Table I. Quantum Yields for Disappearance of Benzyl Diselenide[a] in the Presence of Triphenylphosphine

No.	Ph_3P, M	$-\Phi_{RSeSeR}$
1	0.000	0.16
2	0.050	1.44
3	0.075	2.66
4	0.100	4.70
5	0.200	6.80

[a] 0.1 M RSeSeR in purified, degassed benzene at 298 K exposed with 313-nm light.

of 1 within 1 h. The major primary photoprocess remains facile Se–Se bond cleavage. It appears that benzylselenyl radicals are trapped by 2 to form triphenylphosphine selenide (5) and benzyl radicals which subsequently react to form all photoproducts observed. The following radical chain mechanism is proposed for the reaction:

$$RSe\cdot + Ph_3P \longrightarrow Ph_3\dot{P}SeR \quad (3)$$

$$RSe\dot{P}Ph_3 \longrightarrow R\cdot + Ph_3PSe \quad (4)$$

$$R\cdot + RSeSeR \longrightarrow RSeR + RSe\cdot \quad (5)$$

$$2R\cdot \longrightarrow R{-}R \quad (6)$$

Our results suggest that benzylselenyl radicals formed in reactions 1 and 2 can attack phosphorus atoms to yield a tetracovalent phosphoranyl radical[4,6] with an expanded valence shell (eq 3). Reactions 3, 4, and 5 are the propagation steps with 5 representing the chain transfer reaction. The relatively stable benzyl radicals produced in 4 combine to yield 4 and terminate the radical chain reaction. This reaction mechanism is analogous to that proposed for thiyl radicals in the presence of trialkyl phosphites.[4]

A reviewer has suggested the possible intermediacy of a structure containing a Se=Se moiety:

$$Ph{-}CH_2{-}\underset{\|}{\overset{Se}{Se}}{-}CH_2{-}Ph$$

We have no spectroscopic evidence for such an intermediate. Furthermore, this intermediate is not consistent with the experimental results. Assuming that this intermediate reacts with Ph_3P to yield $Ph_3P{=}Se$ and dibenzyl selenide, no further free-radical chain mechanisms are possible.[7] Thus, the quantum yield for disappearance of 1 could not exceed unity, and no formation of bibenzyl could occur. We may, therefore, rule out this structure as a possible intermediate in the photochemistry of 1.

Experimental Section

General. Melting points were determined using a Thomas-Hoover apparatus and are not corrected. NMR spectra were obtained with a JEOL C60H instrument using tetramethylsilane as internal standard. Uv spectra were measured on a Cary 15 spectrophotometer. GLC analyses were carried out on a Hewlett-Packard 5750 research chromatograph using a 6 ft × 0.125 in. stainless steel column packed with 10% UCON-98 on 80–100 Chromosorb W and temperature programming. EM precoated silica gel F-254 plates (20 × 20 cm) were used for preparative layer chromatography, with benzene–hexane as eluent.

Materials. Benzyl diselenide and dibenzyl selenide were prepared according to previously reported procedures.[1]

Triphenylphosphine selenide was prepared by adapting the procedure of Nicpon and Meek.[8] The crude product was recrystallized from absolute ethanol, mp 187–188° (lit.[8] 187–188 °C).

Solvents. Thiophene-free reagent grade benzene was further purified by storing the solvent over 4A molecular sieves, filtering, and fractionally distilling. Acetonitrile (Burdick & Jackson spectrographic quality) was purified by passing it through a column of alumina (Woelm, activity 1). Deuterated solvents were commercial spectral grade.

General Irradiation Procedures. Preparative photolyses were carried out in water-cooled Pyrex reactors equipped with dry nitrogen purging and magnetic stirring. Solutions containing benzyl diselenide (2×10^{-2} M) and triphenylphosphine (4×10^{-2} M) were deoxygenated by bubbling nitrogen for 50 min and irradiated under nitrogen atmosphere with eight RUL-3500 Å lamps in a Rayonet RPR-208 photochemical reactor. The progress of the reaction was monitored by NMR as described previously.[1] The photoproducts were isolated by preparative layer chromatography on a precoated silica gel plate and identified by comparison with authentic samples. Yields were calculated by using the NMR and GLC integration data. Quantum yield determinations were carried out in degassed benzene and obtained as previously described.[1]

Acknowledgments. We are grateful to Dr. W. H. H. Günther for encouragement and to Mrs. J. Weaver for some experimental assistance.

Registry No.—1, 1482-82-2; 2, 603-35-0; 3, 1842-38-2; 4, 103-29-7; 5, 3878-44-2.

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Steric Effects in the Base-Catalyzed Hydrolysis of *p*-Nitrophenyl Esters. Relative Behavior of Bridged and Nonbridged Trialkyl Acetates

David S. Kristol,* Richard C. Parker, and Howard D. Perlmutter

Department of Chemical Engineering and Chemistry, New Jersey Institute of Technology, Newark, New Jersey 07102

Ku-Chong H. Chen, David H. Hawes, and George H. Wahl, Jr.

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27607

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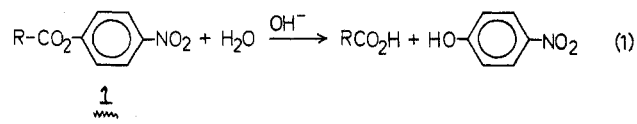
The 1-adamantyl group (1-tricyclo[3.3.1.$3^{3,7}$]decyl) is a substituent which confers a marked increase in lipophilicity on a wide variety of pharmaceuticals without altering their function. The lack of significant information on the substituent effect of this interesting group led us to investigate the base-catalyzed hydrolysis (eq 1) of a series of *p*-nitrophenyl

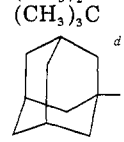
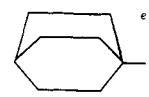


(1)

1

esters (1). In light of Charton's recent findings that alkyl groups do not differ significantly in their electrical effects in base-catalyzed ester hydrolysis,[1] such a study should provide

Table I. Kinetic and Activation Parameters for the Base-Catalyzed Hydrolysis of *p*-Nitrophenyl Alkanoates (1) in 1:1 CH_3CN/0.05 M Aqueous Tris Buffer of pH 9.0

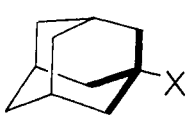
Registry no.	R	Rate constant[a] 23 °C	38 °C	48 °C	Relative rates 23 °C	38 °C	48 °C	$\Delta H^{\ddagger}$[b]	$\Delta S^{\ddagger}$[c]
830-03-5	CH_3	3580 ± 30	9910 ± 70	16800 ± 300	4442	3797	3123	11.2	−22.9
1956-06-5	CH_3CH_2	1130 ± 30	3050 ± 30	5840 ± 10	1402	1169	1086	11.8	−22.7
4195-16-8	$(CH_3)_2CH$	892 ± 30	2330 ± 40	4980 ± 60	1107	893	926	12.3	−21.9
4195-17-9	$(CH_3)_3C$	152 ± 3	484 ± 30	907 ± 20	189	185	169	13.0	−23.1
59711-28-3	 [d]	90.5 ± 1.5	244 ± 2	518 ± 20	112	94	96	12.5	−25.7
59711-27-2	 [e]	83.5 ± 3.1	244 ± 12	500 ± 40	104	94	93	13.0	−24.2
59711-26-1	$(C_2H_5)_3C$[f]	0.806[g]	2.61[g]	5.38[g]	1	1	1	13.7	−30.8

[a] $k_2 \times 10^4$, l. mol^{-1} s^{-1}. [b] kcal mol^{-1}. [c] cal mol^{-1} K^{-1}. [d] Mp 130–131 °C. Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.66: H, 6.12; N, 4.80. [e] Mp 97–98 °C. Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.08. Found: C, 65.08; H, 6.18; N, 4.85. [f] Mp 50–51 °C. Anal. Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.19; H, 7.35; N, 5.43. [g] These are assigned values which were calculated, by means of the Arrhenius equation, from the experimental rate constants of 1.53×10^{-4} at 31 °C and 10.6×10^{-4} at 58 °C.

a direct comparison of the steric requirements ("steric effects") of the various alkyl groups. The compounds studied, along with the second-order rate constants and activation parameters, are shown in Table I.

The data clearly indicate a general decrease in the rate of hydrolysis in the order $CH_3 > C_2H_5 > i\text{-Pr} > t\text{-Bu} > 1\text{-Ad} \sim [2.2.2] > Et_3C$. This is certainly a "steric order" of retardation. The 23 and 38 °C rate data for R = CH_3, CH_3CH_2, $(CH_3)_2CH$, $(CH_3)_3C$, and $(C_2H_5)_3C$ have been correlated with Charton's ν constants by means of his modified Taft equation,[1] with correlation coefficients of greater than 0.99[2].

The *t*-Bu/1-Ad rate ratio of approximately 2 is the same as that observed in the $NaBH_4$ reduction of the ketones $RCOCH_3$ in *i*-PrOH over the temperature range 15–45 °C.[3] In combination, these data argue strongly for a greater steric requirement for the 1-adamantyl (2) and 1-bicyclo[2.2.2]octyl (3) groups, even though they might be considered as con-

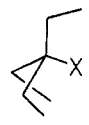


2

3

strained *tert*-butyl groups. A minor contribution may be due to the greater mass ("ponderal effect") of the 1-adamantyl and 1-bicyclo[2.2.2]octyl groups rather than their relative space filling qualities.[4]

It was originally felt that the rigidity of the adamantyl group (as compared with the libration of the *tert*-butyl group) might result in decreased steric interference to attack at a substituent. This now appears unlikely. In fact, it may be this same rigidity which makes for a more congested transition state. The acyclic analogue is free to "bend back" to diminish this strain (Figure 1). Only when the acyclic group is increased in size to the triethyl carbinyl system 4 is steric retardation due to increased hindrance to attack observed.[5]



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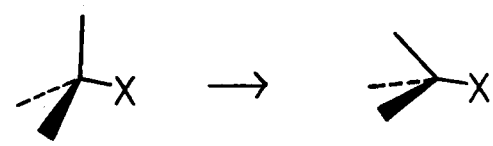

Figure 1.

Charton, using the above correlations, has calculated a ν value of 1.33 for both the 1-adamantyl and 1-bicyclo[2.2.2]-octyl groups,[2] as compared with values of 1.24 and 2.38 for the $(CH_3)_3C$ and $(C_2H_5)_3C$ groups, respectively. Thus the 1-adamantyl and 1-bicyclo[2.2.2]octyl groups appear to have essentially identical steric requirements, and it may be predicted that the latter might also exhibit interesting effects when substituted on pharmaceuticals.

Experimental Section[6]

Materials. Reagent grade acetonitrile was distilled from P_2O_5. Buffer salts and inorganic acids and bases were of analytical grade. The *p*-nitrophenyl esters of acetic and pivalic acids were obtained in reagent grade quality from Aldrich Chemical Co. The esters remaining were prepared by standard synthetic techniques.

Kinetics. In a typical experiment 3 ml of the 1:1 acetonitrile/0.05 M aqueous Tris buffer of pH 9.0 was placed in a cuvette in a Beckmann DU spectrophotometer equipped with a circulating bath that maintained the desired temperature. The reaction was then initiated by injection of 50 μl of the appropriate ester in acetonitrile. The rate was measured by observing the increase in optical density at 400 nm due to the *p*-nitrophenolate ion. The data thus collected were analyzed by the method of initial rates. Regression analysis of the data (ten points) from each run produced correlation coefficients of better than 0.99. Each rate constant reported in Table I is the unweighted average of at least three separate runs.

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