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Structure and Reactivity of Small Ring Compounds. I. Solvolyses of Spiro[2, 4]hept-4-yl and Spiro[2, 5]oct-4-yl 3, 5-Dinitrobenzoates

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The solvolyses of spiro[2, 4]hept-4-yl, spiro[2, 5]oct-4-yl, 2-methylenecyclopentyl, 2-methylenecyclohexyl, 2, 2-dimethylcyclopentyl, and 2, 2-dimethylcyclohexyl 3, 5-dinitrobenzoates have been examined in 60 wt% aqueous dioxane. The solvolysis rate of spiro[2, 4]hept-4-yl 3, 5-dinitrobenzoate was 850 times greater than that of the corresponding allyl derivative, the 2-methylenecyclopentyl ester, and 3.0×10^5 times greater than that of the 2, 2-dimethylcyclopentyl ester. Similarly, in the cyclohexyl series, spiro[2, 5]oct-4-yl 3, 5-dinitrobenzoate solvolyzed 330 times faster than the 2-methylenecyclohexyl ester and 1.9×10^5 times faster than the 2, 2-dimethylcyclohexyl ester. In a buffered solution, the spiro[2, 4]heptyl ester gave a mixture of spiro[2, 4]heptan-4-ol (46%), bicyclo[3, 2, 0]heptan-1-ol (28%), and 3-methylenecyclohexanol (10%), besides internally-returned 3, 5-dinitrobenzoate of bicyclo[3, 2, 0]heptan-1-ol (12%). Under the same conditions, the spiro[2, 5]oct-4-yl ester produced spiro[2, 5]octan-4-ol (71%), bicyclo[4, 2, 0]octan-1-ol (21%), and 3, 5-dinitrobenzoate of bicyclo[4, 2, 0]octan-1-ol (6%), the product of internal return. The implication of these results are discussed.

It has been known that cyclopropane has physical and chemical properties similar to those of a double bond,[1-16] although its π-bond character, observed in the ultraviolet spectra[7-12] and in the dipole moments,[10,13-16] is less than that of a double bond. The cyclopropyl group, however, stabilizes a neighboring electron-deficient center much more than a vinyl or phenyl group does.[17-31] Although particular attention has been paied to this high

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31) T. Sharpe and J. C. Martin, *ibid.*, **88**, 1815 (1966).

reactivity of cyclopropylcarbinyl derivatives, has ever no clear interpretation on this matter been presented. Thus, Roberts32) has proposed the existence of non-classical intermediates, Winstein19) has introduced the concept of a homoconjugation which stabilizes a carbonium ion, and Hart20) interpreted it in terms of the hyperconjugative resonance. Since the cyclopropyl group involves a large steric strain, amounting to 28 kcal/mol, as Brown has33) qualitatively suggested, a principal factor of its unusual high reactivity may be the steric factor.

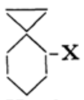
In the present study, the chemical reactivity of a cyclopropylcarbinyl system with a spirane skeleton has been investigated and discussed on the basis of the results of kinetic studies. These compounds have a cyclopropane ring restricted to the particular steric arrangement and are favorable to the obtaining of information on the effect of steric strain. During the course of the investigation, Hanack25) and Closson26) have studied the solvolytic cyclization reactions of cyclopenten-1-yl ethyl and cyclohexen-1-yl ethyl derivatives, and have reported on the rearrangement and the solvolysis rates of the spiro derivatives obtained from those reactions.

The present study includes the solvolyses of spiro[2, 4]hept-4-yl, spiro[2, 5]oct-4-yl, 2-methylenecyclopentyl, 2-methylenecyclohexyl, 2, 2-dimethylcyclopentyl, and 2, 2 - dimethylcyclohexyl 3, 5-dinitrobenzoates; their solvolytic reactivities and reaction products have also been examined.

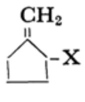
Results

Compounds and Kinetics. The kinetic measurements were carried out on the following esters:

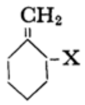
Ia, b



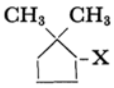
IIa, b



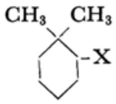
IIIa, b



IVa, b

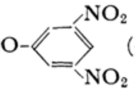


Va, b



VIa, b

a) X=-OH, b) X=-OCO-



$-C_6H_3(NO_2)_2$ (-ODNB)

TABLE 1. SOLVOLYSIS RESULTS IN 60 wt% AQUEOUS DIOXANE

Ester	Temp., °C	$k_1 \times 10^5$ (sec^{-1})	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ e.u.
Ib	55.00a)	2.28 ±0.002	23.2e)	−9.2e)
	70.26a)	12.0 ±0.1		
	75.22a)	23.0 ±0.2c)		
	75.22a)	23.7 ±0.5c,d)		
	85.00a)	49.4 ±0.5		
IIb	64.98a)	1.31 ±0.01	26.7	−2.3
	79.99a)	7.37 ±0.05		
	95.04a)	36.1 ±0.5		
IIIb	100.30a)	0.230±0.003	29.8	−4.9
	130.37a)	4.71 ±0.08		
IVb	100.45a)	0.193±0.001	29.7	−5.6
	116.41a)	1.03 ±0.01		
	130.37a)	4.02 ±0.08		
Vb	130b)	(1.3 ±0.05)$\times 10^{-2}$		
	140b)	(3.4 ±0.4)$\times 10^{-2}$		
VIb	140b)	1.7 $\times 10^{-2}$		

a) Temperature deviation of ±0.02°C.
b) ±0.5°C.
c) Solvolysis rate in the separately prepared 60 wt% aqueous dioxane.
d) Initially 0.0177 M in ester and 0.0200 M is sodium bicarbonate.
e) Activation parameters were calculated from the rates at 55, 70 and 85°C.

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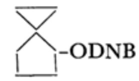
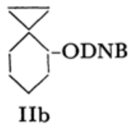
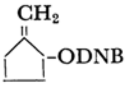
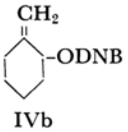
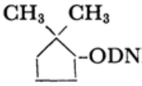
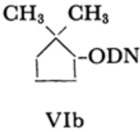
32) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 3542 (1951); R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959); E. Renk and J. D. Roberts, *ibid.*, **83**, 878 (1961); E. F. Cox, M. C. Caserio, M. S. Silver and J. D. Roberts, *ibid.*, **83**, 2719 (1961).

33) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London (1962).

Table 2. Relative solvolysis rates of 3, 5-dinitrobenzoates in 60 wt% aqueous dioxane at 100°C

Compound	 Ib	 IIb	 IIIb	 IVb	 Vb	 VIb
$k_1 \times 10^5$ at 100°C (sec^{-1})	188[a]	59.6[a]	0.222[a]	0.182[a]	6.3×10^{-4} [b]	3.1×10^{-4} [c]
Relative rate	61×10^4	19×10^4	7.2×10^2	6.0×10^2	2.0	1.0
	30×10^4	9.5×10^4	3.4×10^2	2.9×10^2	1.0	
		3.3×10^2		1.0		
	8.5×10^2		1.0			

a) Calculated using the activation parameters.
b) Extrapolated from the rates at 130 and 140°C.
c) Obtained from the ratio k_{VIb}/k_{Vb} at 140°C, which is 0.50.

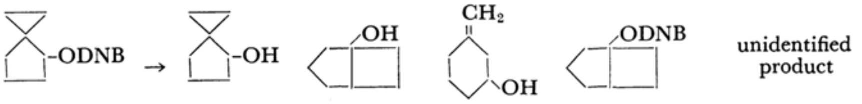


Fig. 1.

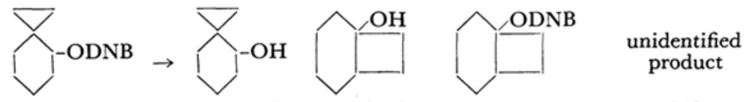


Fig. 2.

Spiro[2, 4]heptan-4-ol (Ia) and spiro[2, 5]octan-4-ol (IIa) were prepared by Dauben's method.[34] We were also successful in preparing 3, 5-dinitrobenzoates, although all attempts to prepare the *p*-toluenesulfonates of these alcohols have failed. The solvolysis rates in 60 wt% aqueous solution of dioxane were measured by titrating the liberated 3, 5-dinitrobenzoic acid potentiometrically with alkali.

There are two possible pathes of the cleavage of 3, 5-dinitrobenzoate, namely, an alkyl-oxygen fission and an acyl-oxygen fission.[35] The kinetic study of spiro [2, 4]hept-4-yl 3, 5-dinitrobenzoate showed a first-order reaction rate throughout the reaction. The addition of sodium bicarbonate to the system caused no change in the reaction rate. Methanolysis, moreover, gave 3, 5-dinitrobenzoic acid, and no alcohol was observed in the products. These results clearly support the idea that the path of the cleavage of this compound involves an alkyl-oxygen fission. The kinetic results are summarized in Table 1 while the relative rates are shown in Table 2.

Solvolysis Products. Since the alcohols formed by the solvolyses of spiro derivatives were found to be unstable under solvolytic conditions, the product analyses were made in the presence of 13% excess sodium bicarbonate in order to avoid any further rearrangement. The presence of a small amount of sodium bicarbonate in a system did not disturb the reaction, as has been described above. In fact, in the absence of sodium bicarbonate, sprio[2, 4]heptan-4-ol was converted to a mixture of 65% bicyclo[3, 2, 0]heptan-1-ol and 35% 3-methylenecyclohexanol, as has been reported by Closson and Kwiatkowski,[26] and also spiro[2, 5]octan-4-ol was converted to bicyclo[4, 2, 0]octan-1-ol under solvolytic conditions. The solvolyses of both the spiro[2, 4]hept-4-yl and spiro[2, 5]oct-4-yl esters gave internally-returned esters of bicyclo[3, 2, 0]heptan-1-ol and bicyclo[4, 2, 0]octan-1-ol in 12% and 6% yields respectively. The carbinol mixture was analyzed by vpc. The results are shown in Fig. 1 and Fig. 2.

Discussion

Table 2 shows that the rates of the solvolyses of spiro cyclopropylcarbinyl derivatives are much faster than those of the allyl derivatives by factors of 850 in cyclopentyl derivatives and 330 in cyclohexyl derivatives. Compared with the saturated homologs, 2, 2-dimethyl derivatives, the spiro ester solvolyzes, surprisingly, 300000 times faster in a cyclopentyl system and 190000 times faster

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[34] W. G. Dauben and H. G. Berezin, *J. Am. Chem. Soc.*, **85**, 468 (1963),

[35] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University, Ithaka, N. Y. (1953), pp. 760—780.

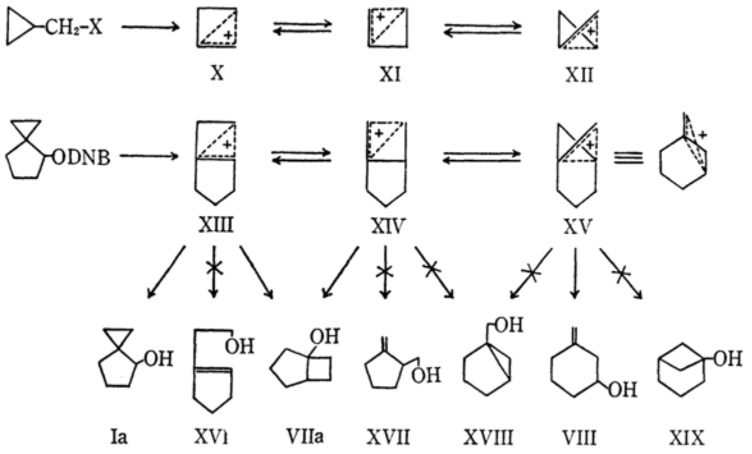

Fig. 3.

in a cyclohexyl system. The high reactivity of cyclopropylcarbinyl derivatives has been interpreted by Hart[20] in terms of the hyperconjugative resonance, and has been attributed by Winstein[19] to homoconjugation. Studies of ultraviolet spectra[7-12] and dipole moments[10,13-16] have revealed that the conjugation ability of a cyclopropyl group is situated between those of carbon-carbon single and double bonds. This finding suggests that cyclopropylcarbinyl derivatives may be expected to be less reactive than allyl derivatives. Solvolyses of the spiro cyclopropylcarbinyl derivatives are, however, much faster than that of the corresponding allyl derivatives. Therefore, it is difficult to understand the high reactivity of cyclopropylcarbinyl derivatives by considering merely the hyperconjugative interaction or homoconjugation between the cyclopropane ring and the electron-deficient center.

As Figs. 1 and 2 show, three alcohols are formed from Ib and two alcohols from IIb. Supposing that the Ib and IIb esters solvolyze through the intermediates corresponding to the bicyclobutonium ions, X, XI, and XII, the existence of which has been proposed by Roberts,[32] one can expect that various products will be formed as in Fig. 3.

Since the positive charge on the XIII, XIV, and XV intermediates is localized mostly on the secondary and tertiary carbon atom, primary alcohols, such as XVI, XVII, and XVIII, may not be formed, while, on the other hand, secondary and tertiary alcohols may be formed. However, the tertiary alcohol XIX was not isolated from the reaction products. Nevertheless, the secondary alcohol VIII was obtained. These compounds may be presumed to be formed from the common intermediate, XV. Moreover, from spiro[2, 5]oct-4-yl 3, 5-dinitrobenzoate, the rearranged product corresponding to VIII was not obtained. Thus, it seems to be difficult to interpret the results obtained in the present study in terms of any hyperconjugative resonance, homoconjugation, or non-classical carbonium ion. We may suppose that the intermediate carbonium ion is essentially classical and that the difference in the hybridization of the carbon atom at the reaction center may result in the high reactivity observed in the solvolyses of cyclopropylcarbinyl derivatives.[36] Other spiro compounds are currently under investigation; the mechanism will be reported in detail in the near future.

Experimental[37]

2 - Methylenecyclopentanol. 2 - *N, N* - Dimethylaminomethylcyclopentanol, prepared by reducing 2 - *N, N* - dimethylaminomethylcyclopentanone[38] with lithium aluminum hydride in the usual manner, was converted to 2-methylenecyclopentanol as follows:[39] To 124 g (0.867 mol) of 2-*N, N*-dimethylaminomethylcyclopentanol in 100 m*l* of methanol, there was added 97.5 g (0.867 mol) of a 30% aqueous hydrogen peroxide solution. As the reaction was considerably exothermic, it was necessary to cool the mixture with an ice bath. After two hours, an additional 97.5 g of a hydrogen peroxide solution were added, after which the mixture was left to stand at room temperature. The completion of the oxidation could be tested by phenolphthalein, as the amine oxide gave no color with this indicator. The excess hydrogen peroxide was destroyed by a small amount of platinum black. The solution was then filtered and concentrated under reduced pressure at a bath temperature of 50—60°C until the amine oxide solidified. The flask containing the amine oxide was

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[36] *Cf*. A. Streitwieser, Jr., *Chem. Revs.*, **56**, 573 (1956); C. S. Foote, *Tetrahedron Lttters*, **1963**, 579.

[37] Melting points were uncorrected. NMR spectra were obtained with a JNM-4H-100. IR spectra were obtained with a Hitachi ESI-S2 infrared spectrophotometer. Hitachi-Horiba pH meter type M-4 was used to measure the solvolysis rate.

[38] C. Mannich and P. Schaller, *Arch. Pharm.*, **276**, 575 (1938).

[39] A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 939 (1953).

connected to a trap cooled in a dry ice - acetone bath and evacuated to *ca.* 10 mmHg. When the flask was heated to 160—170°C, the amine oxide began to decompose. The amine oxide decomposed completely within two hours at this temperature. To the contents of the trap, 500 m*l* of ether were then added. The ether layer was separated and washed successively with a dilute hydrochloric acid solution to remove dimethylhydroxylamine, a 5% sodium bicarbonate solution and a saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. Bp 74—77°C/3 mmHg (lit.39) 77—80°C/50 mmHg), yield 48.7 g (57.3%), n_D^{25} 1.4743 (lit.39) 1.4750), and phenyl urethane mp 81.5—83°C (lit.39) 82.6—83.6°C).

2-Methylenecyclohexanol. Following the same procedure, 2-methylenecyclopentanol was obtained, 2-*N, N*-dimethylaminomethylcyclohexanol40) was oxidized by hydrogen peroxide to the amine oxide, which was then pyrolyzed to 2-methylenecyclohexanol. Bp 73—76°C/16 mmHg (lit.39) 81—85°C/27 mmHg), yield 69%, n_D^{25} 1.4849 (lit.39) 1.4883), and phenyl urethane mp 71—72°C (lit.39) 71.4—72.4°C).

Spiro[2, 4]heptan - 4 - ol. Spiro[2, 4]heptan - 4 - ol was prepared by the method of Dauben and Berezin34) as follows: To a mixture of 500 m*l* of anhydrous ether and 91 g (1.39 mol) of a zinc-copper couple,41) 310 g (1.16 mol) of methylene iodide were added, after which the reaction mixture was refluxed for one hour. Then the flask containing the reaction mixture was immersed in a ice-water bath. To this mixture there was added a solution of 54 g (0.554 mol) of 2-methylenecyclopentanol in 100 m*l* of dry ether over a period of about 30 min. After this addition, the mixture was refluxed for two hours and then cooled. To the reaction mixture 200 m*l* of a saturated ammonium chloride solution were added, and the ethereal layer was separated. The aqueous layer and solid were then washed further with ether. The combined ethereal solutions were washed with two 150-m*l* portions of an ammonium chloride solution, two 150-m*l* portions of a saturated potassium carbonate solution, and two 150-m*l* portions of a saturated sodium chloride solution. The ethereal solution was dried over anhydrous magnesium sulfate and then concentrated. When the residual oil was distilled through a 30 cm Widmer column, a fraction with a bp of 65—67°C/15 mmHg (lit.34) 100°C/68 mmHg) was collected. Yield 44 g (71%). The IR and NMR spectra agreed with those previously reported.23,34)

Spiro[2, 5]octan-4-ol. Using the procedure by which spiro[2, 4]heptan-4-ol was obtained, 2-methylenecyclohexanol was converted to spiro[2, 5]octan-4-ol. Bp 87—88°C/20 mmHg (lit. 76—78°C/20 mmHg,34) 88.5°C/20 mmHg25)) and yield 64%. An NMR spectrum showed absorptions at 6.85 τ (area 1), 7.25 τ(1), *ca.* 8.45 τ (8), and 9.5—9.9 τ (4). The IR spectrum was in agreement with that previously reported.34)

2, 2 - Dimethylcyclopentanol. 2, 2 - Dimethylcyclopentanol was prepared by the lithium aluminum hydride reduction of the corresponding ketone, which has been obtained by the pyrolysis of 2, 2-dimethyladipic acid with barium hydroxide. Bp 153—154°C (lit.42) 153—154°C).

2, 2-Dimethyladipic acid was prepared as follows: To 188 g of 50% nitric acid heated to about 60°C, 500 mg of ammonium vanadate were added, and then 36 g of 2, 2-dimethylcyclohexanol were introduced slowly. 20—30 drops of 2, 2-dimethylcyclohexanol were admitted, after which the reaction mixture was stirred until the reaction had started. Then the reaction flask was placed in an ice-water bath and cooled until the temperature of the mixture fell to 50—55°C. The remaining 2, 2-dimethylcyclohexanol was added as rapidly as possible, while the temperature of the mixture was kept within these limits. Toward the end of the oxidation the ice-water bath had to be removed and sometimes heat had to be applied in order to maintain that temperature. Stirring was continued for about one hour after the addition of alcohol. Then the mixture was cooled in a refrigerator. 2, 2-Dimethyladipic acid was recrystallized from a small amount of water. Mp 88—89°C (lit.43) 85—86°C), and yield 40%. Found: C, 55.16; H, 8.10%. Calcd for $C_8H_{14}O_4$: C, 55.22; H, 8.12.%

2, 2 - Dimethylcyclohexanol. 2, 2 - Dimethylcyclohexanol was obtained by the lithium aluminum hydride reduction of 2, 2-dimethylcyclohexanone prepared by the procedure of Bailey and Madoff.44)

Preparation of the 3, 5-Dinitrobenzoates. The 3, 5-dinitrobenzoates were prepared according to the procedure of Sneen and Baron,21) and were purified by recrystallization from ethanol-water or ether-petroleum ether. The IR and NMR spectra of the esters were fully consistent with the structure. The physical constants and analytical data are given in Table 3.

Kinetic Measurement. *(a) Solvent.* Dioxane was purified as follows:45) Commercial dioxane was boiled under reflux for ten hours with 10% of its volume of 1 N hydrochloric acid, a slow stream of air being meanwhile passed through the condenser in order to remove the acetaldehyde formed. After the same operation has been repeated on the distilled dioxane, in order to remove the water the distilled dioxane was treated with potassium hydroxide and the aqueous layer was removed. The aldehyde-free dioxane was, moreover, shaken with stannous chloride in order to remove the peroxide, and then distilled. Lastly, when the dioxane was refluxed for five hours over sodium, a fraction with a bp of 101—102°C was collected. All distillations were performed through a 30 cm Widmer column.

(b) Standardization of Reagent. Potassium hydroxide was washed with water in order to remove the potassium carbonate formed on the surface, and then made up to approximately 0.02 N in an aqueous solution. It was standardized against potassium biphthalate using phenolphthalein.

(c) Procedure. Approximately 0.02 N solutions of ester were employed, and the reactions were followed by titrating the liberated 3, 5-dinitrobenzoic acid potentiometrically to the pH 8 end point with a standard potassium hydroxide solution.

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TABLE 3. MELTING POINTS AND ANALYTICAL DATA FOR THE 3,5-DINITROBENZOATES

3,5-Dinitrobenzoate	Mp, °C	Carbon, %		Hydrogen, %		Nitrogen, %	
		Calcd	Found	Calcd	Found	Calcd	Found
Ib	87—88	54.90	54.96	4.61	4.76	9.15	9.37
IIb	113—114	56.25	56.42	5.04	5.19	8.72	8.70
IIIb	62.5—63.5[a]	53.43	53.35	4.14	4.26	9.59	9.67
IVb	85—86[b]	54.90	54.91	4.61	4.78	9.15	9.09
Vb	82.5—83.5	54.54	54.56	5.23	5.32	9.09	9.01
VIb	111—112	55.89	56.37	5.63	5.84	8.69	8.86

a) Reported 62.5—65.5°C.[39] b) Reported 86.5—87.5°C.[39]

(c-1) Measurement at Temperatures below 80°C: Exactly 100 m*l* of 60 wt% aqueous dioxane were pipped into a 250 m*l* flask immersed in a constant-temperature bath. After equilibrating the temperature, approximately 0.002 M of ester was placed in the flask, and the solution was thoroughly mixed. At appropriate time intervals, 5 m*l* aliquots were withdrawn, quenched in 50 m*l* of acetone, and titrated immediately. The infinity titers were obtained by heating the solution for a period corresponding to at least ten half-lives, returning it to the bath to equilibrate, and titrating it as has been described above.

(c-2) Measurement at Temperatures above 80°C: For runs at temperatures above 80°C, it was convenient to use ampoules. After dissolving approximately 0.002 M portions of the ester weighed accurately with 100 m*l* of 60 wt% aqueous dioxane in a volumetric flask, the solution was distributed among 14 ampoules and sealed. The time was taken first when the first ampoule was quenched in an ice-salt bath. With 50 m*l* of acetone, 5 m*l* aliquots were diluted and titrated.

The data for a typical kinetic run are listed in Table 4.

TABLE 4. SOLVOLYSIS OF 0.0197 M SPIRO[2,4]HEPT-4-YL 3,5-DINITROBENZOATE IN 60 WT% AQUEOUS DIOXANE AT 70.26±0.02°C

Time, sec	Base, m*l*[a]	$k_1 \times 10^4$ (sec^{-1})
—	0.056	—
1102	0.598	1.21
1895	0.958	1.23
3155	1.426	1.20
4028	1.715	1.19
4620	1.902	1.20
5435	2.135	1.20
6305	2.352	1.19
7390	2.583	1.18
8708	2.869	1.19
10263	3.143	1.20
12258	3.406	1.20
∞	4.407[b]	—
	Mean	1.20±0.01

a) Volume of 0.0197 N potassium hydroxide solution per 4.995 m*l* aliquot.
b) 88.2% of theoretical.

Product Analysis. *(a) Spiro[2,4]hept-4-yl 3,5-Dinitrobenzoate.* A solution of spiro[2,4]hept-4-yl 3,5-dinitrobenzoate (1.077 g, 0.00352 mol) and sodium bicarbonate (0.335 g, 0.00398 mol) in 200 m*l* of 60 wt% aqueous dioxane was maintained at 90°C for three hours; then it was cooled, and 200 m*l* of water was added. The reaction mixture was extracted with five 75 ml portions of ether, and the combined extracted were washed with several portions of water in order to remove the dioxane. After the solution had been dried over anhydrous magnesium sulfate, the solvent was removed through a 15 cm Widmer column. Vapor phase chromatographic analysis (carbowax 20 M on firebrick 25%, 2 m, 113°C) indicated that the solvolysis product consisted of four components (4 : 53 : 32 : 11)[46] with the retention times of 20.5, 45, 57.5, and 68.5 min respectively. The latter three components were isolated and identified as Ia, VIIa, and VIII respectively by comparing their IR and NMR spectra with those of authentic samples.[25] A preliminary experiment showed that, after ten half-lives, Ib liberated only 87.5% of the theoretical amount of 3,5-dinitrobenzoic acid, and that no additional acid was liberated after twenty half-lives. In an isolation experiment, 15.0 g of Ib in 350 m*l* of a solvent was maintained at 90°C for three hours, and then worked up as above. The extracts were concentrated under reduced pressure to *ca.* 10 m*l*. The residual oil was dissolved in 50 m*l* of methanol and cooled. There was thus obtained 1.6 g of an ester, mp 131.5—134°C. The vpc analysis of the product obtained from the hydrolysis of this crude ester gave practically only one peak, with a retention time identical with that of VIIa. The ester purified by recrystallization from ether - petroleum ether had a mp of 136—137°C, and a mixed-melting-point determination with 3,5-dinitrobenzoate of VIIa (mp 135—13y°C) showed no depression.

(b) Spiro[2,5]oct-4-yl 3,5-Dinitrobenzoate. A solution of spiro[2,5]oct-4-yl 3,5-dinitrobenzoate (1.157 g, 0.00362 mol) and sodium bicarbonate (0.344 g, 0.00410 mol) in 200 m*l* of a solvent was heated at 100°C for three hours. The reaction mixture was then worked up as usual. Vpc analysis (glycerol on fireblick 10%, 2 m, 100°C) indicated that the solvolysis product consisted of three components (2 : 76 : 22).[46] The latter two components were isolated and identified as IIa and IXa respectively by comparing their IR and NMR spectra with those of authentic samples.[25] After ten half-lives, IIb liberated only 93.7% of the theoretical amount of 3,5-dinitrobenzoic acid. An isolation experiment of the rearranged ester was performed as has been described above; it was thus identified as IXb.

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[46] It was assumed that the molar response factors of the individual alcohols were identical.