyl azide with cyclohexene proceeded with equal ease to give a quantitative yield of an equilibrium mixture of (5) and (6) (82 : 18).



(1) Ar = *o*-$NO_2C_6H_4$ (2) Ar = *o*-$NO_2C_6H_4$

(3) Ar = *p*-$NO_2C_6H_4$ (4) Ar = *p*-$NO_2C_6H_4$

(5) Ar = Ph (6) Ar = Ph

(7) Ar = *p*-MeC_6H_4 (8) Ar = *p*-MeC_6H_4

(9) Ar = Ferrocenyl (10) Ar = Ferrocenyl

This mixture could not be purified without decomposition and it was hydrolysed to give benzenesulphonamide (87%) and cyclohexanone. Thermal decomposition of toluene-*p*-sulphonyl azide in cyclohexene–cyclohexane was incomplete even after 7 days. Boiling for 7 days in cyclohexene–toluene gave a mixture of (7) and (8) (83 : 17).

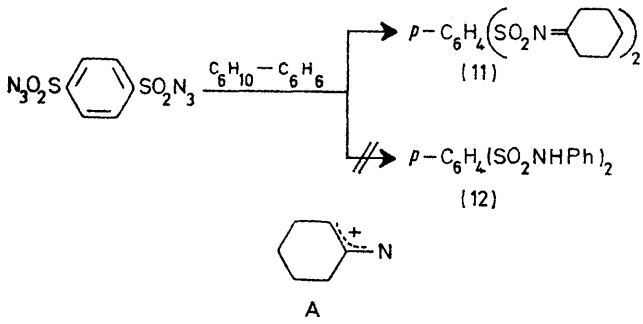
The reaction of ferrocenesulphonyl azide in cyclohexene [1] was repeated. A mixture of the imine (9) and the enamine (10) was obtained which was hydrolysed readily (in moist air) to ferrocenesulphonamide and cyclohexanone. The i.r. spectrum of the neat liquid mixture indicated that the imine was the main product (weak ν_{NH}, strong $\nu_{C=N}$); the n.m.r. spectrum in $CDCl_3$ solution, however, indicated that the enamine (10) was the main (60—80%) tautomer present in that solvent.

When benzene-*p*-disulphonyl diazide was thermolysed in a large excess of an equimolar mixture of cyclohexene and benzene, *NN'*-dicyclohexylidenebenzene-*p*-bis-sulphonamide (11) was obtained in 97% yield, but no benzene-*p*-bis-sulphonanilide (12). No enamine form could be detected. The mass spectrum of (11) exhibited the expected molecular ion at *m/e* 396, and a base peak at *m/e* 96 corresponding to ion A. Hydrolysis of (11) gave benzene-*p*-bis-sulphonamide (92%) and cyclohexanone.

The reaction of sulphonyl azides with other olefins

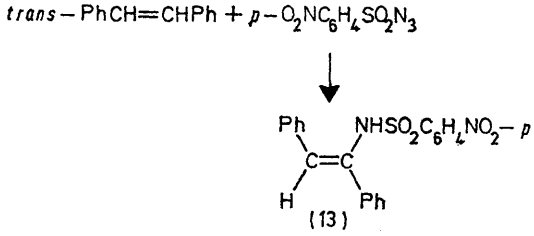
[1] R. A. Abramovitch, C. I. Azogu, and R. G. Sutherland, *Tetrahedron Letters*, 1971, 1637.
[2] R. A. Abramovitch and G. N. Knaus, in preparation; G. N. Knaus, Ph.D. thesis, University of Alabama, 1972.
[3] R. A. Wohl, *J. Org. Chem.*, 1973, **38**, 3862.
[4] A. C. Oehlschlager and L. H. Zalkow, *J. Org. Chem.*, 1965, **30**, 4205.
[5] C. A. Ritchie and M. Rosenberger, *J. Chem. Soc.* (*C*), 1967, 227; R. Fusco, G. Bianchetti, and D. Pocar, *Gazzetta*, 1961, **91**, 849 (*Chem. Abs.*, 1962, **56**, 14,020f).
[6] D. L. Rector and R. E. Harmon, *J. Org. Chem.*, 1966, **31**, 2837.
[7] P. Scheiner, *Tetrahedron*, 1968, **24**, 349.
[8] F. D. Marsh and M. E. Hermes, *J. Amer. Chem. Soc.*, 1964, **86**, 4506; A. G. Anastassiou, *ibid.*, 1965, **87**, 5512.

was investigated briefly. *p*-Nitrobenzenesulphonyl azide was chosen because of its ease of preparation and

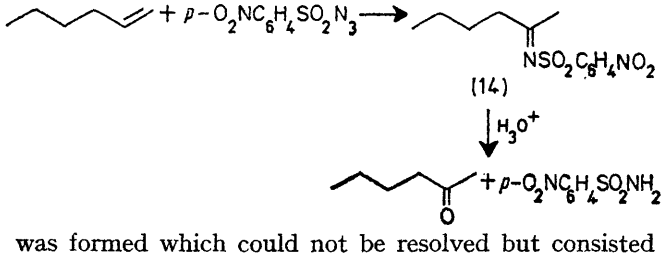


handling, and to avoid any possible participation by an *ortho*-nitro-group in the rate-determining step (*o*-nitrobenzenesulphonyl azide appeared to decompose at a lower temperature in benzene than did other non-*ortho*-substituted sulphonyl azides).

When stilbene and *p*-nitrobenzenesulphonyl azide were heated in benzene, the *N*-(α-phenylstyryl)sulphonamide (13) (64%) was obtained.



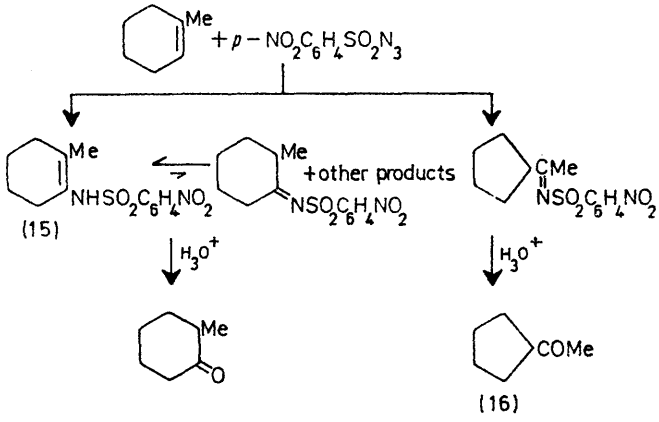
Reaction of *p*-nitrobenzenesulphonyl azide with hex-1-ene gave the *N*-(1-methylpentylidene)sulphonamide (14) (identified by n.m.r., i.r., and mass spectra) which, on hydrolysis, gave *p*-nitrobenzenesulphonamide (100%) and hexan-2-one (70%). The latter was pure by g.l.c., and there was no evidence of hexanal or of rearranged products. This contrasts with the rearrangements observed with methylenecycloalkanes [3] and below. With *trans*-4-methylpent-2-ene a mixture of products



was formed which could not be resolved but consisted mainly of three imines (very weak NH absorption in the i.r., no measurable H–D exchange in the n.m.r.), which, on hydrolysis, gave a mixture of carbonyl compounds and *p*-nitrobenzenesulphonamide. The n.m.r. spectrum of the mixture of carbonyl compounds indicated that it consisted of 4-methylpentan-2-one, 2-methylpentan-3-one, and 2,3-dimethylbutanal in a ratio of *ca.* 1 : 1 : 1·5. When the azide was heated with 2,3-dimethylbut-2-ene in cyclohexane no identifiable product of reaction between the azide and the olefin could be detected; only a small amount of an insertion product into cyclohexane was isolated and identified.

Decomposition of the azide in 4-methylcyclohexene gave a mixture of imines which was hydrolysed to give *p*-nitrobenzenesulphonamide (85%) and at least seven other components. The major ketonic fraction was a 1 : 1 mixture of 3- and 4-methylcyclohexanone (34%). The other products were not identified, but undoubtedly include rearrangement products in view of the high yield of sulphonamide obtained. Decomposition in 1-methylcyclohexene gave mainly the *N*-(2-methylcyclohex-1-enyl)sulphonamide (15) (20% probably in imine form) which could be isolated and purified. Other sulphonylimino-derivatives were also present since hydrolysis of the crude product gave *p*-nitrobenzenesulphonamide (75%) and six other products. Of the latter, the main one (40%) was 2-methylcyclohexanone derived from (15). Cyclopentyl methyl ketone (16) (15%) was also formed, indicating that the corresponding imine and/or enamines must also have been produced in the thermolysis of the azide. The other products observed by g.l.c. analysis were not identified.

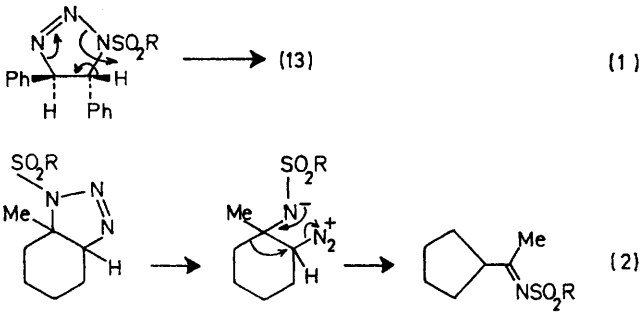
No generalisations can be made at present about the position of equilibrium between the imine and enamine products formed in these reactions (no effort was made to attain equilibrium in most cases), and the products



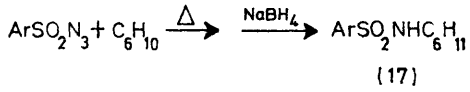
are often very susceptible to hydrolysis (less so if electron-withdrawing substituents are present in the sulphonamide). A ready 1,3-dipolar addition of the azide function to the olefin followed by elimination of nitrogen has been proposed.[3] In some cases, a concerted nitrogen elimination–proton migration can be visualised (*e.g.* cyclohexene, stilbene) [equation (1)], while in the cases where an alkyl group migration is occurring (1-methylcyclohexene, 4-methylpent-2-ene) it is more convenient to view the reaction as proceeding *via* the intermediate diazonium salt [equation (2)]. Except when the olefin was unreactive (2,3-dimethylbut-2-ene) no product of nitrene insertion into cyclohexane or benzene was observed. Indeed, at 80° the thermolysis of sulphonyl azides to give nitrenes would be expected to be very slow.[9]

[9] R. A. Abramovitch and R. G. Sutherland, *Fortschr. Chem. Forsch.*, 1970, **16**, 1.

The use of this reaction as a route to arenesulphonamides was investigated briefly and shows promise. The sulphonyl azide was heated in cyclohexene and the



mixture was treated directly with sodium borohydride. Good yields of sulphonamides (17) were obtained. Some unsubstituted sulphonamide (hydrolysis product



(17)

of imine) was also formed. The results are summarised in the Table.

In situ reduction of sulphonylimines from cyclohexene *

Ar in $ArSO_2N_3$	Reduction temp. (°C)	$ArSO_2NHC_6H_{11}$ (%)	$ArSO_2NH_2$ (%)
Ph	25	85·3	13·0
Ph	82	87·6	10·4
p-Tolyl	25	89·1	9·2
p-Tolyl	82	84·9	14·4
p-$NO_2C_6H_4$	25	72·0	14·5
p-$NO_2C_6H_4$	82	68·3	11·0
Ferrocenyl	25	55·6	35·7

* Thermolysis of the azide at 100° for 24—48 h.

EXPERIMENTAL

General Procedure for Reaction of Sulphonyl Azides in Cyclohexene.—The azide was boiled under reflux with a large excess (45—108 molar) of an equimolar mixture of dry cyclohexene and cyclohexane or cyclohexene and benzene (drying tube). When the decomposition was complete (24 h—7 days) the solvent was evaporated off *in vacuo* and the product was either isolated and purified or, if it was too unstable, its spectroscopic properties were determined and it was then hydrolysed with aqueous ethanolic hydrochloric acid to give the sulphonamide and the ketone.

N-(*Cyclohex-1-enyl*)- (2) *and* N-*cyclohexylidene-o-nitrobenzenesulphonamide* (1) had m.p. 119—120° (from dry ether) (Found: C, 50·9; H, 4·9. $C_{12}H_{14}N_2O_4S$ requires C, 51·0; H, 5·0%); $\nu_{max.}$ (KBr) 3295 (NH), 1615 (C=N), 1545 (NO_2), 1370 (NO_2), 1330 (SO_2), and 1150 cm^{-1} (SO_2); δ 8·35—7·60 (4H, m), 6·48 (NH, D_2O exchange), 5·66—5·47 (0·23H, m, =CH–), 3·3—2·70 (m), and 2·7—1·2 (m); *m/e* 282 ($M^{+\cdot}$, 5%), 186 (100), and 55 (86). A second crop of the equilibrium mixture of enamine and imine was obtained from the mother liquors (overall yield 100%).

The above product (1·31 g) was dissolved in 50% aqueous ethanol (12 ml) and conc. HCl (1·5 ml) was added. The solution was boiled under reflux for 20 min, cooled, and the *o*-nitrobenzenesulphonamide (0·83 g, 88%), m.p. 187—188° (lit.,[10] 186°), filtered off. The filtrate was extracted with ether, the extract dried ($MgSO_4$) and concentrated, and the concentrate analysed by g.l.c. Only cyclohexanone was observed and collected (i.r. spectrum identical with that of an authentic sample).

N-*Cyclohexylidene*-p-*nitrobenzenesulphonamide* (100%), had m.p. 99—100° (Found: C, 51·2; H, 5·1. $C_{12}H_{14}N_2O_4S$ requires C, 51·0; H, 5·0%); $\nu_{max.}$ (KBr) 1610 (C=N), 1525 (NO_2), 1350 (NO_2), 1315 (SO_2), and 1150 cm^{-1} (SO_2); δ ($CDCl_3$) 8·25 (4H, A_2B_2), 3·23—2·75 (m, 2 equatorial allylic H), 2·58—2·17 (m, 2 axial allylic H), and 2·17—1·40 (6H, m); *m/e* 282 ($M^{+\cdot}$, 11%), 186 (31), and 55 ($C_4H_7^+$, 100).

Hydrolysis of the imine (0·74 g) as above gave *p*-nitrobenzenesulphonamide (0·50 g, 94%), m.p. 179—181° (lit.,[10] 178°), and cyclohexanone (yield not determined).

When the azide decomposition was extended to 100 h a quantitative yield of the mixture of tautomers was obtained: $\nu_{max.}$ (film) 3230w (NH), 1610s,br (C=N), 1525 (NO_2), 1350 (NO_2), 1315 (SO_2), and 1150 cm^{-1} (SO_2); δ ($CDCl_3$) 5·6 (0·43H, m, =CH–). Hydrolysis of this sample with aqueous acid gave *p*-nitrobenzenesulphonamide (100%), and cyclohexanone (13·5%). When the hydrolysis was carried out in the presence of 2,4-dinitrophenylhydrazine, cyclohexanone 2,4-dinitrophenylhydrazone was isolated (97%), identical with an authentic sample.

N-Cyclohexylidenebenzenesulphonamide (100%), was obtained as an oil which could not be distilled at 220° (bath temp.) and 0·02 mmHg; $\nu_{max.}$ (film) 3260 (NH) and 1615 cm^{-1} (C=N); δ 8·12—7·77 (5H), 6·20 (NH, D_2O exchange), 5·45 (0·18H, m, =CH–), 3·28—2·8 (m), 2·5—2·1 (m), and 2·1—1·2 (m) (aliphatic CH); *m/e* 237 ($M^{+\cdot}$, 9%), 96 ($C_6H_{10}N^+$, 47), and 77 (Ph^+, 100). Hydrolysis with aqueous ethanolic acid gave benzenesulphonamide (87%), m.p. 155—156° (lit.,[11] 156°).

N-Cyclohexylidene- (7) and *N*-(cyclohex-1-enyl)-toluene-*p*-sulphonamide (8) were obtained by boiling toluene-*p*-sulphonyl azide (0·876 g) in a mixture (30 ml) of equimolar amounts of cyclohexene and toluene for 7 days. Evaporation of the solvent under high vacuum gave the product (1·1 g) as an oil which did not distil at 220° and 0·02 mmHg. Attempted crystallisation from CCl_4–hexane (1 : 2 v/v) or $CHCl_3$–light petroleum caused its hydrolysis (by adventitious moisture) to toluene-*p*-sulphonamide. The oil showed $\nu_{max.}$ (film) 3260 (NH), 1615 (C=N), 1350 (SO_2), and 1155 cm^{-1} (SO_2); δ ($CDCl_3$) 7·95—7·65 (2H, m), 7·42—7·05 (2H, m), 5·67 (NH, D_2O exchange), 5·45 (0·17H, m, =CH–), 3·2—2·8 (m), 2·8—2·6 (m), 2·38 (3H, s), and 2·15—1·05 (m); *m/e* 251 ($M^{+\cdot}$, 2%), 96 (14), and 91 (100).

Acidic hydrolysis of the imine gave toluene-*p*-sulphonamide (84%), identical with an authentic sample.

NN′-*Dicyclohexylidenebenzene*-p-*bis-sulphonamide* (11), had m.p. 134—135° (Found: C, 54·3; H, 6·1. $C_{18}H_{24}N_2O_4S_2$ requires C, 54·5; H, 6·1%); $\nu_{max.}$ (KBr) 1610 (C=N), 1330 (SO_2), and 1155 cm^{-1} (SO_2); δ ($CDCl_3$) 8·14 (4H, s), 3·24—2·83 (4H, m, equatorial allylic H), 2·70—2·18 (4H, m, axial allylic H), and 2·18—1·42 (12H, aliphatic H); *m/e* 396 ($M^{+\cdot}$, 8%), 98 (65), 96 (100), and 55 (83).

Hydrolysis of the imine (0·63 g) with aqueous ethanolic acid gave benzene-*p*-bis-sulphonamide (0·35 g, 92%), m.p. 285—286° (lit.,[12] 286—288°) and cyclohexanone (yield not determined).

[10] L. Demeny, *Rec. Trav. chim.*, 1929, **48**, 1145.
[11] 'Handbook of Chemistry and Physics,' The Chemical Rubber Co., Cleveland, Ohio, 50th edn., 1969—1970.
[12] A. V. Kirsanov and N. A. Kirsanova, *Zhur. obshchei Khim.*, 1959, **29**, 1802 (*Chem. Abs.*, 1960, **54**, 8693h).

Reaction of Ferrocenesulphonyl Azide with Cyclohexene.—The azide (1·02 g) in freshly distilled cyclohexene (60 ml) was heated in a glass-lined bomb at 120° for 9 h. An aliquot portion was then evaporated under dry nitrogen and the spectral properties of the residue were determined rapidly; $\nu_{max.}$ (film) 3260w (NH), 1615s (C=N), 1315 (SO_2), and 1135 cm^{-1} (SO_2); as the film was exposed to air the smell of cyclohexanone became evident and the i.r. spectrum of the sample gradually changed to that of ferrocenesulphonamide. The n.m.r. spectrum of the fresh dry product in $CDCl_3$ showed δ 5·71—5·59 (=CH−, NH), 4·78—4·47 (9H, m, ferrocene protons), 3·16—2·85br (m), 2·55—2·28br (m), and 2·2—1·35br (m); on addition of D_2O and rapid scanning the area of the δ 5·71—5·59 peak decreased and the area ratio =CH− : ferrocene protons was 0·65 : 9·0 indicating that, in $CDCl_3$, the enamine : imine ratio is 65 : 35. On repeated runs this ratio varied from 60 : 40 to 80 : 20. The cyclohexene solution was chromatographed on a column of neutral alumina (2·3 × 24 cm). Elution with benzene–ethyl acetate (95 : 5 v/v) gave a yellow solid (0·024 g) which immediately began to be hydrolysed in contact with air (smell of cyclohexanone, i.r. spectrum gradually changing to that of ferrocenesulphonamide) and which could not be purified further. Elution with benzene–ethyl acetate (1 : 1 v/v) gave a yellow gum (0·01 g) whose i.r. spectrum [3280 cm^{-1} (NH), no C=N band] indicated that it was the insertion product reported previously.[1] Elution with ethyl acetate and ethyl acetate–ethanol (97 : 3 v/v) gave ferrocenesulphonamide (0·76 g, 82%), identical with an authentic sample.

N-(α-*Phenylstyryl*)-p-*nitrobenzenesulphonamide* (13).—*p*-Nitrobenzenesulphonyl azide (1·0 g) and *trans*-stilbene (1·34 g) in cyclohexane (25 ml) were boiled under reflux ($CaCl_2$ guard tube) for 94 h, the solvent was evaporated off, and the residue chromatographed on a column of silica gel (100 g; 60—200 mesh). Elution with benzene gave *trans*-stilbene (1·09 g), m.p. 123—125°, then unchanged azide (0·51 g), and finally the *product* (0·54 g, 64·9% based on azide consumed), m.p. 150—152° (from 50% aqueous EtOH) (Found: C, 63·3; H, 4·3. $C_{20}H_{16}N_2O_4S$ requires C, 63·1; H, 4·2%); $\nu_{max.}$ (KBr) 3270 (NH) and 1627 cm^{-1} (C=C); δ [$(CD_3)_2SO$] 10·2br (1H, s, NH, exchangeable), 8·4 (4H, A_2B_2), 7·3 (10H, m), and 6·7 (1H, s, =CH−); *m/e* 380 ($M^{+\cdot}$, 3·3%) and 194 (100).

N-(1-*Methylpentylidene*)-p-*nitrobenzenesulphonamide* (14).—This was obtained as an oil (100%) from the azide (2·0 g) and hex-1-ene (200 ml); $\nu_{max.}$ (film) 1615 (C=N), 1605 (Ar), 1525 (NO_2), 1345 (NO_2), 1325 (SO_2), and 1160 cm^{-1} (SO_2); δ ($CDCl_3$) 8·58—8·15 (4H, A_2B_2), 2·7—2·19 (5H, CH_3–$\overset{|}{C}$=, –CH_2–$\overset{|}{C}$=), and 1·9—0·9 (7H, m); *m/e* 284 ($M^{+\cdot}$, 0·2%) and 42 (100). Hydrolysis with boiling aqueous acid gave *p*-nitrobenzenesulphonamide (100%) and hexan-2-one (70·3% by g.l.c.), identical (i.r. and n.m.r.) with an authentic sample.

Reaction of p-*Nitrobenzenesulphonyl Azide with* trans-4-*Methylpent-2-ene.*—The mixture of imines gave a parent ion at *m/e* 284; $\nu_{max.}$ (film) 3280vw,br (NH), 1615 (C=N), 1525 (NO_2), 1345 (NO_2), 1320 (SO_2), and 1160 cm^{-1} (SO_2); δ ($CDCl_3$) 8·8 (0·3H, d, −N=CH−?), 8·35 (4H, A_2B_2), 3·0—2·3 (<3H, m), and 1·5—0·8 (9H, m). This oil was hydrolysed with boiling 10% HCl mixed with an excess of CCl_4 and stirred vigorously for 15 h. *p*-Nitrobenzenesulphonamide (81%) was filtered off, and the CCl_4 layer was dried ($MgSO_4$) and analysed by g.l.c. (10 ft × 1/4 in Apiezon L on Anachrome, 95°). Only one peak was observed but this was a mixture of at least three carbonyl compounds. The i.r. and n.m.r. spectra of this mixture were very similar to those of a synthetic mixture of 4-methylpentan-2-one, 2-methylpentan-3-one, and 2,3-dimethylbutanal in the approximate molar ratio 1 : 1 : 1·5. The presence of the aldehyde function was confirmed by the i.r. and n.m.r. spectra; $\nu_{max.}$ 2700 cm^{-1} and at δ (CCl_4) 9·7 (d).

Reaction of p-*Nitrobenzenesulphonyl Azide with* 4-*Methylcyclohexene.*—The mixture of imines was hydrolysed as above to give *p*-nitrobenzenesulphonamide (75%). Concentration of the CCl_4 extract and analysis by g.l.c. on an Apiezon L column indicated the presence of seven components in the approximate (by area only) ratio of 2 : 1 : 1 : 2 : 1 : 25 : 1 (in order of increasing retention times). The major component was collected and identified (i.r. and n.m.r.) as a 1 : 1 mixture of 3- and 4-methylcyclohexanone (32·4%) by comparison with the spectra of authentic samples. The other components were not identified.

Reaction of p-*Nitrobenzenesulphonyl Azide with* 1-*Methylcyclohexene.*—The oily mixture of imines was hydrolysed as above to give *p*-nitrobenzenesulphonamide (75%). The organic layer was separated, the aqueous layer was salted out, and the solution extracted with ether. The combined organic extracts were evaporated and analysed by g.l.c. (10 ft × 1/4 in Apiezon L on Anachrome, 95°). Six components were resolved, and the major one (which had the longest retention time) was collected and characterised as 2-methylcyclohexanone (40% yield) by comparison with an authentic sample. The penultimate component was cyclopentyl methyl ketone (15%) (i.r. identical with that of an authentic sample); *m/e* 112 ($M^{+\cdot}$). The other components were not identified.

In one run, the mixtures of imines was treated with dry ether and the solution kept at 0°, when N-(2-*methylcyclohex*-1-*enyl*)-p-*nitrobenzenesulphonamide* (15) separated as yellow crystals, m.p. 127—130° (Found: C, 52·5; H, 5·6. $C_{13}H_{16}N_2O_4S$ requires C, 52·7; H, 5·4%); $\nu_{max.}$ (KBr) 3240s (NH), 1520 (NO_2), 1340 (NO_2), 1305 (SO_2), and 1160 cm^{-1} (SO_2); δ ($CDCl_3$) 8·3 (4H, A_2B_2), 6·15br (s, NH, exchangeable), 2·1br (4H, s), and 1·5br (7H, m); *m/e* 296 ($M^{+\cdot}$, 2·6%) and 59 (100).

Reduction of Imine–Enamine Mixtures.—The decomposition of benzenesulphonyl azide is typical of the method used.

The azide (1·064 g) in freshly distilled cyclohexene (40 ml; dried over molecular sieves) was heated in a glass-lined bomb at 100° for 24—48 h. The clear solution was then treated under nitrogen with sodium borohydride (0·45 g) in acetonitrile (20 ml; dried over molecular sieves) and boiled under reflux ($CaCl_2$ drying tube) for 2 h. The cooled solution was treated with water (50 ml), acidified with 3N-hydrochloric acid, and the aqueous layer extracted with benzene. The combined, dried ($CaCl_2$) organic layers were evaporated onto neutral alumina (10 g) and added to a column of neutral alumina (15 × 2 cm). Elution with benzene–ethyl acetate (1 : 1 v/v) gave *N*-cyclohexylbenzenesulphonamide (1·218 g, 87·6%), identical (m.p. and i.r.) with an authentic sample. Elution with ethyl acetate–ethanol (4 : 1 v/v) gave benzenesulphonamide (10·4%).

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