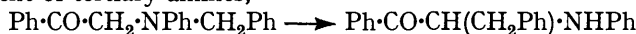


339. Rearrangement of Sulphonhydrazides.

By P. CARTER and T. S. STEVENS.

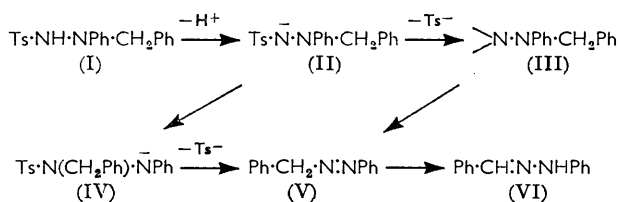
A series of sulphonhydrazides, $R\cdot CH_2\cdot NR'\cdot NH\cdot SO_2R''$, with alkali gave hydrazones, $R\cdot CH\cdot N\cdot NHR'$, and sulphinic acid, $H\cdot SO_2R''$. The change is intramolecular and shows first-order kinetics with respect to the anion of the hydrazide. The effect of substitution on the rate of reaction is discussed.

THE rearrangement of tertiary amines,¹

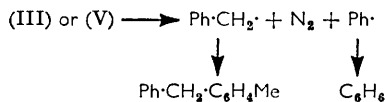


suggests the possibility of an analogous transformation in which the methylene group of the phenacyl radical is replaced by NH, *i.e.*, a rearrangement of *N'*-acyl-*N*-aryl-*N*-benzylhydrazines. Compounds of this type in which the acyl group was benzoyl were very resistant to alkali, but *N*-benzyl-*N*-phenyl-*N'*-toluene-*p*-sulphonylhydrazine afforded benzaldehyde phenylhydrazone with alkali toluenesulphinate: $Ts\cdot NH\cdot NPh\cdot CH_2Ph \longrightarrow Ph\cdot NH\cdot N\cdot CHPh + TsH$ ($Ts = p\text{-}C_6H_4Me\cdot SO_2$).

The reaction is rapid in hot dilute aqueous or alcoholic alkali, giving >60 moles % of benzaldehyde phenylhydrazone with ~30% of benzene. An oily by-product (~20% as $C_{14}H_{14}$), free from nitrogen and sulphur, resembles diphenylmethane and may be mixed phenyltolylmethanes from dimerisation of benzyl radicals. It seems admissible to write the alternative formulations



with the side-reactions:



The sequence (I) \longrightarrow (II) \longrightarrow (IV), analogous to the significant stages of the rearrangement of tertiary amines, seems an improbable mechanism, as it would be expected to be a slower process than the amine transformation (unless the tardiness of the latter is improbably attributed to difficulty in the initial extraction of a proton from the

¹ Cockburn, Johnstone, and Stevens, *J.*, 1960, 3340.

phenacyl-methylene group), whereas the production of (VI) from (I) is very easy. The effect of substitution on the rate of reaction (see below) also tells against this view. The alternative scheme by way of (III) is taken as a provisional basis for discussion, with some reservations. While it is hard to avoid the assumption that the azo-compound (V) is an intermediate, there is no evidence for this; indeed, substituted *N*-benzyl-*N*-phenylhydrazines are oxidised by mercuric oxide to aldehyde arylhydrazones² under conditions unlikely to effect the isomerisation of the azo-compound (V), suggesting the possibility that the ion (II) yields the product (VI) otherwise than *via* (V). There is, further, no formal proof that it is the benzyl and not the phenyl group in (I) which migrates to the adjacent nitrogen atom, though this is no doubt more likely.

A similar reaction was shown by analogues of (I) substituted in either phenyl group or with sulphonyl radicals other than toluene-*p*-sulphonyl. *N*-Benzyl-*N*-2-naphthyl-*N'*-toluenesulphonylhydrazine gave benzaldehyde 2-naphthylhydrazone in moderate yield, with much naphthalene. *N*-Allyl-*N*-phenyl-*N'*-toluenesulphonylhydrazine* gave what appeared to be acetaldehyde phenylhydrazone. On the other hand, the *N*-methyl and *N*-phenethyl analogues were hydrolysed without recognisable production of hydrazone, while *NN*-diphenyl-*N'*-toluenesulphonylhydrazine was unaffected by boiling dilute alkali. *NN*-Dibenzyl-*N'*-toluenesulphonylhydrazine gave, very easily, nitrogen and dibenzyl, as observed by Carpino.³

The process is substantially intramolecular. A mixture of *N*-benzyl-*N*-*p*-chlorophenyl-*N'*-toluenesulphonylhydrazine and *N*-*p*-chlorobenzyl-*N*-phenyl-*N'*-toluenesulphonylhydrazine (which react separately at a rather similar rate) gave with alkali a mixture of benzaldehyde *p*-chlorophenylhydrazone and *p*-chlorobenzaldehyde phenylhydrazone in which no benzaldehyde phenylhydrazone could be detected.

The kinetics of the reactions were examined, rather roughly, by titration with acid, the progressive replacement of the more basic anions (II) by toluenesulphinate being determined. On the scheme formulated, this involves following the process as far as (III) or (V), the stages (II) \longrightarrow (III) or (II) \longrightarrow (IV) being presumably rate-determining. The reaction is of the first order with respect to the anion of the hydrazide, and the velocity is unaffected by alkali in excess of one molecular proportion.

The effect of structural changes on the velocity of reaction is summarised in Table 1.

TABLE 1. *Alkaline decomposition of RR'N·NH·SO₂R''.*

No.	R	R'	R''	10 ⁴ k ₁
1	Benzyl	Phenyl	<i>p</i> -Tolyl	3·3
2	4-Chlorobenzyl	Phenyl	<i>p</i> -Tolyl	1·9
3	4-Methylbenzyl	Phenyl	<i>p</i> -Tolyl	2·9
4	4-Methoxybenzyl	Phenyl	<i>p</i> -Tolyl	4·0
5	2-Methylbenzyl	Phenyl	<i>p</i> -Tolyl	3·4
6	Benzyl	<i>p</i> -Chlorophenyl	<i>p</i> -Tolyl	1·5
7	Benzyl	<i>p</i> -Tolyl	<i>p</i> -Tolyl	7·2
8	Benzyl	<i>o</i> -Tolyl	<i>p</i> -Tolyl	9·3
9	Benzyl	Phenyl	Phenyl	3·3
10	Benzyl	Phenyl	<i>p</i> -Nitrophenyl	3·6
11	Benzyl	Phenyl	<i>p</i> -Chlorophenyl	3·4
12	Benzyl	Phenyl	<i>o</i> -Tolyl	5·7
13	Benzyl	Phenyl	Methyl	1·2
14	Benzyl	Phenyl	Ethyl	1·6
15	Benzyl	Phenyl	Isopropyl	4·7

The reaction is somewhat hindered by electron-attracting substituents in the *N*-phenyl group, and to a less extent by such substituents in the benzyl radical. Electron-attracting substituents in the sulphonyl radical have a small accelerating effect; while such a

* Here and elsewhere the *para*-compound.

² Busch and Lang, *J. prakt. Chem.*, 1936, **144**, 291.

³ Carpino, *J. Amer. Chem. Soc.*, 1957, **79**, 4427.

phenylhydrazine). With sodium hydroxide, the hydrochloride gave *N*-diphenylmethyl-*N*-phenylhydrazine, prisms from ethanol-water (Found: C, 82.9; H, 6.8; N, 10.3. $C_{18}H_{18}N_2$ requires C, 83.2; H, 6.6; N, 10.2%). The acetyl derivative, crystallised from ethanol, had m. p. 165–166° (Found: C, 79.7; H, 6.4; N, 8.9. $C_{21}H_{20}N_2O$ requires C, 79.8; H, 6.3; N, 8.9%).

Other hydrazines were prepared by reducing the appropriate nitrosamine (method B). These, if liquid, were used without purification; *N*-benzyl-*N*-nitroso-*p*-toluidine¹¹ had

TABLE 2. *NN*-Disubstituted *N'*-benzylidenehydrazines.^a

Substituents	M. p.	Found (%)			Formula	Required (%)			Parent hydrazine	
		C	H	N		C	H	N	Method	Properties
2-Methylbenzyl phenyl	92° ^b	83.9	6.9	9.3	$C_{21}H_{22}N_2$	84.0	6.7	9.3	A	M. p. 52–53°
4-Methylbenzyl phenyl	94° ^c	83.8	7.2	9.6	"	"	"	"	A	B. p. 116°/0.01 mm.
4-Methoxybenzyl phenyl ^d	70–71	73.4	7.2	12.9	$C_{14}H_{16}N_2O$	73.7	7.0	12.3	A	
Diphenylmethyl phenyl	112° ^b	86.1	6.2	8.0	$C_{26}H_{22}N_2$	86.2	6.1	7.7	A	M. p. 74°
4-Chlorobenzyl phenyl	100° ^c	74.6	5.5	8.9	$C_{20}H_{17}ClN_2$	74.9	5.3	8.7		M. p. 40–42° ^{14, e}
Benzyl <i>p</i> -chloro-phenyl	120° ^{b, f}	74.9	5.4	—	"	"	"	"	B	B. p. 195–198°/15 mm.
Benzyl 2-naphthyl	175–176° ^{f, g}	85.4	6.1	8.6	$C_{24}H_{20}N_2$	85.7	6.0	8.3	B	M. p. 76–78° ^e
α -Methylbenzyl phenyl ^h	160° ^b	79.5	6.6	9.2	$C_{21}H_{20}N_2O$	79.7	6.3	8.9	B ⁱ	B. p. 175–180°/13 mm.

^a All compounds in this Table were crystallised from ethanol and are colourless unless otherwise stated. ^b Prisms. ^c Needles. ^d All data refer to the simple disubstituted hydrazine. ^e Prepared by refluxing 4-chlorobenzyl bromide (1 mol.) with phenylhydrazine (2 mols.) in benzene for 8 hr. Pale yellow. ^f Plates. ^g All data for *N*-benzyl-*N'*- α -methylbenzylphenylhydrazine. ^h Method A gave mainly styrene.

m. p. 52°, and *N*-benzyl-*N*-nitroso-2-naphthylamine, 110°. *N*-Benzyl-*N*-nitroso-*p*-chloroaniline crystallised from ethanol in pale yellow prisms, m. p. 58° (Found: C, 63.4; H, 4.9; N, 10.8. $C_{13}H_{11}ClN_2O$ requires C, 63.3; H, 4.5; N, 11.4%). 9,10-Dihydro-10-nitrosophenanthridine,¹² yellow plates (from ethanol), m. p. 95–96°, gave a positive Liebermann reaction (Found: C, 73.8; H, 4.7; N, 13.4. $C_{13}H_{10}N_2O$ requires C, 74.3; H, 4.3; N, 13.3%). In general, the nitrosamine (1 mol.) in acetic acid (4 mols.) was added to a stirred suspension of zinc dust (excess) in water, the temperature being kept below 30° (the high-melting, sparingly soluble *N*-benzyl-*N*-nitroso-2-naphthylamine was reduced at 70°). After several hours' stirring, the base was extracted from the filtered solution by ether; some secondary amine was often produced as well. 9,10-Dihydro-10-nitrosophenanthridine gave mixtures containing much dihydrophenanthridine; it was not reduced by lithium aluminium hydride. Known *NN*-disubstituted hydrazines prepared in this way were: benzyl *o*-tolyl,^{2, 13} m. p. 36–38° (benzylidene derivative, m. p. 93°); benzyl *p*-tolyl,¹³ m. p. 36° (benzylidene derivative, m. p. 138°). In other cases the hydrazine was characterised as benzylidene derivative (Table 2).

Preparation of Sulphonhydrazides.—Not unexpectedly, the Schotten-Baumann procedure was unsuitable, and reaction of the hydrazine with sulphonyl chloride in presence of a tertiary base was usually unsatisfactory. Unless otherwise stated, the hydrazines named in Tables 3 and 4 were prepared by refluxing the hydrazine (2 mols.) in benzene with the sulphonyl chloride (1 mol.) for 3–8 hr. The benzene solution then contained hydrazide; the precipitate was the water-soluble hydrazine hydrochloride, sometimes accompanied by further, water-insoluble hydrazide. The hydrazide was usually recrystallised from ethanol. In some cases, unless a lower temperature was used, the hydrazine $R\cdot CH_2\cdot NR'\cdot NH_2$ gave much of the hydrazone, $R\cdot CH_2\cdot NR'\cdot N\cdot CHR$; it is significant that *N'*-benzenesulphonyl-*N*-benzyl-*N*-phenylhydrazine

¹¹ Kohler, *Annalen*, 1887, **241**, 360.

¹² Cf. Pictet and Ankersmit, *Annalen*, 1891, **266**, 151.

¹³ Votoček and Allan, *Coll. Czech. Chem. Comm.*, 1936, **8**, 313.

¹⁴ Cf. Hörlein, *Chem. Ber.*, 1954, **87**, 463.

TABLE 3. NN-Disubstituted N'-toluene-p-sulphonylhydrazines.

Substituents	Yield (%)	M. p.	Found (%)				Formula	Required (%)			
			C	H	N	S		C	H	N	S
Benzyl phenyl	55 ^a	142—143°	68.0	5.6	8.2	9.2	C ₂₀ H ₂₀ N ₂ O ₂ S	68.2	5.7	8.0	9.1
2-Methylbenzyl phenyl	60 ^a	129	68.8	6.2	7.7	—	C ₂₁ H ₂₂ N ₂ O ₂ S	68.9	6.0	7.7	8.7
4-Methylbenzyl phenyl	75 ^a	140	68.6	6.1	7.5	8.5	—	—	—	—	—
4-Methoxybenzyl phenyl	68 ^b	97—98	65.9	6.0	7.6	8.0	C ₂₁ H ₂₂ N ₂ O ₂ S	66.0	5.8	7.3	8.4
4-Chlorobenzyl phenyl	70 ^a	135—136	62.1	5.1	7.4	8.4 ^c	C ₂₀ H ₁₈ ClN ₂ O ₂ S	62.1	4.9	7.3	8.3
4-Nitrobenzyl phenyl ^d	20 ^a	161	60.3	4.9	10.8	7.8	C ₂₀ H ₁₈ N ₂ O ₂ S	60.5	4.8	10.6	8.0
Benzyl o-tolyl ^e	50 ^b	117	68.8	5.9	7.6	—	C ₂₁ H ₂₂ N ₂ O ₂ S	68.9	6.0	7.7	—
Benzyl p-tolyl	30 ^b	149	68.7	6.1	7.7	—	—	—	—	—	—
Benzyl p-chlorophenyl ^f	25 ^b	161	61.9	5.1	7.4	8.7	C ₂₀ H ₁₆ ClN ₂ O ₂ S	62.1	4.9	7.3	8.3
Benzyl 2-naphthyl	35 ^b	167	71.4	5.6	7.0	7.9	C ₂₄ H ₂₂ N ₂ O ₂ S	71.7	5.5	7.0	8.0
Allyl phenyl ^g	70 ^a	101	63.5	6.1	9.1	—	C ₁₆ H ₁₈ N ₂ O ₂ S	63.5	6.0	9.3	—
Methyl phenyl ^h	20 ^a	135—136	60.7	5.9	10.1	—	C ₁₄ H ₁₆ N ₂ O ₂ S	60.9	5.8	10.1	—
Phenethyl phenyl	48 ^a	105—106	68.6	6.1	7.7	8.4	C ₂₁ H ₂₂ N ₂ O ₂ S	68.9	6.0	7.7	8.7
Dibenzyl	80 ⁱ	125	68.9	6.0	7.7	8.9	—	—	—	—	—
Diphenyl	—	139—141 ^j	—	—	8.4	—	C ₁₉ H ₁₆ N ₂ O ₂ S	—	—	8.3	—

^a Prisms. ^b Needles. ^c Found: Cl, 9.3. Req.: Cl, 9.2%. ^d Prepared in pyridine (95%; 3 hr.); yellow. ^e Prepared in boiling ether (48 hr.). ^f Reaction product separated by carbon tetrachloride into less-soluble hydrazide and more-soluble N-benzyl-N-toluenesulphonyl-p-chloroaniline (mixed m. p.). ^g Prepared in boiling ether (24 hr.). ^h Prepared in boiling ether (30 min.). ⁱ Plates. ^j Cubes.

TABLE 4. N-Benzyl-N-phenyl-N'-sulphonylhydrazines.

Acyl group	Yield (%)	M. p.	Found (%)				Formula	Required (%)		
			C	H	N	S		C	H	N
Benzenesulphonyl	50	119° ^a	67.2	5.4	8.3	8.3	C ₁₉ H ₁₆ N ₂ O ₂ S	67.5	5.3	8.3
Toluene-o-sulphonyl ^b	60	111 ^c	67.8	5.7	7.8	—	C ₂₀ H ₂₀ N ₂ O ₂ S	68.2	5.7	8.0
p-Chlorobenzenesulphonyl	60	157 ^d	60.8	4.6	7.4	—	C ₁₉ H ₁₄ ClN ₂ O ₂ S	61.2	4.6	7.5
p-Nitrobenzenesulphonyl ^e	70	178—179 ^a	59.5	4.6	11.3	—	C ₁₉ H ₁₄ N ₂ O ₂ S	59.5	4.4	11.0
Methanesulphonyl	35	119—120 ^a	60.8	5.7	9.7	—	C ₁₄ H ₁₆ N ₂ O ₂ S	60.8	5.8	10.0
Ethanesulphonyl	—	119—120 ^a	62.0	6.2	9.7	—	C ₁₅ H ₁₈ N ₂ O ₂ S	62.1	6.2	9.7
Propane-2-sulphonyl	45	100 ^a	63.0	6.7	9.4	—	C ₁₆ H ₂₀ N ₂ O ₂ S	63.2	6.6	9.2

^a Needles. ^b Prepared in boiling ether (3 days). ^c Prisms. ^d Plates. ^e Yellow. ^f Found: S, 10.3. Req.: S, 10.5%.

decomposes at 120° with vigorous effervescence, giving benzaldehyde, recognised as 2,4-dinitrophenylhydrazone (18%). p-Chlorobenzene,¹⁵ p-nitrobenzene,¹⁶ methane,¹⁷ ethane,¹⁷ and propane-2-sulphonyl¹⁷ chlorides were prepared by known methods.

Neither toluenesulphonyl chloride nor methanesulphonyl chloride gave a hydrazide with N-diphenylmethyl-N-phenylhydrazine. Reaction in benzene or in pyridine gave only sym-tetraphenylethane and unchanged hydrazine. N-α-Methylbenzyl-N-phenylhydrazine gave no hydrazide with toluenesulphonyl chloride; with p-nitrobenzenesulphonyl chloride it gave no hydrazide, a little acetophenone (identified as 2,4-dinitrophenylhydrazone), and some 6% of N-α-methylbenzyl-p-nitrobenzenesulphonanilide, pale yellow needles (from ethanol), m. p. 182—184° (Found: C, 62.4; H, 4.8; N, 7.4. C₂₀H₁₈N₂O₄S requires C, 62.8; H, 4.7; N, 7.3%).

Decomposition of Sulphonhydrazides.—(i) N-Benzyl-N-phenyl-N'-toluene-p-sulphonylhydrazine (2 g.) and 5% aqueous sodium hydroxide (30 ml.) were heated at 100° for 1 hr. with occasional shaking. The solid crystallised from ethanol-water, giving benzaldehyde phenylhydrazone (mixed m. p.; 740 mg.). Chlorination of the aqueous filtrate at 0° gave toluenesulphonyl chloride (mixed m. p.).

(ii) The sulphonhydrazide (4 g.) was decomposed with aqueous alkali, and the crude hydrazone shaken with ligroin (b. p. 40—60°; 20 ml.). This extracted a yellow oil which after chromatography on alumina (elution by ligroin) gave 200 mg. of a colourless, nitrogen-free oil smelling like diphenylmethane. Nitration with concentrated sulphuric acid-fuming nitric acid gave a solid, m. p. 160—165° (from ethanol). With alcoholic sodium hydroxide this gave the blue colour characteristic of 2,4,2',4'-tetranitrodiphenylmethane (m. p. 172°; mixed m. p. 140°).

¹⁵ Chem. Fabr. Weiler-Ter Meer, G.P. 385,049.

¹⁶ Bell, J., 1928, 2770.

¹⁷ Johnson and Sprague, J. Amer. Chem. Soc., 1936, 58, 1348.

(iii) The sulphonhydrazone (4 g.) was refluxed with 2% aqueous sodium hydroxide (150 ml.) for 1 hr., and 60 ml. were distilled. The distillate was shaken with ligroin (b. p. 60–80°) (30 ml.), and the extract distilled. Nitration of the fraction boiling below 80° gave *m*-dinitrobenzene (600 mg.; mixed m. p.); the higher-boiling portion gave benzaldehyde 2,4-dinitrophenylhydrazone (60 mg.; mixed m. p.).

Benzaldehyde phenylhydrazone was also produced in quantity by heating the sulphonhydrazone with solid potassium hydroxide at 140°, or by refluxing it for 2 hr. with sodium hydroxide in ethanol-water (2 : 1).

The other sulphonhydrazides were treated as in (i) above (aqueous ethanol was used as solvent in case 6 of Table 1), and the hydrazones had the properties described in the literature. In cases 2–5 and 7, identity was confirmed by mixed m. p. with authentic material.

N-p-Nitrobenzyl-*N*-phenyl-*N'*-toluenesulphonylhydrazine, with an excess of hot aqueous-ethanolic sodium hydroxide, gave a dark brown powder, m. p. >250°, insoluble in ethanol. Heated with 1 equiv. of alkali, the hydrazone yielded a red, uncrystallisable gum which gave a green colour with ethanolic alkali. With ethanolic sodium hydroxide, *p*-nitrobenzaldehyde phenylhydrazone gave a similar green colour and, on refluxing, an insoluble solid resembling that obtained from the hydrazone.

N-Benzyl-*N*-2-naphthyl-*N'*-toluenesulphonylhydrazine (3 g.) was refluxed for 2 hr. in ethanol with 10% aqueous sodium hydroxide (10 ml.). Ethanol was distilled off, water added, and the solid produced separated by ligroin into soluble naphthalene (420 mg.; mixed m. p.) and insoluble benzaldehyde 2-naphthylhydrazone (650 mg.; m. p. 194°).

N-Allyl-*N*-phenyl-*N'*-toluenesulphonylhydrazine (2 g.) gave with warm aqueous sodium hydroxide a steam-volatile oil which crystallised from ligroin as yellow plates (550 mg.), m. p. 47–48°. The compound, which is insoluble in dilute acid, does not give the violet colour with chromic acid characteristic of pyrazolines,⁸ and immediately liquefies when mixed with 1-phenylpyrazoline (m. p. 52°), is regarded as *acraldehyde phenylhydrazone* (Found: C, 73.8; H, 7.0; N, 18.8. C₉H₁₀N₂ requires C, 73.9; H, 6.9; N, 19.2%). The infrared spectrum shows high maxima at 999 and 907 cm.⁻¹, consistent with the presence of a vinyl group.

N-Methyl-*N*-phenyl-*N'*-toluenesulphonylhydrazine (1 g.), with hot aqueous alkali, gave a steam-volatile, basic oil (200 mg.) which with benzaldehyde yielded benzaldehyde methylhydrazone.

N-Phenethyl-*N*-phenyl-*N'*-toluenesulphonylhydrazine (1 g.), refluxed with 20% aqueous sodium hydroxide (50 ml.) for 4 hr., gave an oil, the basic portion of which yielded with benzaldehyde, benzaldehyde *N*-phenethyl-*N*-phenylhydrazone¹⁰ (200 mg.; mixed m. p.).

Intramolecular Mechanism.—Equal amounts of *N*-benzyl-*N-p*-chlorophenyl-*N'*-toluenesulphonylhydrazine and *N*-4-chlorobenzyl-*N*-phenyl-*N'*-toluenesulphonylhydrazine were refluxed together with sodium hydroxide solution and the product (A) examined chromatographically, by capillary ascent on Whatman No. 1 paper, ethanol-water (1 : 2 by vol.) being used as solvent. The behaviour of product A was indistinguishable from that of a mixture of benzaldehyde *p*-chlorophenylhydrazone and *p*-chlorobenzaldehyde phenylhydrazone, and addition of 2% of benzaldehyde phenylhydrazone was easily detected. Spots were recognised by their fluorescence under ultraviolet light. Benzaldehyde phenylhydrazone had the *R_F* value 0.45, and each chlorinated hydrazone, 0.30.

Kinetics of the Reaction.—*N*-Benzyl-*N*-phenyl-*N'*-toluene-*p*-sulphonylhydrazine (1.00 g.) in ethanol (50 ml.) was mixed with 0.5N-aqueous sodium hydroxide (10 ml.: 1.77 equiv.) at 74.5° ± 0.1°. Successive portions (5 ml.) were withdrawn, added to cold water (20 ml.), and titrated with hydrochloric acid against phenolphthalein. Results of a typical run are given below; x = diminution in titre (equiv.) after time t (sec.).

t	600	1200	1800	2400	3000	3600	4800	6000	
x	0.20	0.34	0.45	0.52	0.63	0.69	0.76	0.86	
$10^4 k_1$	3.7	3.5	3.3	3.1	3.3	3.3	2.9	3.3	Mean 3.3

An experiment in which one equiv. of alkali was used gave indistinguishable results. The results recorded in Table 1 were obtained in the same way.

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