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$$\%\ \text{D in } \mathbf{9}Z \text{ from } \mathbf{11b} = \frac{k_c}{k_c + k_{eH}}\left(\frac{R}{R+1}\right) + \frac{k_{eH}}{k_c + k_{eH}} = \left(\frac{1}{P_H + 1}\right)\left(\frac{R}{R+1}\right) + \frac{P_H}{P_H + 1}$$

$$\%\ \text{D in } \mathbf{9}Z \text{ from } \mathbf{11c} = \frac{k_c}{k_c + k_{eD}}\left(\frac{R}{R+1}\right) = \left(\frac{1}{P_D + 1}\right)\left(\frac{R}{R+1}\right)$$

where $R = k_H/k_D$ for deprotonation of chlorolium ion **13**; k_c = rate constant for **12** → **13**; k_{eH} = rate constant for **12** → **9Z**, k_{eD} = rate constant for **12** → **9Z** where **12** is deuterated; $P_H = k_{eH}/k_c$ and $P_D = k_{eD}/k_c$; and $P_H/P_D = k_{eH}/k_{eD}$, which is the isotope effect for deprotonation of vinyl cation **12**. To solve these equations, it is necessary to assume a value for either R or P_H/P_D. Once the equation is solved, the fraction of **9Z** formed from chlorolium ion is given by $1/(1 + P_H)$.
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Synthetic and Kinetic Studies on Tricarbonates and Dicarbonates[1]

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The synthesis and properties of di-1-adamantyl tricarbonate (**5**), dicarbonate (**6**), and monocarbonate (**7**) are described. The kinetics of the thermal conversion of **6** to **7** have been measured and the activation parameters determined. Some systematic errors in the previously reported kinetics of the tri- and dicarbonates **1**, **2**, **3**, and **4** are corrected and the mechanisms of the thermal reactions are discussed. Some substituted phenoxycarbonyl derivatives of amino acids, prepared from *tert*-butyl aryl dicarbonates, are described.

In earlier studies,[3-7] the preparation and reactions of a hitherto unknown class of compounds, the di-*tert*-butyl tricarbonates **1** and **2**, were described, along with convenient syntheses of the corresponding dicarbonates **3** and **4**. The utility of the latter for preparing *t*-BOC and thio-*t*-BOC derivatives of amino acids was pointed out;[8] the oxygen dicarbonate[4] has been widely adopted for this purpose,[9] and the reagent is commercially available[10] as well as readily synthesizable in the laboratory.[7,8] The present paper reports further studies on the novel tricarbonates and on other carbonate derivatives.

Di-1-adamantyl tricarbonate (**5**) was prepared as a pure crystalline compound from the sodium salt of 1-adamantanol as shown in eq 1. When heated to approximately 110 °C, **5** melted with decomposition to yield approximately 75% of 2 equiv of carbon dioxide and a mixture of di-1-adamantyl dicarbonate (**6**) and di-1-admantyl carbonate (**7**). Subsequent heating of this mixture above 150 °C led to the formation of only the monocarbonate **7** and 2 equiv of carbon dioxide. Attempts to effect the thermal stepwise transformation of **5** to **6** to **7** were not successful, although a variety of solvents and temperatures was utilized. Thermal decomposition of **5** always led to a mixture of **6** and **7** in addition to carbon dioxide. However, as was the case with **2**, reaction of **5** with a tertiary base in carbon tetrachloride gave solely the corresponding dicarbonate **6** (eq 2).

Examination of the decomposition of pure dicarbonate **6** at approximately 170 °C indicated that the monocarbonate

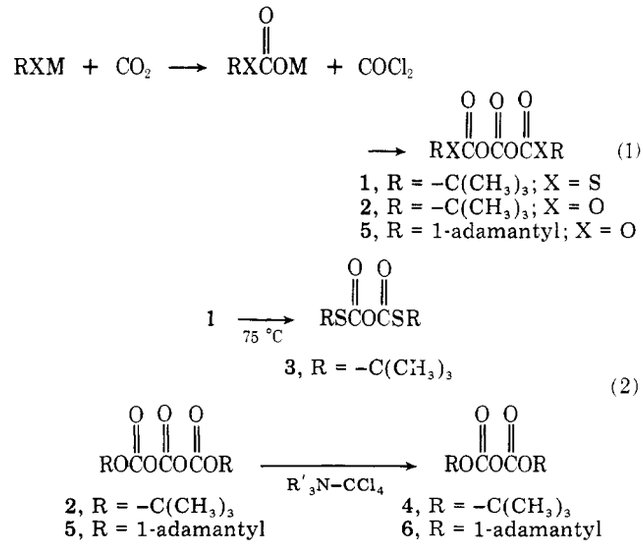

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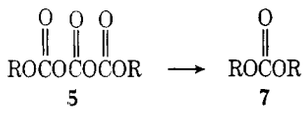
Table I. Kinetics of the Decomposition of 1-Adamantyl Dicarbonate 6 to 1-Adamantyl Monocarbonate 7

Temp,[a] °C	Concn[b]	First order $k \times 10^5$ s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
135.9 ± 0.2	0.0164	9.16 ± 0.05		
	0.0316	9.62 ± 0.18		
146.1 ± 0.1	0.0214	25.5 ± 0.3	32.2	1.2
	0.0229	63.7 ± 0.3		
156.3 ± 0.1	0.0273	66.6 ± 0.6		
100[c]		0.19		

[a] Corrected temperatures. [b] Molar concentration in benzonitrile. [c] Extrapolated.

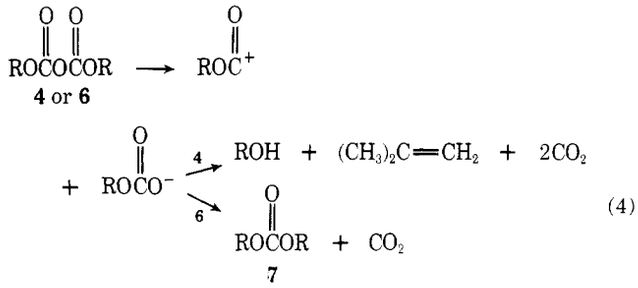
7 and carbon dioxide were the only products (eq 3). Therefore, a kinetic study of this decomposition, in which the decrease



in the carbonyl absorption at 1806 cm^{-1} with benzonitrile as solvent was followed, led to the kinetic results in Table I.

$$6 \xrightarrow{170\ °C} 7 + CO_2 \qquad (3)$$

During this study, we reexamined the original kinetic study on the compounds **1**, **2**, **3**, and **4** and found that a systematic error had been made in the calculation of the rate constants. Therefore, all rate constants and activation parameters have been recalculated from the original data and the corrected results are presented in Table II. There are some interesting implications which can be drawn from the comparision of the decomposition of the 1-adamantyl dicarbonate **6** with the *tert*-butyl dicarbonate **4**. The very similar activation parameters for the two decompositions support a similar mechanism for decomposition. Since the adamantyl system would not be expected to form a free carbonium ion, decomposition probably occurs by initial scission of an internal carbonyl oxygen bond and subsequent loss of carbon dioxide followed by either recombination or proton abstraction and decarboxylation again (eq 4). Furthermore, the corresponding

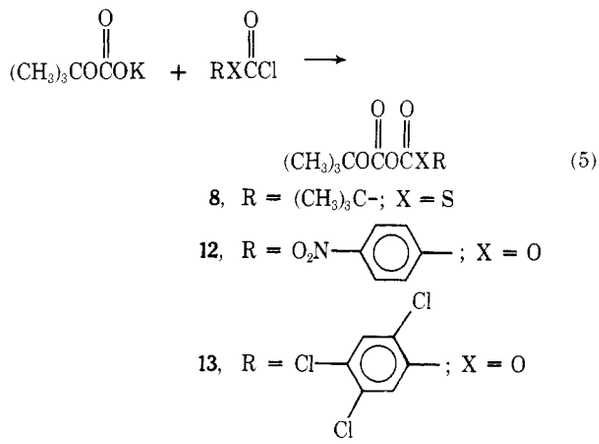


(4)

thiol dicarbonate **3**, the thiol tricarbonate **1**, and the oxygen tricarbonate **2** would appear thus to decompose via a concerted process such as the originally suggested cyclic transition states,[5] on the basis of thier activation parameters.

Attempts to prepare the di- and tricarbonates from 2-adamantanol led to the desired product as evidenced by IR, but analytically pure material could not be obtained. Decomposition of these materials appeared to parallel the corresponding 1-adamantyl system, although quantitative amounts of carbon dioxide were not obtained.

Because of the differences in the mode of decomposition of **3** and **4**, *tert*-butylthiol *tert*-butyl dicarbonate (**8**) was prepared for study following eq 5. It was obtained analytically



(5)

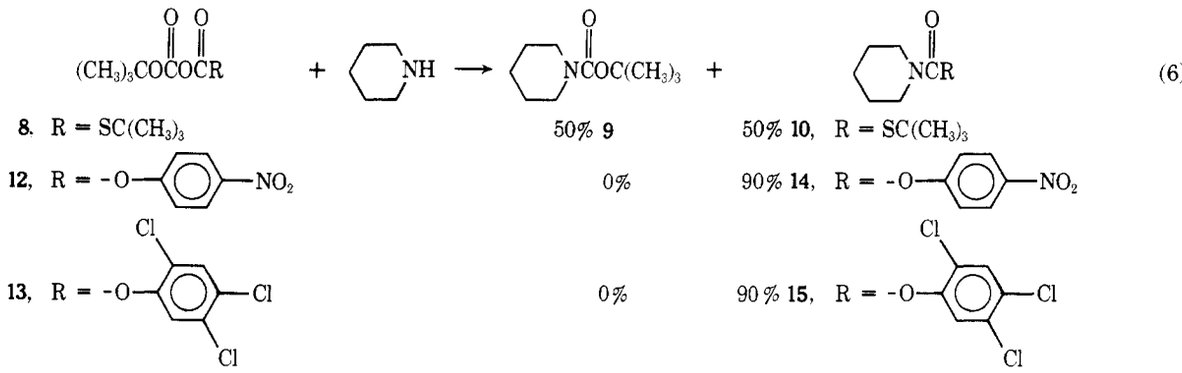
pure and was characterized as having carbonyl absorptions at 1795 and 1730 cm^{-1}.[8,11] Reaction of **8** with piperidine gave an approximately equimolar ratio of carbamate **9** and thiocarbamate **10** (eq 6) as shown by IR.

A crude determination of the decomposition rate of **8** at 162 °C gave a first-order rate constant of 2.0×10^{-4} s^{-1}, a figure which is quite similar to the rate constants for the symmetrical

Table II. Corrected Kinetics[3] of the Decomposition of tert-butyl Di- and Tricarbonates[a] (Each Published[3] First-Order Rate Constant Should Be Multiplied by 2.303; Revised Activation Parameters Are Given Below)

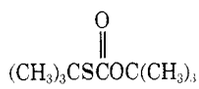
	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
A. RSCOCOCSR → RSCOCSR + CO_2		
In decalin	27.1	−5.2 (105.5 °C)[b]
In chlorobenzene	24.2	−7.2 (82.4 °C)[b]
B. ROCOCOCOR → ROH + $(CH_3)_2C{=}CH_2$ + $3CO_2$		
In decalin	27.8	−4.1 (114.4 °C)[a]
C. RSCOCSR → RSCSR + CO_2		
In decalin	28.8	−9.0 (151.8 °C)[b]
D. ROCOCOR → ROH + $(CH_3)_2C{=}CH_2$ + $2CO_2$		
In decalin	33.7	2.5 (149.4 °C)

[a] R = *tert*-butyl. [b] Corrected temperature ±0.1 °C.



(6)

dicarbonates **3** and **4** at equivalent temperatures. Four separate measurements of the carbon dioxide evolved during decomposition gave a range of 172 to 130% with an average of 147% of 1 equiv. Observed products from the decomposition included carbon dioxide, *tert*-butyl dithiocarbonate, *tert*-butyl alcohol, isobutene, di-butyl carbonate, and *tert*-butyl mercaptan. During the rate determination, a peak at 1710 cm^{-1} increased in intensity through about half the reaction period and then decreased during the remainder of the reaction. This peak did not correspond to any of the above compounds; therefore we suggest that it is due to *tert*-butylthiol *tert*-butyl carbonate (**11**); further, we demonstrated that this



11

can be obtained as the major product with only minor amounts of other materials when the decomposition was carried out overnight at room temperature with Dabco present. All of this information suggests some decomposition by both an ionic chain process and an intramolecular pathway, with the chain process controlling the final product distribution. A change to a polar solvent led to a rapid increase in the decomposition rate and strongly supports the occurrence of an ionic chain process. We feel that these experiments add support to the earlier suggestion that these tertiary di- and tricarbonates containing sulfur can decompose via an intramolecular route, while the corresponding oxygen systems decompose only by the ionic chain.

As an extension of the above study, *tert*-butyl *p*-nitrophenyl dicarbonate (**12**) and *tert*-butyl 2,4,5-trichlorophenyl dicarbonate (**13**) were prepared as shown in eq 5 and their reactivity with amino compounds was examined. Contrary to the reactivity of **8**, both **12** and **13** reacted with piperidine to yield exclusively the corresponding phenoxycarbamates **14** and **15** (eq 6). Subsequently, dicarbonates **12** and **13** were treated with a series of amino acid esters to give the results shown in Table III. Several points are worthy of note. First, **12** and **13** did not attack primary or phenolic hydroxyl groups, primary thiols, or indole nitrogens and attacked only α-amino nitrogens, except for histidine, where the imidazole imino group reacted along with the α-amino group. All of the derivatives were crystalline compounds except for the serine and proline esters. Also, the reaction was carried out very easily at room temperature under mild conditions except for the alanine ester which was refluxed overnight. Attempts to remove the *N*-*p*-nitrophenoxycarbonyl group from **16** with aqueous sodium carbonate and piperidine led to a quantitative yield of *p*-nitrophenol but no isolable glycine ester. However, Wieland[12] reports the removal of the analogous *m*-nitrophenoxycarbonyl grouping by photolysis in the presence of trifluoroacetic acid.

Although chemically interesting, these new dicarbonates are inferior to **3** and **4** as blocking agents. Investigations toward the production of dicarbonates with greater water solubility such as those from 2-hydroxypyridine and numerous other compounds were undertaken, but we were unable to isolate any new dicarbonates with superior physical properties. A water-soluble dicarbonate would be of considerable usefulness in selective alteration of enzymes or proteins.

Experimental Section

Instrumentation was as previously described;[5,13] analyses were by Galbraith Laboratories.

Di-1-adamantyl Tricarbonate (5). A three-necked 1000-mL flask was fitted with a mechanical stirrer, a calibrated addition funnel, and a glass tube for introducing N_2 or CO_2 under the solution surface. This system was flamed while being flushed with dry N_2. A 50% suspension of NaH in mineral oil (5.3 g, 0.11 mol) was washed with three 25-mL portions of freshly distilled THF to remove the mineral oil. The

Table III. R'OC(O)NHCH(R)COOR''; Prepared from *tert*-Butyl *p*-Nitrophenyl Dicarbonate (12) or *tert*-Butyl 2,4,5-Trichlorophenyl Dicarbonate (13)

Registry no.	Compound	R'	Amino acid	R''	Characterization	Mp,[f] °C	Yield
2185-07-1	**16**	NPC[a]	Gly	Et	*c,d,e*	95.5–97	87
65815-64-7	**17**	NPC	L-Ala	Me	*c,d,e*	98–101	78
65815-65-8	**18**	NPC	L-Ser	Me	*c*	—	65[g]
65815-66-9	**19**	NPC	D-Try	Et	*c,d,e*	132–133	89
65815-67-0	**20**	NPC	L-Tyr	Me	*c,d,e*	110–111.5	93
51247-40-6	**21**	TPC[b]	Gly	Et	*c,d,e*	116–117	86
65815-68-1	**22**	TPC	L-Ala	Me	*c,d,e*	101–102	86
65815-69-2	**23**	TPC	D-Try	Et	*c,d,e*	143–144	88
65815-70-5	**24**	TPC	L-Tyr	Me	*c,d,e*	157.5–158.5	96
65815-71-6	**25**	TPC	L-Pro	$C_6H_5CH_2$	*c,d*	—	105[g]
65815-72-7	**26**	TPC	L-CysH	Et	*c,d,e*	90–91	97
65859-22-5	**27**	TPC	L-His	Me	*c,d,e*	67–70	52

[a] *p*-$NO_2C_6H_4$. [b] 2,4,5-$Cl_3C_6H_2$. [c] Correct IR spectrum. . [d] Correct NMR spectrum. [e] Correct elemental analysis. [f] Recrystallized from chloroform–hexane. [g] Did not purify.

washed NaH was placed in 100 mL of THF and 15.2 g (0.1 mol) of 1-adamantanol in 50 mL of THF, and 150 mL of benzene was added over a 30-min period. The solution was heated under reflux for 2 h. It then was cooled by an ice–salt bath, at −15 to −20 °C, and CO_2 was bubbled into the solution for 1 h. A thick gel resulted. A solution of 8 mL of phosgene in 28 mL of benzene was added dropwise to the resulting gel with vigorous stirring over a period 10–15 min. The cooled solution was stirred for 1 h and N_2 was bubbled through the cooled solution for an additional hour.

A yellow solid remained after solvent was removed at or below 0 °C. The solid was washed with pentane to give a white solid. Evaporation of the filtrate yielded additional white solid. The combined total was 16.0 g (80%) of di-1-adamantyl tricarbonate, which decomposed on melting at 109–110 °C with gas evolution. Recrystallization from a small amount of CCl_4 and large amount of pentane did not change the melting point. The IR spectrum (CCl_4) showed carbonyl bands at 1840, 1800, and 1775 cm^{-1} and the NMR spectrum (CCl_4) showed two broad peaks at 1.72 and 2.20 ppm.

Anal. Calcd for $C_{23}H_{30}O_7$: C, 66.01; H, 7.23. Found: C, 66.28; H, 7.24.

Di-1-adamantyl Dicarbonate (6) from the Tricarbonate and Dabco. A solution of 1.27 g of di-1-adamantyl tricarbonate in 8 mL of CCl_4 was placed in a 25-mL flask fitted with a magnetic stirrer and 0.004 g of freshly sublimed Dabco was added. Rapid evolution of carbon dioxide began at once. The reaction mixture was stirred at room temperature for 45 min to complete the loss of CO_2 and then 4 mL of water, containing sufficient citric acid to make the aqueous layer slightly acidic, was added. The layers were separated, the organic layer was dried, and the solvent was removed at room temperature with a rotary evaporator. Recrystallization from a small amount of chloroform and a large amount of pentane solution gave 0.82 g (74%) of white solid of dicarbonate, mp 120–121.5 °C. The IR spectrum ($CHCl_3$) showed carbonyl absorptions at 1806 and 1755 cm^{-1} and the NMR spectrum ($CDCl_3$) showed two broad peaks at 1.65 and 2.16 ppm.

Anal. Calcd for $C_{22}H_{30}O_5$: C, 70.56; H, 8.07. Found: C, 70.36; H, 7.95.

Similar results were obtained with triethylamine as catalyst instead of Dabco.

Thermal Decomposition of Di-1-adamantyl Tricarbonate. a. In the Absence of Solvent. The apparatus consisted of a two-necked flask equipped with a condenser attached to the top of which were a $CaSO_4$ drying trap and a U tube, containing ascarite, connected in series. Di-1-adamantyl tricarbonate (0.525 g) was placed in the flask and a stream of pure dry nitrogen passed through the apparatus slowly via the side arm. (The nitrogen was passed through a concentrated sulfuric acid trap and tubes of ascarite prior to entry into the apparatus.) Then the decomposition flask was immersed in an oil bath and heated at approximately 112–114 °C. The passage of nitrogen was continued until the weight of ascarite in the U tube, which was attached to the top of the condenser, remained constant (1.5 h). The weight of carbon dioxide evolved was 0.0842 g (76% of 2 molecules). Raising the oil bath temperature to 150 °C and continuing to pass the nitrogen for another 2 h, the weight of carbon dioxide evolved totally was 0.1151 g (104% of 2 mol).

b. In Solvent. In an attempt to limit the reaction to the formation of dicarbonate only, a number of runs were made using various solvents (carbon tetrachloride, chlorobenzene, toluene, dioxane, and methylcyclohexane) at their boiling points. In all cases, the tricarbonate, **5**, decomposed to a mixture of dicarbonate, **6**, and monocarbonate, **7**, in various ratios. This mixture was separated by high-pressure liquid chromatography and was compared to the IR spectra of pure di- and monocarbonate.

Kinetic Studies on Di-1-adamatyl Dicarbonate. Commercially available benzonitrile was dried with $CaCl_2$ and distilled from P_2O_5 in an all-glass apparatus. The middle portion of 96 °C (40 mm) of the distillate was collected, n^{25}_D 1.5258 (lit.[14] n^{20}_D 1.5282).

The kinetic runs were carried out essentially as described previously.[5,13]

***tert*-Butyl *tert*-Butylthiol Dicarbonate (8).** The following is a modification of the procedure of Degering.[15] For 30 min dry carbon dioxide was passed into an ice bath cooled three-necked round-bottomed flasked equipped with a mechanical stirrer charged with potassium *tert*-butoxide (4.5 g, 0.04 mol) in 100 mL of dry THF. A solution of *tert*-butylthiol chlorocarbonate (6.1 g, 0.04 mol) in 30 mL of dry THF was then added dropwise with vigorous stirring over a 30-min period and the resulting mixture was refluxed for 3 h. The solution was filtered through a medium-fritted filter and the volume was reduced in vacuo to yield 5.85 g of a material which appeared to be a mixture of at least three components on the basis of its IR spectrum. Distillation under reduced pressure led to three different fractions: the first mainly *tert*-butylthiol chlorocarbonate, bp 45 °C (12 mm); the second a mixture of di-*tert*-butyldithiol carbonate and the title compound, 55–75 °C (1 mm); and the third a fraction of 2.4 g (26%), bp 76–78 °C (1 mm), whose IR spectrum was consistent with the title compound. The NMR spectrum[16] showed a broad singlet at 1.54 ppm in carbon tetrachloride and the neat IR spectrum showed a carbonyl doublet at 1795 (s) and 1730 cm^{-1} (m). A correct elemental analysis was obtained.

Decomposition of *tert*-Butyl *tert*-Butylthiol Dicarbonate (8). These studies were carried out in the same manner which has been described previously.[5,13]

Representative Studies Utilizing *tert*-Butyl *p*-Nitrophenyl Dicarbonate (12) and *tert*-Butyl 2,4,5-Trichlorophenyl Dicarbonate (13). The following are representative of each of the reactions utilizing **12** and **13**.

1. *p*-Nitrophenyl Chloroformate. A stirred solution of 40 g (0.4 mol, ~32 mL) of phosgene in 200 mL of benzene at −10 °C was treated with 48.0 g (0.345 mol) of *p*-nitrophenol, followed by 42 g (0.348 mol) of *N,N*-dimethylaniline at such a rate that the reaction temperature was maintained at 5–10 °C during the addition. The mixture was stirred at room temperature overnight, then was poured into 40 g of ice, and the suspension was filtered. The organic layer in the filtrate was separated, washed with 10% brine (30 mL), 2 N HCl (30 mL), and 10% brine (3 × 30 mL), and dried with $MgSO_4$. The benzene solution was evaporated and yielded 59 g of *p*-nitrophenol chloroformate. The crude product was washed with hexane to give 56 g (80%) of white solid, mp 78.5–80 °C (lit.[17] 81–82 °C). The IR spectrum (CCl_4) showed carbonyl band at 1790 cm^{-1}.

2. *tert*-Butyl *p*-Nitrophenyl Dicarbonate (12). Potassium *tert*-butoxide (9.0 g, 0.08 mol) was dissolved in 140 mL of freshly distilled THF at room temperature in a three-necked 500-mL flask which had been flamed and flushed with dry nitrogen. Dry carbon dioxide was passed through the solution, which was cooled with an ice–salt bath (−15 to about −20 °C), with vigorous stirring for 30 min. A solution of 16.1 g (0.08 mol) of *p*-nitrophenyl chloroformate in 80 mL of THF was added dropwise over a 15-min period. The reaction mixture was stirred at 0 °C for 2 h and then raised to 5–10 °C for another hour. The precipitate was removed by suction filtration through a fritted-glass filter funnel of medium porosity, which had previously been cooled with ice-cold pentane. The precipitate was washed thoroughly with ice-cold pentane and the solution was completely evaporated at a temperature below 0 °C in a rotary evaporator under reduced pressure by a rotary pump to give a white crude product. This product was dissolved in CCl_4 and then filtered. A white solid of 2.6 g of di-(*p*-nitrophenyl) carbonate was isolated, showing a carbonyl band at 1780 cm^- ($CHCl_3$).

The filtrate was evaporated at or below 0 °C by a vacuum pump, washed with pentane, and 14.4 g (64%) of *tert*-butyl *p*-nitrophenyl dicarbonate was obtained. The dicarbonate decomposed on melting at 69.5–70.5 °C with gas evolution. The IR spectrum ($CHCl_3$) showed carbonyl bands at 1835 and 1780 cm^{-1}, and the NMR spectrum (CCl_4) showed peaks at 1.6 (s, 9 H), 7.6 (d, 2 H), and 8.5 (d, 2 H) ppm.

Anal. Calcd for $C_{12}H_{13}NO_7$: C, 50.88; H, 4.59. Found: c, 51.07; H, 4.44.

***N*-(*p*-Nitrophenoxycarbonyl)piperidine (14).** To a solution of 1.13 g (0.004 mol) of *tert*-butyl *p*-nitrophenyl dicarbonate in 3 mL of THF was added dropwise a solution of 0.68 g (0.008 mol) of piperidine in 4 mL of THF, with stirring at 0 °C. The reaction mixture was stirred at room temperature overnight. The solvent was evaporated at a reduced pressure, and the residue was washed with pentane and was recrystallized from chloroform–pentane giving 0.90 g (90%) of yellowish crystals of *N*-(*p*-nitrophenoxycarbonyl)piperidine, mp 91.5–93 °C. The IR spectrum ($CHCl_3$) contained a band at 1720 cm^{-1}. The NMR spectrum ($CDCl_3$) in ppm: 1.70 (broad s, 6 H); 3.75 (broad m, 4 H); 7.60 (d, 2 H); 8.55 (d, 2 H).

Anal. Calcd for $C_{12}H_{14}N_2O_4$: C, 57.60; H, 5.60. Found: C, 57.59; H, 5.69.

***N*-(*p*-Nitrophenoxycarbonyl)glycine Ethyl Ester.** Glycine ethyl ester hydrochloride (1.40 g) was suspended in 20 mL of $CHCl_3$, and 0.84 g of $NaHCO_3$ in 20 mL of H_2O was added. Sodium chloride (2 g) was added, and then 2.83 g of *tert*-butyl *p*-nitrophenyl dicarbonate dissolved in a few milliliters of $CHCl_3$; the mixture was stirred at room temperature overnight. The two layers were separated, and the aqueous layer was extracted with $CHCl_3$; the $CHCl_3$ solution was dried, filtered, and evaporated at room temperature. The milk-white solid was recrystallized from $CHCl_3$–hexane to give 2.3 g (87%) of white crystals of *N*-(*p*-nitrophenoxycarbonyl)glycine ethyl ester, mp 95.5–97 °C.

The IR spectrum (CCl_4) showed –NH stretch at 3440 cm^{-1} and

carbonyl bands at 1740 and 1760 cm^{-1}. The NMR spectrum ($CDCl_3$) in ppm: 1.33 (t, 3 H); 4.10 (d, 2 H); 4.30 (q, 2 H); 5.73 (broad, 1 H); 7.38 (d, 2 H); 8.30 (d, 2 H).

Anal. Calcd for $C_{11}H_{12}N_2O_6$: C, 49.25; H, 4.48, Found: C, 49.05; H, 4.54.

***tert*-Butyl 2,4,5-Trichlorophenyl Dicarbonate (13).** A suspension of 18.3 g (0.15 mol) of potassium *tert*-butoxide in 200 mL of THF was cooled with ice–salt. Carbon dioxide was passed into the suspension with vigorous stirring for 30 min. A solution of 39.0 g (0.15 mol) of 2,4,5-trichlorophenyl chloroformate in 120 mL of THF was added dropwise. The reaction mixture was stirred at 0 °C for 2 h and 5–10 °C for another 1–5 h. Insoluble materials were removed, and the filtrate was evaporated at reduced pressure. The crude product was recrystallized from 400 mL of pentane and then from 280 mL of pentane to give 21.1 g (41%) of *tert*-butyl 2,4,5-trichlorophenyl dicarbonate, mp 65.5–66.5 °C.

The IR spectrum (CCl_4) showed carbonyl bands at 1835 and 1770 cm^{-1}, and the NMR spectrum (CCl_4) showed peaks at 1.62 (s, 9), 7.66 (s, 1 H), and 7.81 (s, 1 H) ppm.

Anal. Calcd for $C_{12}H_{11}Cl_3O_5$: C, 42.17; H, 3.22. Found: C, 42.21; H, 3.28.

Registry No.—**1**, 22085-39-8; **2**, 24424-95-1; **3**, 22085-40-1; **4**, 24424-99-5; **5**, 65815-73-8; **6**, 65815-74-9; **7**, 65815-75-0; **12**, 60416-11-7; **13**, 60450-67-1; **14**, 65815-76-1; glycine ethyl ester HCl, 623-33-6; 1-adamantanol, 768-95-6; *tert*-butylthiol chlorocarbonate, 13889-95-7; di-*tert*-butyldithiol carbonate, 16118-32-4; *p*-nitrophenyl chloroformate, 7693-46-1; *p*-nitrophenol, 100-02-7; di-*p*-nitrophenyl carbonate, 5070-13-3; 2,4,5-trichlorophenyl chloroformate, 4511-19-7.

References and Notes

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Influence of the Steric Requirements of the Nucleophile on the Transition State Structure of E2 Reactions. A Kinetic Study of the Eliminations from 1-Bromo-2-arylethanes and 1-Chloro-1-phenyl-2-arylethanes Promoted by Sodium 2,6-Di-*tert*-Butylphenoxide

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The kinetics of the eliminations from 1-bromo-2-arylethanes and 1-chloro-1-phenyl-2-arylethanes promoted by sodium 2,6-di-*tert*-butylphenoxide in DMF–Me_2SO (9:1 v/v) have been investigated. With the first series of substrates values of ρ (+2.44), k_H/k_D (9.0), and Br/Cl leaving-group effect (146) have been evaluated which turn out to be quite similar to those (+2.64, 7.6, and 120, respectively) calculated for the corresponding reactions promoted by sodium phenoxide. The reaction of 1-chloro-2-arylethanes with sodium 2,6-di-*tert*-butyl phenoxide also exhibits a ρ value (+2.30) which is very similar to that (+ 2.40) of the same reaction with sodium phenoxide. From these results it is possible to conclude that with both series, the transition state structure of the E2 reaction is substantially unaffected by the steric requirements of the nucleophile. The influence of steric effects on the elimination rate is also not very large, sodium 2,6-di-*tert*-butylphenoxide being only 200-fold less reactive than sodium phenoxide.

The study of elimination reactions promoted by sodium phenoxides in a dipolar aprotic solvent provides a very useful tool for investigating the effect of the nature of the nucleophile on the mechanism of E2 reactions. Accordingly, unequivocal information on the effect of the nucleophile basicity upon the transition state structure of E2 reactions has been recently obtained by the study of eliminations from 2-arylethyl derivatives[1-3] induced by phenoxides of different basicity in DMF.

A continuation of this investigation with the purpose of acquiring information also on the effects of the steric requirements of the nucleophile appears worthwhile since it is recognized that these effects can be of importance in determining geometrical and positional orientation of E2 reactions.[4-9] Moreover it has been recently suggested[10] that the steric requirements of the base might play a significant role in producing the "anti-Thornton" behaviors observed in several reactions involving slow proton transfer.[11]

In this paper we report the results of a kinetic study of the eliminations from 1-bromo-2-arylethanes, 1-chloro-1-phenyl-2-arylethanes, and 1-chloro-2-phenylethane promoted by sodium 2,6-di-*tert*-butylphenoxide in DMF–Me_2SO mixed solvent. 2,6-Di-*tert*-butylphenoxide is a sterically very hindered base that has been found to produce a positional orientation much different from that anticipated by its basic strength in the reaction with 2-iodobutane.[6] In the case of

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