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THE DECOMPOSITION OF SULPHONYLHYDRAZONE SALTS: MECHANISM AND STEREOCHEMISTRY—II

THE PYROLYSIS OF THE DIAZODECALINS

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Abstract—Sulphonylhydrazones have been prepared from the four decalones and decomposed under conditions favouring the pyrolysis of the intermediate diazodecalins (a) as such and (b) after initial C-protonation. Mixtures of octalins were formed exclusively in each case. Quantitative analysis indicated that in the uncatalysed decomposition of the diazo-compounds the migration of an adjacent proton took place from a position antiparallel to that of the expelled nitrogen molecule. This implies that *free* carbenes are not intermediates in these reactions.

IN Part I of the present Series[1] it was shown that decomposition of sulphonylhydrazones under alkaline conditions involves a rate-determining, unimolecular elimination of sulphinate anion from the conjugate base to give the diazo-compound. This can decompose either directly or, in proton rich solvents, by initial C-protonation to a diazonium ion which then undergoes the expected substitution and elimination reactions. In a brief note submitted shortly after our paper, Friedman and Shechter[2] came to essentially similar conclusions. The direct decomposition of the diazo-compound, called "carbenoid decomposition" by Friedman and Shechter[2], is of course the more novel reaction. To clarify its mechanism we have prepared and decomposed *in situ* the four diazodecalins, using the sodium-acetamide reagent previously described[1] and the four decalone methanesulphonylhydrazones as progenitors.

The mixtures of hydrocarbons obtained from the methanesulphonylhydrazones in a solution of sodium in acetamide at 156° were analysed by gas-chromatography, as described in the previous paper.[3] In no case was any hydrocarbon formed (>1 per cent yield) which could not be identified as one of the octalins; almost certainly a cyclodecalin, formed by intramolecular insertion,[2] would have had a markedly different R_D value from the olefines and would have been observed as such. On hydrogenation it would almost certainly have given, at least as a minor product, some hydrocarbon other than a decalin—if, indeed, it reacted at all. No products, other than *cis* and *trans* decalins, were in fact detected (>1 per cent) in the hydrogenation products; thus olefines possessing the skeleton of bicyclo-[5:3:0]-decane, which might have been formed by carbon participation in the decomposition of the 1-diazodecalins, were also absent.[3]

These results, and those reported by the American workers for 2-diazobutane,[2] imply that "intramolecular insertion" is essentially a reaction of *primary* diazo-compounds, decomposition to an olefine by hydrogen migration taking place without

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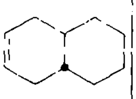
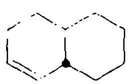
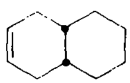
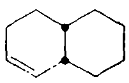
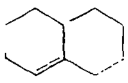
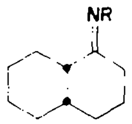
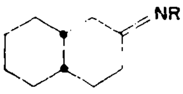
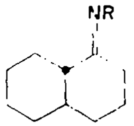
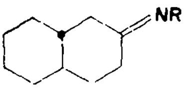
[1] J. W. Powell and M. C. Whiting, *Tetrahedron* 7, 305 (1959).
[2] L. Friedman and H. Shechter, *J. Amer. Chem. Soc.* **81**, 5512 (1959).
[3] J. W. Powell and M. C. Whiting, *Tetrahedron* **12**, 163 (1961).

complications at least with simple secondary diazo-alkanes or -cycloalkanes. The proportions of the two isomers formed in each pyrolysis are indicated in Table 1. With one exception, they are consistent with the view[2] that a carbene is formed first and then rearranges to an olefine. One would predict in these circumstances that the product would be a statistical mixture of olefines, modified in the direction of an increased proportion of the more stable compound. It is to be expected that $\Delta^{1,9}$-octalin would be more stable than *trans*-Δ^{1}-octalin (and this is in fact true[4]); it is entirely plausible that *trans*-Δ^{2}-octalin should be slightly more stable than *trans*-Δ^{1}-octalin, and that there should be no significant difference in stability between *cis*-Δ^{1}- and *cis*-Δ^{2}-octalins.[5] The analysis of the products from 1-diazo-*cis*-decalin, however, suggests a different explanation for all these results, as *cis*-Δ^{1}-octalin predominates over $\Delta^{1,9}$-octalin although the latter would be expected to be, and in fact is,[4] the more stable hydrocarbon. In 1-diazo-*cis*-decalin, two conformations, I and II, exist; the

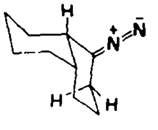
TABLE 1. PRODUCTS OF THE ALKALINE DECOMPOSITION OF THE DECALONE METHANESULPHONYLHYDRAZONES

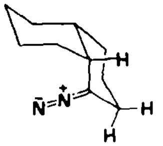
Decalone Methane-sulphonyl-hydrazone	Reagent					
	A G	25% 27%	75% 73%			
	A G		51% 48%	49% 52%		
	A G	74% 82%			26% 18%	
	A G				35% 45%	65% 55%

=NR is =N.NH.SO$_2$.CH$_3$, giving =N$^+$=N$^-$

Reagent A: 1·3 N solution of sodium in acetamide, at 156°.

Reagent G: 1·3 N solution of sodium in ethylene glycol, at 156°.





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[4] J. W. Powell and M. C. Whiting, *Proc. Chem. Soc.* In press.

[5] R. B. Turner, W. R. Meador and R. E. Winkler, *J. Amer. Chem. Soc.* **79**, 4122 (1957).

first should be the more stable and, having the polar diazo-group exposed, might be more effectively solvated in acetamide and so able to react more rapidly. If it is assumed that the migrating hydrogen atom moves, from an axial position approximately antiparallel with the breaking $C{=}N_2$ bond, synchronously with the fission of the latter, then conformation I could give only *cis*-Δ^1-octalin while conformation II would probably give *cis*-Δ^1-and $\Delta^{1,9}$-octalins in about the same proportions as does 1-diazo-*trans*-decalin in giving *trans*-Δ^1- and $\Delta^{1,9}$-octalins. A 2:1-predominance of conformation I in the reaction, plus the above stereo-electronic hypothesis, would explain the results obtained with 1-diazo-*cis*-decalin. This hypothesis would also explain, as well as the free carbene hypothesis, the results obtained with the other diazodecalins, as in these cases there are no stereoelectronic restrictions and energetic factors would determine the products.

The view that secondary diazo-compounds decompose when possible by a synchronous mechanism might also account for some of the results reported by Friedman and Shechter,[2] notably the wide spacing (67:28:5) in the proportions of *trans*-Δ^2-, *cis*-Δ^2-, and Δ^1-butenes obtained from 2-diazobutanes. These are very different from typical reaction-product ratios obtained in the reactions of carbene itself.[6] Generalization of our results to acyclic systems would, however, be premature.

The decomposition reactions of the decalone sulphonylhydrazones were also carried out under Bamford–Stevens conditions, i.e. with the sodium derivative of ethylene glycol in excess of glycol.[7] The olefinic products did not differ greatly in composition from those obtained in acetamide, although in the preparative runs the total yields of olefines were only 30–40 per cent as against ca. 70 per cent in acetamide. The β-hydroxyethyl ethers were formed in ca. 30 per cent yield, whereas in acetamide no substitution products could be detected; this agrees with our earlier observations.[1] Probably the diazodecalins decompose in glycol mainly by the proton-catalysed route; equatorial diazonium cations would then be expected[8,10] to give, at least very largely, equatorial substitution products, while axial diazonium ions would mainly undergo diaxial 1:2-elimination, giving mixtures of olefines quite similar to those obtained from the similarly stereospecific decompositions of the diazo-compounds themselves, as observed in acetamide.

"The reaction of *p*-toluenesulphonhydrazones with base" was recently criticized as a method of preparing olefines by DePuy and Froemsdorf[9] on the grounds of low total yield and the formation of rearrangement products. These criticisms are justified as applied to the reaction in ethylene glycol,[7] the only solvent used by these workers; they are not justified if applied to the reaction in acetamide,[1] which is convenient and gives good yields of olefine-mixtures similar to those obtained, less conveniently except perhaps on a very large scale, by the pyrolysis of esters of the corresponding secondary alcohols.

EXPERIMENTAL

The preparation of the α-decalols and of the *cis*-β-decalol from commercial α- and β- naphthols by literature methods proved difficult, apparently because of catalyst poisons, possibly hydroxybenzthiophenes, in the latter. A standardized purification procedure was evolved: the naphthol was first

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[6] W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *J. Amer. Chem. Soc.* **78**, 3224 (1956); cf. H. M. Frey, *Ibid.* **80**, 5005 (1957).

[7] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.* 4735 (1952).

[8] J. A. Mills, *J. Chem. Soc.* 260 (1953); A. K. Bose, *Experientia*, **9**, 256 (1953).

[9] C. H. DePuy and D. H. Froemsdorf, *J. Amer. Chem. Soc.* **82**, 634 (1960).

[10] W. G. Dauben, R. C. Tweit and C. Mannerskantz, *J. Amer. Chem. Soc.* **76**, 4420 (1954).

distilled at atm press, then heated under reflux with Raney nickel (0·1 part) in ethanol (2 parts) for several hours, when a very dark solution was obtained. Filtration, removal of solvent and redistillation gave a specimen of naphthol with a reasonably high and reproducible rate of hydrogenation.

cis-β-*Decalone methanesulphonylhydrazone*

cis, *cis*-β-Decalol[10] (5 g) in acetone[11] (100 ml) was treated with a solution of chromic acid (6 N) in sulphuric acid (12 N) with external water-cooling until a strong yellow colour persisted in the acetone layer. After 15 min, water (500 ml) was added and the ketone was isolated with ether; without purification, it was dissolved in ethanol (5 ml) and added to a solution of methanesulphonylhydrazine (3·7 g) in ethanol at 60°. After 14 hr at 20° the product (5·65 g, 69%) separated, m.p. 99–102°; recrystallization from ethanol gave the *hydrazone* as needles, m.p. 104–105° (Found: C, 54·05; H, 8·25; N, 11·5. $C_{11}H_{20}N_2O_2S$ requires: C, 54·1; H, 8·25; N, 11·5%).

cis-α-*Decalone methanesulphonylhydrazone* was prepared by a similar method from *cis*, *cis*-α-decalol[12] (1·15 g). The crude product, m.p. 156–158°, had an infra-red spectrum free from the characteristic bands of *trans*-α-decalone methanesulphonylhydrazone at 1203, 1053 and 1029 cm^{-1}. On crystallization from 2-methoxyethanol, the temp being kept below 100°, it gave the desired *hydrazone* (4·5 g, 55%), m.p. 165·5° (Found: C, 54·2; H, 7·9; N, 11·64%).

trans-β-*Decalone methanesulphonylhydrazone*

$\Delta^{1,9}$-2-Octalone was prepared in 30% yield by condensation[13] of cyclohexanone (196 g) with methyl vinyl ketone (70 g) at 0° in the presence of benzyltrimethylammonium hydroxide (6 g). The product, b.p. 90–95°/1 mm, n_D^{20} 1·5262 (40 g) was reduced[14] with lithium (10 g) in liquid ammonia (1 l.) and ether (200 ml), giving material which showed an infra-red band of appreciable intensity at 1660 cm^{-1} as well as a stronger band at 1700 cm^{-1}. It was again reduced, lithium (ca. 4 g) being added to a solution in ammonia (750 ml) and ether (100 ml) until a deep blue colour persisted. After a further 10 min the product was isolated and distilled; it (20·8 g) had b.p. 65–68°/0·8 mm, n_D^{25} 1·4830 (Hückel[15] gives n_D^{19} 1·4809), and showed infra-red bands indicating the presence of a trace of the αβ-unsaturated ketone, as well as appreciable amounts of hydroxylic material. This crude ketone (5 g) was converted to the methanesulphonylhydrazone as described above; crystallization was not immediate, but the separated *hydrazone* (6·25 g, 78%) had m.p. 123°, unchanged on recrystallization (Found: C, 53·7; H, 7·9; N, 11·85%).

trans-α-*Decalone methanesulphonylhydrazone*

(a) Hydrogenation of purified α-naphthol (75 g) in ethanol (50 ml) over W-7 Raney nickel at 145° and 145 atm was complete after 8 hr. Filtration and distillation gave a fraction, b.p. 120–125°/14 mm, n_D^{25} 1·500 (38·4 g) consisting of a mixture of α-decalols. This was dissolved in acetone (200 ml) and treated with chromic acid solution (60 ml) as described above. The mixture of α-decalones obtained on isolation was equilibrated by heating under reflux with sodium hydroxide (33 g) in water (50 ml) and methanol (70 ml) for 18 hr. Isolation and distillation through a 20 cm Dufton column gave essentially pure *trans*-α-decalone (27·7 g), b.p. 112–113°/15 mm, n_D^{25} 1·4850, which largely crystallized on standing (Gutsche and Peter[12] give n_D^{20} 1·4852 (supercooled), b.p. 58°/0·8 mm, m.p. 31°). This material (15·4 g) in ethanol (25 ml) was added to methanesulphonylhydrazine (11 g) in hot ethanol (75 ml) and the solid which separated on cooling was recrystallized from β-methoxyethanol below 100°. The *hydrazone* (17·3 g, 51% from the α-decalol mixture) had m.p. 181–182° (Found: C, 54·5; H, 8·3; N, 11·6%).

(b) The crude α-decalone mixture obtained by oxidation (9 g) was added to methanesulphonylhydrazine (6·5 g) in hot ethanol (45 ml). A solid separated on cooling which, from its infra-red spectrum, was a mixture of the *cis*- and *trans*-α-decalone derivatives. It was heated under reflux for 3 hr in ethyl acetate (200 ml) and acetic acid (10 ml); on cooling the *trans*-α-decalone derivative (7·65 g, 54% from the decalol mixture) separated, m.p. 180–181°.

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[11] cf. K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.* 39 (1946).

[12] C. D. Gutsche and H. H. Peter, *J. Amer. Chem. Soc.* **77**, 5971 (1955).

[13] E. E. van Tamelen, personal communication.

[14] E. E. van Tamelen and W. C. Proost, *J. Amer. Chem. Soc.* **76**, 3632 (1954).

[15] W. Hückel, *Liebigs Ann.* **444**, 1 (1925).

Decomposition of the decalone methanesulphonylhydrazones

The methanesulphonylhydrazone (0·4 g) was added to a solution of sodium (0·15 g) in the appropriate solvent (5 g) (in the case of acetamide, dissolution of the sodium was carried out *in vacuo* to avoid combustion). The mixture was heated at 156° in a vapour-bath until nitrogen evolution slackened. Water (5 ml) was added while the reaction mixture was still warm, and the product was extracted into light petroleum (b.p. 60–80°, 1·5 ml). This extract was used directly for gas-liquid chromatography, after the addition of *trans*-decalin as internal indicator in appropriate cases.

The following is a typical preparative run, using the glycol reagent: *trans*-α-Decalone methanesulphonylhydrazone (5 g) was added to a solution of sodium (1·5 g) in ethylene glycol (50 ml). The mixture was heated to 155–160° until nitrogen evolution slackened (15 min). After cooling, water (100 ml) was added, and the product was extracted into ether (50 + 3 × 25 ml). The combined extracts were washed with water (4 × 25 ml), dried (magnesium sulphate), and the solvent was removed through a short column. The resulting oil was then distilled under reduced press, the fractions being obtained:

Fraction A B.p. 67–71°/7 mm, 1·00 g, n_D^{20} 1·4835.
Fraction B B.p. 85–87°/0·02 mm, 1·41 g, n_D^{20} 1·4871.

Fraction A was shown, by infra-red spectroscopy and gas-liquid chromatography, to be a mixture of $\Delta^{1,9}$-and *trans*-Δ^1-octalins, whilst the infra-red spectrum of fraction B showed it to be a hydroxyether, presumably 1-(β-hydroxyethoxy)-*trans*-decalin.

The results of this reaction, and the other preparative reactions which were carried out on the decalone methanesulphonylhydrazones, are summarized in the following table.

TABLE 2. PREPARATIVE REACTIONS ON THE DECALONE METHANESULPHONYLHYDRAZONES

Sulphonyl-hydrazone	Reagent	Olefine		Hydroxyether	
		Yield	Refractive index	Yield	Refractive index
cis-α	Acetamide	67%	1·4943 (18°)		
cis-α	Glycol	26	1·4925 (20°)	35%	1·4939 (20°)
trans-α	Acetamide	72	1·4933 (20°)		
trans-α	Glycol	36	1·4933 (20°)	34	1·4871 (20°)
cis-β	Glycol	43	1·4938 (17°)	29	1·4966 (17°)

A portion of the hydroxyether from the *cis*-β-hydrazone, after redistillation, was submitted for analysis, with the following result: (Found: C, 73·4; H, 10·9% $C_{12}H_{22}O_2$ requires: C, 72·7; H, 11·2%).

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