Table I
Products from Ruthenium Tetroxide Oxidation of Substituted Naphthalenes

Compd[a]	Registry no.	Reaction time[b]	Products	Yield, %
Naphthalene (3)	91-20-3	60 hr	Phthalic acid	70
α-Naphthol (3)	90-15-3	1 hr	Phthalic acid	82
β-Naphthol (2)	135-19-3	1 hr	Phthalic acid	60
1-Methylnaphthalene (7)	90-12-0	24 hr	Phthalic acid	24
			3-Methylphthalic acid	6
2-Methylnaphthalene (5)	91-57-6	24 hr	Phthalic acid	50
			4-Methylphthalic acid	5
1-Methoxynaphthalene (3)	2216-69-5	4 days	Phthalic acid	85
2-Methoxynaphthalene (1)	93-04-9	4 days	Phthalic acid	72
			4-Methoxyphthalic acid	6
2,3-Dimethylnaphthalene (2)	581-40-8	3 days	Phthalic acid	25
1,4-Dimethylnaphthalene (2)	571-58-4	3 days	Phthalic acid	10
			3,6-Dimethylphthalic acid	15
2-Chloronaphthalene (2)	91-58-7	5 days	Phthalic acid	7
			4-Chlorophthalic acid	70
1-Fluoronaphthalene (3)	321-38-0	3 days	Phthalic acid	44
			3-Fluorophthalic acid	11
1-Nitronaphthalene (4)	86-57-7	7 days	Phthalic acid	7
			3-Nitrophthalic acid	63
1-Naphthoic acid (2)	86-55-5	36 hr	Phthalic acid	38
			1,2,3-Tricarboxybenzene	16
2-Naphthoic acid (3)	93-09-4	48 hr	Phthalic acid	28
			1,2,4-Tricarboxybenzene	24
2-Naphthaldehyde (2)	66-99-9	48 hr	Phthalic acid	29
			1,2,4-Tricarboxybenzene	29
			2-Naphthoic acid	2
Tetralin (6)	119-64-2	60 hr	Adipic acid[c]	36
3-Hydroxy-2-naphthoic acid (2)	92-70-6	48 hr	Phthalic acid	85

[a] Numbers in parentheses indicate number of trials. [b] The reaction time can be reduced if more $RuO_2 \cdot 2H_2O$ is used, but this causes large decreases in yields. [c] Large amounts of tars present.

All materials were available commercially; the substituted naphthalenes were purified prior to use by crystallization and/or sublimation.

Acknowledgments. The authors are grateful to Mrs. L. Dabeka for skillful technical assistance and to the National Research Council for financial support.

Registry No.—Ruthenium tetroxide, 20427-56-9.

References and Notes

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Dominance of an Ionic Mechanism over a Cyclic Concerted Process in a Hydrocarbon Solvent

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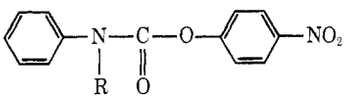
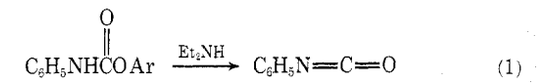
We have investigated the mechanism for the aminolysis of *p*-nitrophenyl *N*-phenylcarbamate (Ia) in toluene.[2] As will be shown below, Ia reacts in the nonpolar solvent through an ionic mechanism to the exclusion of a cyclic six-center process that generates little or no charge.



Ia, R = H
b, R = CH_3

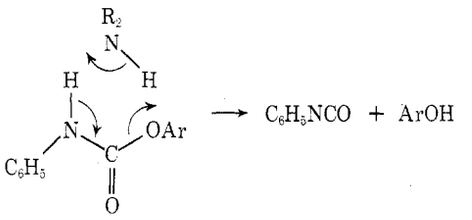
The observed rate constant (as measured by *p*-nitrophenol release) for the reaction of 0.053 *M* diethylamine with 8.7×10^{-5} *M* Ia in toluene at 25.0° was found to equal 1.50×10^{-3} sec^{-1}. This is at least 10^4 faster than that between diethylamine and Ib.[3] If the amine attacked the carbamate carbonyl (to eject *p*-nitrophenol and form a urea *via* a BAC2 mechanism), then Ia and Ib would not differ so widely in their rates.[4] The requirement of an N proton for a facile reaction demands that Ia eliminate to give an isocyanate intermediate (eq 1).[5,6] The intermediate subsequently reacts with amine to produce a urea.



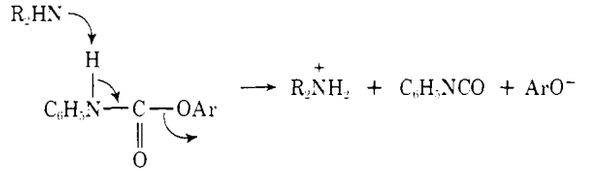
(1)

Formation of the isocyanate in toluene could conceivably occur by one of three mechanisms.

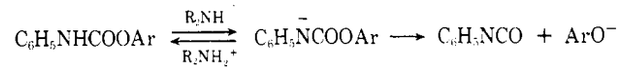
(1) Six-membered cyclic concerted process



(2) E2 mechanism



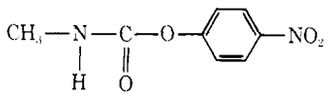
(3) E1cB mechanism



The following results remove the cyclic concerted mechanism as an acceptable possibility. Both diethylamine and triethylamine were found to catalyze the formation of isocyanate from Ia. The triethylamine-catalyzed elimination is first order in amine below 0.1 M amine ($k_2 = 4.5 \times 10^{-2}$ M^{-1} sec^{-1}, toluene, 25.0°).[7] The diethylamine reaction is both first order and second order in amine with the former predominating below 0.1 M amine ($k_2 = 2.2 \times 10^{-2}$ M^{-1} sec^{-1}, toluene, 25.0°). Comparison of the corresponding bimolecular rate constants for the secondary and tertiary amines shows that triethylamine is a twofold better catalyst than diethylamine. Of the three mechanisms above, only the first is inconsistent with this comparison. Triethylamine lacks the necessary N proton to participate in the cyclic pathway. We conclude that the concerted mechanism is incorrect.

Both of the remaining mechanisms entail charge formation. One would predict, therefore, that carbamate aminolysis should be subject to a sizable solvent effect, and this was found to be the case. The reaction of triethylamine with Ia is three orders of magnitude faster in acetonitrile than in toluene.

No evidence was collected which distinguishes the E2 from the E1cB-type mechanism. There does seem, however, to be considerable N–H breakage in the transition state, because Ia reacts over 200 times faster than p-nitrophenyl N-methylcarbamate (II) with triethylamine in toluene.



II

In conclusion, we have found that the aminolysis of Ia prefers an ionic mechanism despite the nonpolar medium and despite the availability of a seemingly feasible concerted pathway. The lack of a concerted proton transfer from a secondary amine to the "ether" oxygen of Ia during the proton abstraction suggests that there is little carbonyl carbon–oxygen bond cleavage in the transition state. If bond cleavage were appreciable, then the cyclic mechanism would be favored because p-nitrophenoxide is undoubtedly a stronger base than an aliphatic amine in a hydrocarbon solvent.[8,9] Our results can also be viewed in terms of the postulate that intramolecular proton transfer is most probable when a cyclic transition state can accommodate a linear arrangement of the donor atom, proton, and acceptor atom.[10] The absence of a cyclic mechanism for aminolysis of Ia might, therefore, stem from the inability of a six-membered ring to attain such a relationship.

Experimental Section

Materials. p-Nitrophenyl N-phenylcarbamate was prepared by refluxing equimolar amounts of p-nitrophenol and phenyl isocyanate in dry toluene for 3 hr. Recrystallization and drying gave pale yellow crystals, mp 148–150° (lit. mp 153–155°,[11] 149–150° [12]).

Anal. Calcd for $C_{13}H_{10}N_2O_4$: C, 60.46; H, 3.90; N, 10.85. Found: C, 60.50; H, 3.91; N, 10.87.

p-Nitrophenyl N-methyl-N-phenylcarbamatewas prepared from p-nitrophenol, N-methyl-N-phenylcarbamoylchloride, and triethylamine in toluene. The product was purified by liquid chromatography and by crystallization to give a 6% yield of product melting at 62–64°.

Anal. Calcd for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.44; N, 10.29. Found: C, 61.83; H, 4.50; N, 10.36.

p-Nitrophenyl N-methylcarbamate was obtained by mixing p-nitrophenol and methyl isocyanate in anhydrous diethyl ether with a trace of triethylamine, mp 162–163° (lit.[2a] mp 157.5–159°).

Kinetics. A stoppered cuvette containing 3.00 ml of a toluene solution of an aliphatic amine (0.01–0.1 M) was equilibrated at 25.0° within the thermostated cell comparment of a Cary 14 spectrophotometer. A small amount (25 μl) of a toluene solution of Ia was then added to the cuvette such that the initial substrate concentration was 8.7×10^{-5} M. The production of p-nitrophenol (measured by the increase in absorbance at 322 nm) was then traced as a function of time.[13] Pseudo-first-order rate constants were secured by processing the absorbance–time data in the usual manner.

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Registry No.—Ia, 6320-72-5; Ib, 49839-35-2; II, 5819-21-6; diethylamine, 109-89-7; triethylamine, 121-44-8.

References and Notes

(1) Recipient of a Camille and Henry Dreyfus Foundation Teacher–Scholar Grant and a National Institutes of Health Research Career Development Award.
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(3) The reaction of Ib is too slow to measure under our reaction conditions; therefore 10^4 is only a *minimum* rate difference.
(4) The rate difference cannot be attributed to steric effects on a BAC2 mechanism because diisopropylamine reacts with Ia nearly as rapidly as does diethylamine.
(5) The same argument has been used in a study of the alkaline hydrolysis of carbamates (ref 2a).
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(7) At concentrations well above 0.1 M triethylamine, the k_{obsd} *vs.* [amine] plot curves downward. The origin of this effect has not yet been established.
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(13) Analysis of the infinity spectra of the triethylamine-catalyzed reaction showed that the production of p-nitrophenol is quantitative.

Selectivity in the Free-Radical Reduction of Lactones with Trichlorosilane[1]

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Each of the generally recognized methods for converting lactones to cyclic ethers suffers from distinct structural limitations. For instance, Adams catalyst in an acidic medium will reduce δ-lactones to the corresponding ethers but fails completely with γ- and ϵ-lactones.[2] Pettit's reagents derived from complex metal hydrides and boron trifluoride are very effective when the alcohol portion of the lactone is tertiary, but the yields of ethers decrease