Structural Effects in Solvolytic Reactions. 28. Solvolysis of 1-Aryl-1-cyclopropyl 3,5-Dinitrobenzoates Containing Strongly Electron-Supplying Aryl Groups. Evidence for Two Distinct Reaction Processes Involving Assisted (K_Δ) and Unassisted (K_c) Mechanisms

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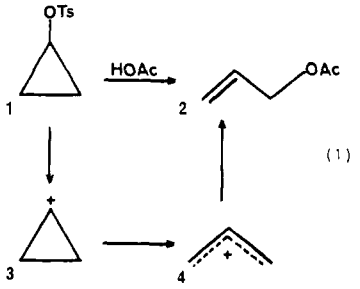
Abstract: New σ^+ constants for the 3,4-methylenedioxy, *p*-ethoxy, and *p*-isopropoxy substituents were determined from the rates of solvolysis of the corresponding 2-aryl-2-propyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C. Moreover, the σ^+ constant for the *p*-dimethylamino substituent was calculated from other data reported in this study. The availability of a greatly expanded series of σ^+ constants in the highly activating region, −1.74 for *p*-Me_2N-, −0.984 for 3,4-ethanooxy(5′-coumaranyl), −0.848 for *p*-*i*-PrO-, −0.811 for *p*-EtO-, −0.778 for *p*-MeO-, −0.676 for 3,4-OCH_2O-, and −0.542 for *p*-MeS-, made possible a detailed examination of the rates of solvolysis of the 1-aryl-1-cyclopropyl 3,5-dinitrobenzoate in 80% aqueous acetone as a function of the electron supply from the activated aryl group. A plot of log *k* vs. σ^+ revealed definite deviation from the usual linear correlation, indicating a change in the mechanism as the electron demand at the cationic center becomes enhanced. The more activating groups, *p*-dimethylaminophenyl and 5′-coumaranyl, yield products which are solely the unrearranged 1-aryl-1-cyclopropanols. With decreasing electron supply (increasing electron demand), the products reveal increasing amounts of the rearranged product, the ring-opened allyl alcohol. Thus, the *p*-MeO derivative gives 13%, *p*-MeS 30%, and *p*-Me 95% of the allyl alcohol product. The rates and the products of solvolysis were determined at two temperatures. From these results the titrimetric rate constants could be dissected into the assisted (k_Δ) and the unassisted (k_c) components. Both log k_Δ and log k_c plot linearly against σ^+. The log k_Δ vs. σ^+ plot yields a value of ρ_Δ + of −2.47. On the other hand, the plot of log k_c vs. σ^+ yields a value of $\rho_c{}^+$ of −7.07, the most negative value of ρ^+ yet observed. This value of $\rho_c{}^+$ correlates nicely with the linear plot of log *k* (for the 1-anisyl-1-cycloalkyl *p*-nitrobenzoates) vs. ρ^+ for the ring derivatives (ring members 3–8), removing the discrepancy previously noted for the cyclopropyl system. Extrapolation of the data for the tertiary derivatives to the parent secondary cyclopropyl system by the Peters' procedure indicates that the solvolysis of the secondary derivative must be enhanced by huge anchimeric assistance, in the neighborhood of $\sim 10^{12}$, much larger than the values estimated previously.

The chemical reactivity of cyclic carbon compounds is influenced markedly by variations in the size of the ring.[2,3] Of these ring compounds, the most extreme in behavior is the cyclopropyl system. Thus, it has been known for many years that cyclopropyl derivatives undergo nucleophilic substitution with the greatest reluctance.[4] This exceptional inertness has been accounted for in terms of I-strain—the highly unfavorable increase in angle strain accompanying the change from the ground state to the transition state.[2,5]

For example, the acetolysis of cyclopropyl tosylate (**1**) proceeds at a rate some 10^5 times slower[6] than that of cyclohexyl tosylate, itself a relatively slow derivative.[3] The acetolysis product is entirely the ring-opened species, allyl acetate (**2**) (eq 1).



(1)

It was suggested that the cyclopropyl tosylate undergoes very slow ionization to a cyclopropyl cation (**3**) followed by a fast opening of **3** to the allyl cation (**4**) (eq 1). However, Schleyer and Nicholas[7] raised objections to this interpretation, pointing out that the rate of acetolysis of **1** was actually faster than that of 7-norbornyl tosylate, despite the considerably larger bond angle at the 7 position. They suggested that the rate of solvolysis of cyclopropyl tosylate must be enhanced and proposed that ionization must be concerted with ring opening.[8]

The precise mechanism of ring opening in carbonium reactions of cyclopropyl derivatives has received widespread attention. It was predicted that the ring opening must be stereospecific and disrotatory,[9] with the direction of ring opening depending upon the stereochemistry of the leaving group.[10] These predictions have received experimental support,[10b,11,12] based largely upon indirect kinetic evidence from cyclopropyl solvolyses and thermolyses. These studies led Schleyer and his co-workers to estimate the anchimeric assistance in the acetolysis of cyclopropyl tosylate to be huge, in the range of $10^{4.7-7}$ [13]

Such enhanced reaction rates with associated ring openings should not be a factor under circumstances where (1) the required disrotatory motion is precluded by geometrical constraints[14,15] or (2) the cyclopropyl cation is stabilized by a substituent which is sufficiently electron rich.[16-18]

The latter appeared to be a promising avenue to explore. It should be possible to introduce highly activating groups which would permit the solvolysis of the cyclopropyl derivatives to proceed without anchimeric assistance or rearrangement. Then, by modifying the substituents, the electron demand could be increased and the effects of anchimeric assistance observed. In this way it should be possible to achieve a quantitative understanding of the importance of anchimeric assistance and rate of solvolysis as a function of the electron demand. Indeed, DePuy and his co-workers pioneered such a study. They examined the acetolysis of 1-aryl-1-cyclopropyl tosylates and reported ρ^+ values both for the normal solvolysis and that involving internal return.[10b,19] Unfortunately, their study was handicapped by the lack of σ^+ values for highly activating groups. Consequently, their study was limited to

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Table I. Rates of Solvolyses of 2-Aryl-2-propyl Derivatives in 80% Aqueous Acetone

aryl group	leaving group	10^6k_1, s^{-1} T_1, °C	T_2, °C	25.0 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	σ^+
p-dimethylaminophenyl[a]							−1.74
5′-coumaranyl	OBz	5.48 (0)		154	21.0	−5.5	
	OPNB			3203[b,c]			−0.984
p-isopropoxyphenyl	OBz	132 (0)		38.0	21.2	−7.8	
	OPNB			790[c]			−0.848
p-ethoxyphenyl	OBz	0.9 (0)		25.2	21.0	−9.2	
	OPNB			524[c]			−0.811
p-methoxyphenyl	OBz			17.2[d]			
	OPNB			372[e]			−0.778
3,4-methylenedioxy-phenyl	OBz			5.76			
	OPNB			199[c]			−0.676
p-methylthiophenyl	OPNB	504 (50)		26.1[b]	22.1	−5.5	−0.542
p-methyl phenyl	OPNB	391 (100)	33.6 (75)	0.072[e,f]	24.8	−8.2	−0.311 0.0

[a] See text. [b] Reference 26. [c] Calculated by multiplying the rate constant for the benzoate by the factor 20.8. [d] These values give k_{OPNB}/k_{OBz} = 21.6, in good agreement, within the experimental uncertainty, with the earlier value 20.8 we have been using. For consistency the value 20.8 will continue to be used. [e] Reference 31. [f] Calculated from the data at higher temperatures.

p-Me and *p*-H as the more activating groups, and neither achieved a solvolysis that was free of anchimeric assistance and rearrangement.

We have recently been exploring the tool of increasing electron demand[20] as a means of achieving understanding of such structure-reactivity questions. Indeed, the tool of increasing electron demand appears to offer major promise for exploring the effect of structure on the stability of carbocations produced in solvolytic processes.[21] It appears to minimize the serious difficulty in structural studies arising from the need to select an appropriate model system for comparison of the rates.[22-24] Representative systems have now been subjected to examination by this tool to establish the effect on the developing carbocationic center of typical cyclic and acyclic groups.

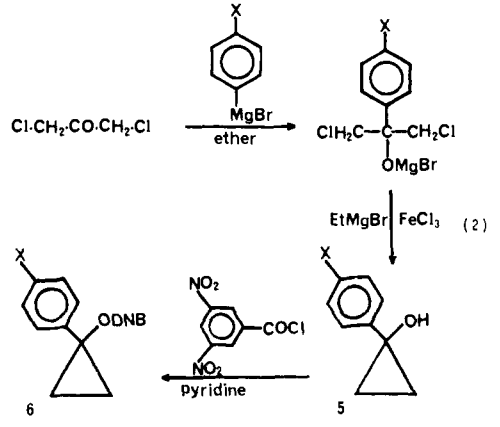
Recently, we applied the tool to the study of the effect of ring size on solvolysis.[25,26] We observed a remarkable parallelism between the ρ^+ values realized for rings of four to eight members and the relative reactivities exhibited by these ring systems.[25] But the cyclopropyl point deviated badly.[26]

The question arose as to whether the relationship between ring size and ρ^+ breaks down with the cyclopropyl ring system or whether the ρ^+ value, based on the titrimetric rate constants, was not the correct value. In all other cases, the 1-aryl-1-cycloalkyl derivatives underwent solvolysis without detectable rearrangement. However, rearranged products were present in the products from all of the 1-aryl-1-cyclopropyl derivatives examined.

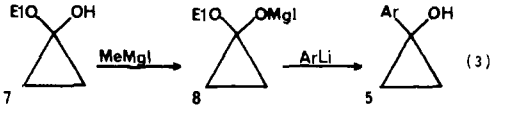
We decided that a full understanding of this system would require σ^+ values for highly activating aryl groups and solvolytic data, both rate and product, for 1-aryl-1-cyclopropyl dinitrobenzoates containing such highly activating groups. That study is here reported. The results provide full clarification of the behavior of the 1-aryl-1-cyclopropyl derivatives.

Results

Synthesis. 2-*p*-Methylthiophenyl-2-propyl *p*-nitrobenzoate, 2-(5′-benzo-1,3-dioxazole)-2-propyl benzoate, 2-*p*-ethoxyphenyl-2-propyl benzoate, 2-*p*-isopropoxyphenyl-2-propyl benzoate, and 2-(5′-coumaranyl)-2-propyl benzoate were prepared by standard methods. 1-Aryl-1-cyclopropanols (**5**, X = *p*-Me, *p*-SMe, 3,4-OCH_2O, *p*-OMe, and *p*-O-*i*-Pr) were synthesized following the general method described by DePuy et al.[27] (eq 2) and converted into the corresponding 3,5-dinitrobenzoates (**6**). The 1-aryl-1-cyclopropanols, *p*-dimethylaminophenyl and 5′-coumaranyl, were synthesized by the following method. Treatment of 1-ethoxycyclopropanol (**7**) with



1 molar equiv of methylmagnesium iodide yielded a species (**8**) which readily reacted with *p*-dimethylaminophenyllithium and 5′-coumaranyllithium to yield the desired 1-aryl-1-cyclopropanol (**5**) in good yield[28] (eq 3). The tertiary alcohols (**5**) were converted into the 3,5-dinitrobenzoates (**6**) by treating them with 3,5-dinitrobenzoyl chloride in pyridine (eq 2). The



properties of the dinitrobenzoates are reported in the Experimental Section.

Solvolysis. The rates of solvolysis of the 2-aryl-2-propyl *p*-nitrobenzoates were determined in 80% aqueous acetone. The rate constants for 2-(5′-benzo-3,4-dioxazole)-2-propyl, 2-(*p*-ethoxyphenyl)-2-propyl, 2-(*p*-isopropoxyphenyl)-2-propyl, and 2-(5′-coumaranyl)-2-propyl *p*-nitrobenzoates were calculated by multiplying the rate of the benzoate by a factor of 20.8,[29] confirmed by comparing the rates of solvolysis of the 2-anisyl-2-propyl derivatives.[26] The pertinent rate data and σ^+ constants are summarized in Table I.

Rates of solvolysis of the 1-aryl-1-cyclopropyl 3,5-dinitrobenzoates were determined in 80% aqueous acetone. The rate constants and the activation parameters for the solvolysis of the various 1-aryl-1-cyclopropyl 3,5-dinitrobenzoates are tabulated in Table II.

Product Studies. The products of solvolysis of 1-aryl-1-cyclopropyl 3,5-dinitrobenzoates were determined in buffered aqueous acetone. The products were analyzed by GC and by ^1H NMR. The results are summarized in Table III.

Table II. Rates of Solvolyses of 1-Aryl-1-cyclopropyl 3,5-Dinitrobenzoates in 80% Aqueous Acetone

aryl group	10^6k_1, s^{-1} T_1, °C	T_2, °C	25 °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
p-dimethylaminophenyl			399		
5′-coumaranyl	399 (125)	33.0 (100)	1.52×10^{-3} [a]	28.84	−2.2
p-isopropoxyphenyl	40.3 (125)	42.6 (125)	1.23×10^{-4} [a]	29.3	−5.5
p-methoxyphenyl	212 (150)	21.4 (125)	4.7×10^{-5} [a]	29.9	−11.0
	11.8 (150)[b]	1.21 (125)[b]	2.93×10^{-6} [a,b]	29.8	−11.0
3,4-methylenedioxyphenyl	102 (150)	9.62 (125)	1.45×10^{-5} [a]	31.03	−4.1
p-methylthiophenyl	22.7 (150)	2.1 (125)	2.87×10^{-6} [a,b]	31.3	−6.5
p-methylphenyl	86.2 (175)	8.23 (150)	1.78×10^{-7} [a,b]	34.8	−0.1

[a] Extrapolated from data at higher temperatures. [b] *p*-Nitrobenzoate. This gives $k_{ODNB}/k_{OPNB} = 16.0$. Reference 26.

Table III. Products of Solvolyses of 1-Aryl-1-cyclopropyl 3,5-Dinitrobenzoates in 80% Aqueous Acetone[a]

aryl group	temp, °C	product, %[b] unrearranged alcohol	rearranged alcohol
p-dimethylaminophenyl	25	100	0
5′-coumaranyl	125	100	0
p-isopropoxyphenyl	150	97.5	2.5
	125	100	0
p-methoxyphenyl	150	87.0	13.0
	125	89.0	11.0
3,4-methylenedioxyphenyl	150	78.5	21.5
	125	80.8	19.2
p-methylthiophenyl	150	70.0	30.0
	125	72.6	27.4
p-methylphenyl	175	5.0	95.0
	150	5.5	94.5

[a] Solvolyzed in 80% aqueous acetone containing 10% molar excess of NaOAc. Solvolyzed for 10 half-lives, except in the case of *p*-CH_3 at 150 °C, where the solvolysis was run only for 2.5–3 half-lives. [b] The products were analyzed by NMR and GC.

Discussion

In our earlier study[26] we had examined the solvolysis of 1-aryl-1-cyclopropyl 3,5-dinitrobenzoates containing moderately activating substituents in the phenyl group (*p*-MeO, *p*-MeS, and *p*-Me). The titrimetric rate constants, over the limited range of σ^+ values available (σ^+ −0.778, −0.542, and −0.311, respectively), plotted linearly against σ^+, providing a ρ^+ value of −5.19, considerably more negative even than the unusual value of −4.91 observed for the related cyclobutyl derivatives,[25] and approaching the exceptional value of −5.27 noted for 7-norbornyl.[20]

However, the failure of this ρ^+ value for cyclopropyl to fit the linear plot we had achieved for the other ring compounds[25] persuaded us of the need to examine the solvolysis of the 1-aryl-1-cyclopropyl 3,5-dinitrobenzoates over a much greater range of electron supply, especially toward the higher range. Previous problems had emphasized examination of the effect of increasing electron demand on various systems. Consequently, we had emphasized obtaining σ^+ constants for substituents toward the lower end of electron supply. Now we undertook to remedy this oversight and provide a full range of σ^+ values in the highly activating region.

σ^+ Constants for Activating Substituents. Determination of the rates of solvolysis of appropriately substituted *tert*-cumyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C (or extrapolated to 25 °C) provided data for the calculation of the σ^+ values for substituents in the activating range. The usual expression, $\log (k/k_H) = \rho^+\sigma^+$,[30] with $\rho^+ = -4.72$[31] was used. For convenience, both the present data and earlier values for substituents in the activating range are listed in Table I.

Because of the extreme reactivity of 2-*p*-dimethylaminophenyl-2-propyl *p*-nitrobenzoate, it was not possible to utilize this method to establish the σ^+ value for the *p*-dimethylamino group. We had to resort to less direct methods.

The σ^+ constant for the *p*-dimethylamino group has been estimated to be −1.58 (uncatalyzed bromination),[32] −1.74 (protonolysis of $ArSiMe_3$),[33] −2.0 (ionization of Ar_2CHOH),[34] −1.55 (ionization of Ar_3COH).[34] An average value of −1.7 had been assigned as the σ^+ value for the dimethylamino group on the basis of these values.[30]

An analysis of the solvolytic rate data for the 7-aryl-7-norbornyl *p*-nitrobenzoates[20] provides a σ^+ value of −1.73 for the *p*-dimethylamino group. Moreover, analysis of our data on the solvolysis of the 1-aryl-1-cyclopropyl dinitrobenzoates gave an almost identical σ^+ value of −1.74 for this group. Consequently, we are adopting a value for σ^+ for the *p*-dimethylamino group of −1.74 (Table I).

Correlation of the Rate Constants. We previously had examined the solvolysis of the 1-arylcyclopropyl dinitrobenzoates containing as activating substituents in the 1-aryl groups *p*-methoxy, *p*-methylthio, and *p*-methyl.[26] The logarithms of these titrimetric rate constants at 25 °C plotted linearly against σ^+ (Figure 1[26]), yielding a ρ^+ value of −5.19.

The present σ^+ values provide a far greater range of reactivity. The rate data for these derivatives are summarized in Table II. However, with this far greater range of reactivities, the log k-σ^+ plot (Figure 1) reveals a definite deviation from a linear correlation.

The plot is clearly reminiscent of the log k-σ^+ treatment of the data for the solvolysis of the 7-aryl-*anti*-norbornenyl derivatives[20] and the corresponding plots for the 3-aryl-2-butyl derivatives.[35,36] In each of these cases the deviations from a linear correlation were quantitatively accounted for in terms of a change in mechanism from k_Δ to k_c for the 7-aryl-*anti*-norbornenyl derivatives and from k_Δ to k_s for the 3-aryl-2-butyl compounds. Accordingly, we were encouraged to undertake a similar analysis of the data for the 1-aryl-1-cyclopropyl dinitrobenzoates.

Solvolysis Products for the 1-Aryl-1-cyclopropyl Dinitrobenzoates. The two derivatives at the upper range of reactivity (electron supply), *p*-dimethylaminophenyl (**9**) and 3,4-ethanooxy (**12**), undergo solvolysis to give 1-aryl-1-cyclopropanols (**11, 14**) with no detectable rearrangement or ring opening (eq 4, 5). To our knowledge, these are the first 1-aryl-1-cyclopropanyl derivatives to undergo solvolysis without detectable rearrangement.

This result is in accord with a simple ionization without anchimeric assistance (a k_c process) to the corresponding carbonium ions, **10** and **13**, which undergo capture of water in the solvent to yield the unrearranged products, **11** and **14**.

With increasing electron demand there appears in the product increasing amounts of the ring-opened derivatives (150 °C): 2.5% for *p*-isopropoxy, 13% for *p*-methoxy, 21.5% for

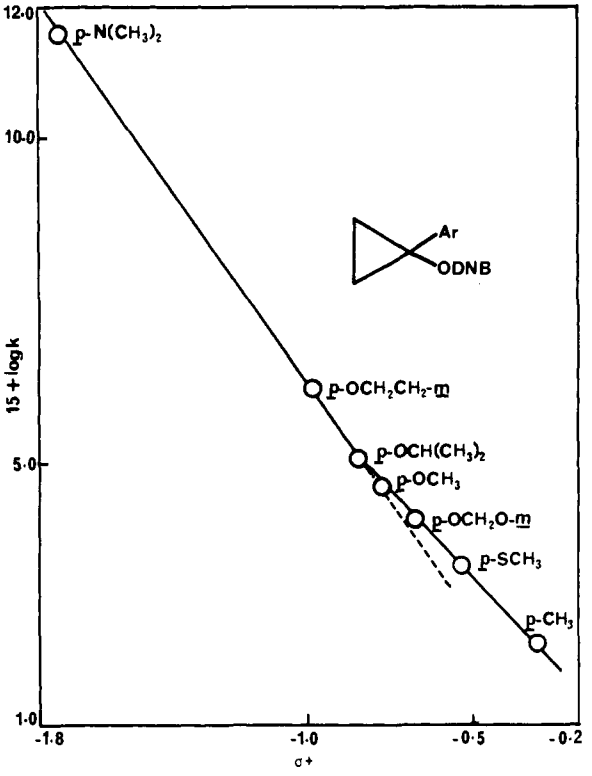


Figure 1. Log k–σ^+ plot at 25 °C for the 1-aryl-1-cyclopropyl 3,5-dinitrobenzoates in 80% aqueous acetone.

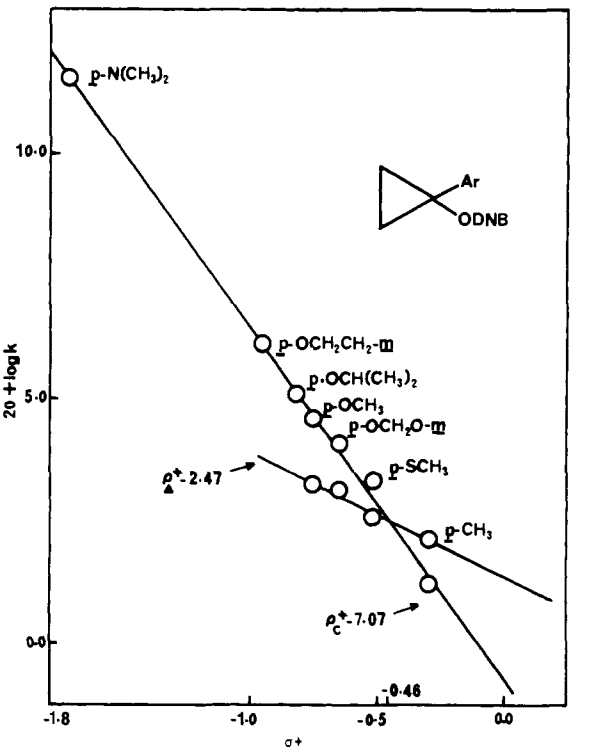
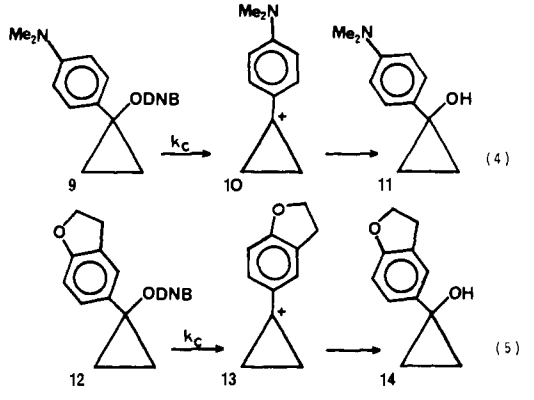
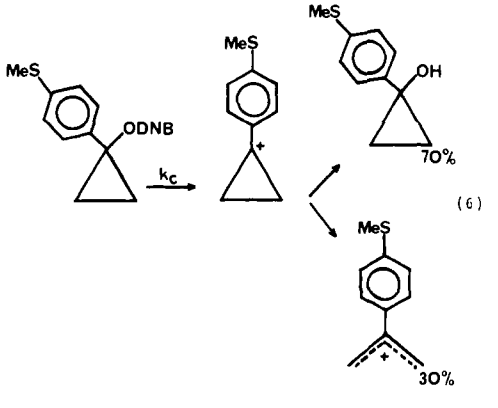


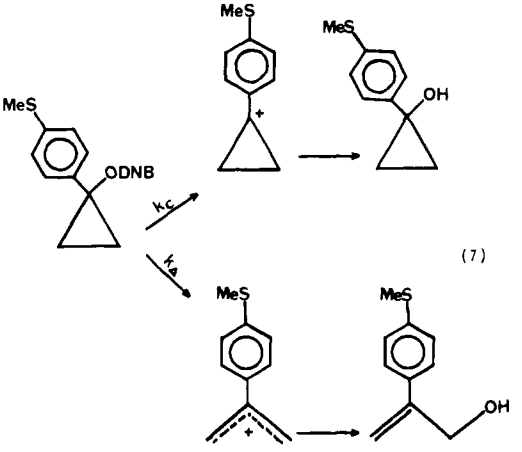
Figure 2. Plots of log k_c–σ^+ and log k_Δ–σ^+ at 25 °C for the 1-aryl-1-cyclopropyl 3,5-dinitrobenzoates in 80% aqueous acetone.



3,4-methylenedioxy, 30% for *p*-methylthio, and 95% for *p*-methyl (Table III).

The question arises as to whether the two products arise from a rate-determining ionization to the cation, followed by a distribution of the cation to the two products (eq 6), or whether the ionization itself follows two pathways, one without anchimeric assistance and the other with (eq 7).





With the considerable confidence engendered by the numerous successful applications of the $\rho^+\sigma^+$ relationship,[30,21] one can predict that a simple ionization process of the kind represented by eq 6 should provide a simple linear log k vs. σ^+ correlation. That is clearly not the case here (Figure 1). On the other hand, concurrent k_c and k_Δ processes should permit an analysis into linear log k_c vs. σ^+ and log k_Δ vs. σ^+. We undertook to test this possibility.

Correlation of the Separated Rate Constants. We assumed that the unrearranged alcohol arises from a k_c process and the rearranged alcohol from a k_Δ process:

$$k_1 = k_c + k_\Delta \qquad (8)$$

The observed value of k_1 at each experimental temperature was multiplied by the fractions of the two products to yield calculated values of k_c and k_Δ at those temperatures. These values could then be extrapolated to 25 °C to obtain individual values of k_c and k_Δ at that standard temperature. The data and results are summarized in Tables IV and V.

A plot of the logarithms of these constants against σ^+ yields two linear correlations which intersect at $\sigma^+ = -0.46$ (Figure 2). That would be the σ^+ value of a substituent which would

Table IV. Dissection of the Titrimetric Rate Constants into the k_c Component

aryl group	10^6k_c, s^{-1} T_1, °C	T_2, °C	25 °C[a]	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
p-dimethylaminophenyl			399		
5′-coumaranyl	399 (125)	33 (100)	1.52×10^{-3}	28.8	−2.2
p-isopropoxyphenyl	393 (150)	42.6 (125)	1.42×10^{-4}	29.2	−5.8
p-methoxyphenyl	184 (150)	19.1 (125)	4.82×10^{-5}	29.8	−5.8
3,4-methylenedioxyphenyl	80 (150)	7.77 (125)	1.39×10^{-5}	30.6	−5.4
p-methylthiophenyl	15.9 (150)	1.53 (125)	2.53×10^{-6}	30.8	−8.3
p-methylphenyl	4.31 (175)	0.45 (150)	2.0×10^{-8}	33.4	−9.3

[a] $\rho_c^+ = -7.07$; correlation coefficient −0.996.

Table V. Dissection of the Titrimetric Rate Constants into the k_Δ Component

aryl group	10^6k_Δ, s^{-1} T_1, °C	T_2, °C	25 °C[a]	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
p-dimethylaminophenyl			~0		
5′-coumaranyl			~0		
p-isopropoxyphenyl	19.4 (150)	very small (125)	~0		
p-methoxyphenyl	27.6 (150)	2.35 (125)	2.02×10^{-6}	32.4	−3.5
3,4-methylenedioxyphenyl	21.9 (150)	1.85 (125)	1.49×10^{-6}	32.5	−3.6
p-methylthiophenyl	6.8 (150)	0.57 (125)	4.65×10^{-7}	32.5	−5.9
p-methylphenyl	81.7 (175)	7.77 (150)	1.59×10^{-7}	34.9	−0.1

[a] $\rho_\Delta^+ = -2.47$; correlation coefficient −0.989.

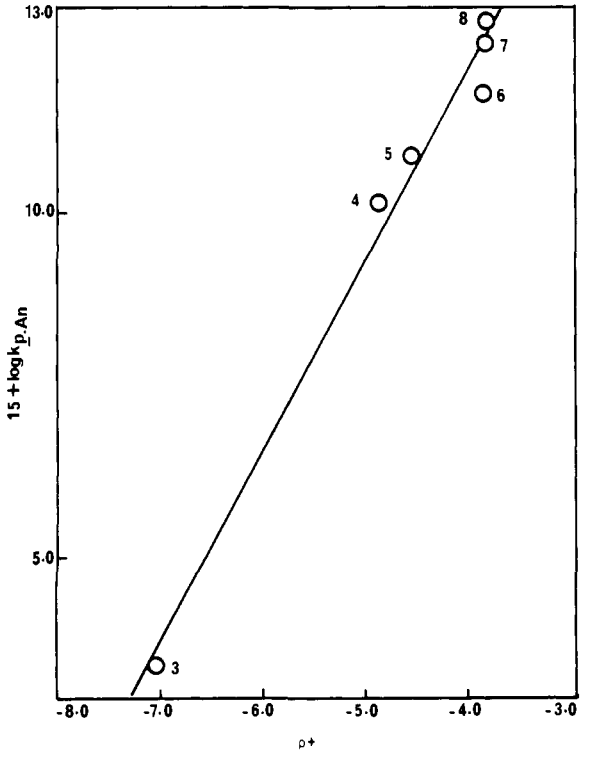


Figure 3. Log k–ρ^+ at 25 °C for the 1-*p*-anisyl-1-cycloalkyl *p*-nitrobenzoates in 80% aqueous acetone.

provide equal values of k_c and k_Δ, i.e., 50% of rearranged and 50% of unrearranged alcohol.

The assisted pathway provides a value of ρ_Δ^+ of −2.47. The unassisted pathway provides a ρ_c^+ of −7.07. This is by far the most negative value of ρ^+ to be encountered in the examination of some 50 systems. It should be compared with the value for 7-norbornyl, the next most negative value which has been encountered, −5.27.[20]

Questions might be raised as to how reliable this value, −7.07, is in view of the manipulations and extrapolations which were necessary to arrive at this quantity. If we utilize the two most reactive derivatives, *p*-dimethylaminophenyl and 5′-coumaranyl (Table II), the temperature extrapolations are far smaller. Moreover, since the products are 100% unrearranged, the observed values of k_1 can be taken as the values of k_c. Utilizing the σ^+ values for these two groups of −1.74 and −0.984 (Table I) yields a ρ_c^+ value of −7.2. Consequently, there would appear to be no reason to be uncertain that ρ_c^+ for the solvolysis of the 1-aryl-1-cyclopropyl dinitrobenzoates is a reaction that is exceptionally sensitive to the substituents in the aromatic ring.

We have been utilizing the tool of increasing electron demand to search for carbon participation (π,[20,37,38] $\pi\sigma$,[39] and σ[40]) in various systems.[21] It is of interest that ρ_Δ^+ reveals a major increase in value over ρ_c^+, with $\Delta\rho^+ = 4.6$ units, even larger than the $\Delta\rho^+$ value of 3.0 realized in the 7-norbornenyl system.[20]

Log k–ρ^+ Correlation for Cyclic Systems. We had previously observed that the logarithm of the rate constants for the solvolysis of the 1-*p*-anisyl-1-cycloalkyl *p*-nitrobenzoates plotted linearly against ρ^+ for rings of four to eight members.[25] However, the ρ^+ value previously realized for the 1-aryl-1-cyclopropyl derivatives, ρ^+ −5.19, based on the assumption of a simple ionization with subsequent rearrangement (eq 6),[26] failed to fit this correlation. It is gratifying to note that the new value realized in this study, −7.07, provides a reasonable fit (Figure 3).

Extrapolation to Secondary Cyclopropyl. As was pointed out earlier, Schleyer and his co-workers had recognized that the rate of acetolysis of cyclopropyl tosylate must involve a large contribution from anchimeric assistance. He had estimated the anchimeric assistance to be in the range of $10^{4.6}$–10^7.[13] We had previously attempted to extrapolate from the tertiary 1-arylcyclopropyl derivatives to the secondary derivatives using the Peters technique[41-44] with γ^+ for hydrogen taken as 2.53. We arrived at a rate enhancement of $\sim 10^6$.

However, the rate constants used in the extrapolation were $k_1 = k_c + k_\Delta$ (eq 8). We now have values for the individual k_c and k_Δ components, with considerably more values than before. Accordingly, we reexamined the extrapolations (Figure 4). It indicates that the acetolysis of the secondary tosylate is enhanced by a factor far larger than has been estimated in the past—a rate enhancement by a factor of $\sim 10^{12}$!

Table VI. Properties of 1-Aryl-1-cyclopropanols

aryl group	yield, %	mp or bp (mm), °C	molecular formula	anal., %		
				C	H	N
p-dimethylaminophenyl	57	113-114	$C_{11}H_{15}NO$	C[a] 74.58	8.47	7.9
				F[b] 74.70	8.24	7.96
5′-coumaranyl	51	130-132 (0.3)	$C_{11}H_{12}O_2$	C 75.0	6.82	
				F 75.09	6.78	
p-isopropoxyphenyl	19	65-66	$C_{12}H_{16}O_2$	C 75.0	8.33	
				F 75.09	8.49	
3,4-methylenedioxyphenyl	40	120-121 (0.1)	$C_{10}H_{10}O_3$	C 67.42	5.62	
				F 67.28	5.50	

[a] Calculated. [b] Found.

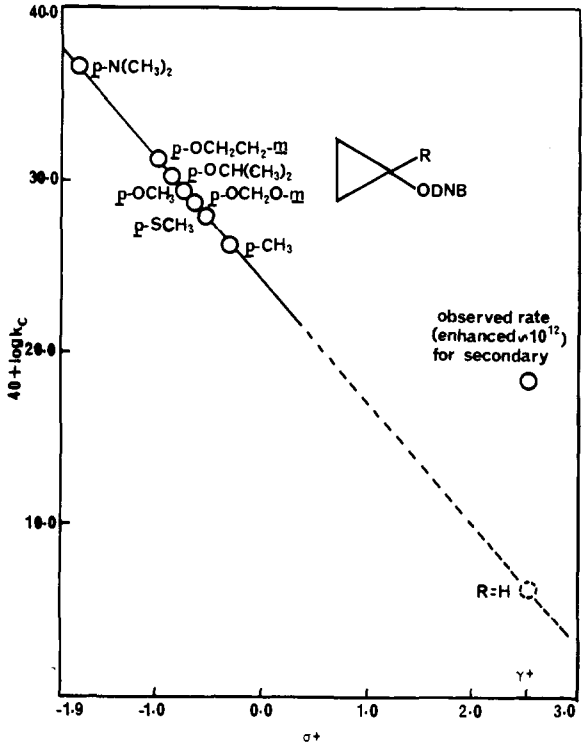


Figure 4. Correlation of the rates for unassisted solvolyses (k_c) of the tertiary cyclopropyl derivatives with that of the secondary.

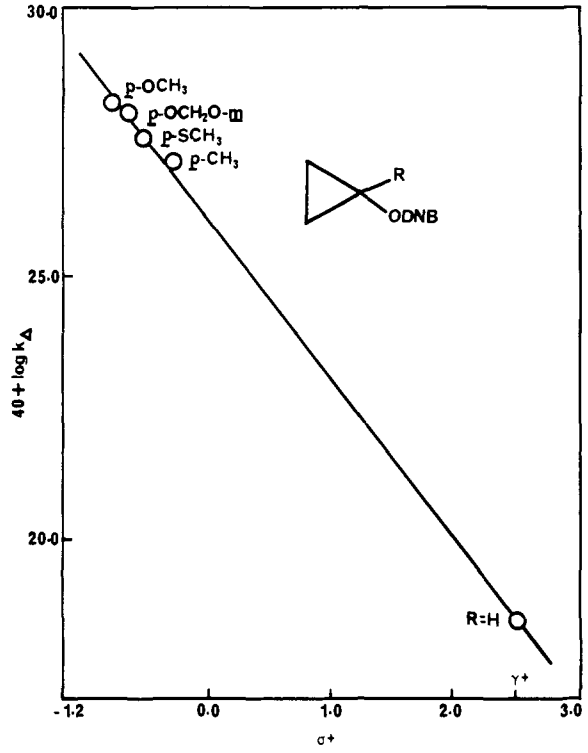
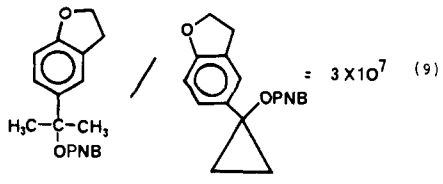


Figure 5. Correlation of the rates for assisted solvolyses (k_Δ) of the tertiary cyclopropyl derivatives with that of the secondary.

It was also of interest to examine the extrapolation of the k_Δ values to cyclopropyl. Here we have fewer data and the extrapolation proceeds from a shorter base. Consequently, the confidence level in this extrapolation must be lower. Nevertheless, the data provide a reasonable correlation of the k_Δ values for the tertiary derivatives with the observed rate constant, presumably k_Δ, for the acetolysis of secondary cyclopropyl tosylate (Figure 5).

Rate Retardation Induced by the Cyclopropyl System. We now have rate data for the 5-coumaranyl derivatives in the *tert*-cumyl system (Table I) and in the 1-aryl-1-cyclopropyl system (Table II). Both systems solvolyze without rearrangement, presumably by a k_c process. A direct comparison of the rates should provide a reasonable estimate for the I-strain retardation induced by the three-ring system[45] (eq 9).



Conclusion

It has been established that 1-aryl-1-cyclopropyl derivatives containing highly electron-supplying aryl groups (*p*-dimethylaminophenyl and 5′-coumaranyl) undergo solvolysis without rearrangement. Derivatives containing poorer electron-supplying groups undergo solvolysis with partial rearrangement. The data permit analysis of the rate constants into two distinct processes, k_Δ and k_c, each of which correlates linearly against σ^+. Consequently, it is concluded that the system undergoes solvolysis with concurrent k_Δ and k_c processes. The value of ρ_c^+, −7.07, is the most negative value yet noted, an indication of the enormous electron demand made as a result of I-strain by the developing cationic center in the three-membered ring. The much less negative value of ρ_Δ^+, −2.47, reveals the effect of carbon participation in partially satisfying this electron demand. With this new value of ρ_c^+, the anomaly previously noted in correlating the reactivities of the 1-*p*-anisyl-1-cycloalkyl derivatives vs. ρ^+ is resolved. Finally, extrapolation of the values of k_c for the tertiary derivatives to the secondary by the Peters' procedure indicates anchimeric assistance in the secondary compound of $\sim 10^{12}$!

Table VII. Properties of 1-Aryl-1-cyclopropyl 3,5-Dinitrobenzoates

aryl group	yield, %	mp, °C	molecular formula	anal., %		
				C	H	N
p-dimethylaminophenyl	76	137–138	$C_{18}H_{17}N_3O_6$	C[a] 58.22	4.58	11.32
				F[b] 58.32	4.62	11.05
5′-coumaranyl	76	147–148	$C_{18}H_{14}N_2O_7$	C 58.32	3.78	7.57
				F 58.19	4.04	7.48
p-isopropoxyphenyl	62	105–106	$C_{19}H_{18}N_2O_7$	C 59.06	4.66	7.25
				F 58.77	4.66	7.06
3,4-methylenedioxyphenyl	60	152–153	$C_{17}H_{12}N_2O_8$	C 54.83	3.23	7.53
				F 55.02	3.42	7.29

[a] Calculated. [b] Found.

Experimental Section

The preparations of 2-(*p*-methylthiophenyl)-2-propyl *p*-nitrobenzoate and 2-(5′-coumaranyl)-2-propyl benzoate were described in an earlier publication.[26]

5-Bromo-1,3-benzodioxazole. The procedure followed is essentially the same as described in the literature.[47] The bromo compound was obtained in 90% yield, bp 85–86 °C (0.9 mm) [lit.[47] bp 85–86 °C (1 mm)].

2-(5′-Benzo-1,3-dioxazole)-2-propanol. 5-Bromo-1,3-benzodioxazole (6 g, 30 mmol) was converted into the Grignard reagent by treatment with ethylene dibromide (5.64 g, 30 mmol) and magnesium (1.66 g, 60 mmol) in ether. To this was added acetone (2.32 g, 40 mmol) in ether at 0 °C. After the usual workup and distillation in vacuo, the pure tertiary alcohol was obtained, bp 102–103 °C (0.05 mm) (50% yield).

2-(5′-Benzo-1,3-dioxazole)-2-propyl Benzoate. The benzoate was prepared by treating the tertiary alcohol with *n*-butyllithium and benzoyl chloride in THF.[48] Examination by NMR indicated that the benzoate was 98% pure. This was used without further purification for the solvolytic studies.

2-*p*-Ethoxyphenyl-2-propanol. To *p*-bromoethoxybenzene (6.03 g, 30 mmol) in ether at 0 °C was added *n*-BuLi (16.7 mL of 1.8 M, 30 mmol). To the lithium derivative thus formed was added acetone (2.32 g, 40 mmol) in ether. After the usual workup, the crude alcohol was obtained as a colorless oil.

2-*p*-Ethoxyphenyl-2-propyl Benzoate. This benzoate was prepared by treating the crude alcohol, 2-*p*-ethoxyphenyl-2-propanol, in THF with *n*-BuLi and benzoyl chloride.[48] The benzoate was obtained as an oil. NMR examination indicated a purity ≥95%. The product was used as such for the rate study.

2-*p*-Isopropoxyphenyl-2-propanol. To *p*-bromoisopropoxybenzene (6.45 g, 30 mmol) in ether at 0 °C was added *n*-BuLi (16.7 mL of 1.8 M, 30 mmol). To the lithium derivative formed was added acetone (2.32 g, 40 mmol) in ether. After the usual workup and distillation in vacuo, the pure tertiary alcohol was obtained, bp 100–102 °C (0.02 mm) (56% yield).

2-*p*-Isopropoxyphenyl-2-propyl Benzoate. This benzoate was prepared by treating the tertiary alcohol with *n*-butyllithium and benzoyl chloride in THF.[48] The benzoate was a liquid, more than 95% pure by NMR. It was used for the rate study without further purification.

1-Aryl-1-cyclopropanols. The 1-aryl-1-cyclopropanols with the substituents *p*-isopropoxy, *p*-methoxy, 3,4-methylenedioxy, *p*-methylthio, and *p*-methyl in the aryl group were synthesized by the procedure described by DePuy et al.[27] The 1-aryl-1-cyclopropanols with the substituents *p*-dimethylamino and 5′-coumaranyl in the aryl group were synthesized by a new method (eq 3). The details of this new synthetic procedure are being reported elsewhere.[28] The properties of the 1-aryl-1-cyclopropanols synthesized are summarized in Table VI.

1-Aryl-1-cyclopropyl 3,5-Dinitrobenzoates. The dinitrobenzoates of the tertiary alcohols were prepared by treating them with 3,5-dinitrobenzoyl chloride in pyridine following the general procedure described earlier.[49] The properties of the dinitrobenzoates are listed in Table VII.

Kinetic Procedure. The procedure employed in determining the rate constants followed that described earlier.[48] All temperatures in the kinetic measurements were controlled to within ±0.02 °C.

Product Analysis. The 3,5-dinitrobenzoates (1 mmol) were solvolyzed in 80% aqueous acetone containing a 10% molar excess of sodium acetate. Sealed ampules were used. After 10 half-lives, ampules were cooled and opened. The acetone was evaporated and the residue extracted with ether. Because of the extreme slowness of the reaction, the *p*-methyl derivative was solvolyzed (150 °C) only for 2–3 half-lives. The solvent was removed and the products were analyzed by GC and ^{1}H NMR. The product compositions are tabulated in Table III.

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Radical Production from the Interaction of Closed-Shell Molecules. 9. Reaction of Ozone with *tert*-Butyl Hydroperoxide[1a]

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Abstract: Ozone reacts rapidly at −60 to 24 °C with *tert*-butyl hydroperoxide (TBH) in various halogenated solvents to produce *tert*-butyl alcohol (70%), acetone (2-10%), and di-*tert*-butyl peroxide (1-9%). A reaction scheme involving both peroxy and alkoxy radicals in radical chain reactions is proposed to account for the products. Evidence for the involvement of the *tert*-butoxy radical in this system was obtained by determining relative rates of hydrogen abstraction from added cyclohexane (to form *tert*-butyl alcohol) vs. β-cleavage (to form acetone). Kinetic studies were carried out for both TBH and *tert*-butyl hydroperoxide-d_1 by two methods: (1) by monitoring the disappearance of dissolved ozone by UV in the presence of excess hydroperoxide; and (2) by measuring peroxide decomposition in an ozone air-flow system. A mechanism is suggested consisting of eq 1-5 (see Scheme I). In addition, the data require a reaction between peroxy radicals and ozone to yield alkoxy radicals and O_2, eq 6. A primary kinetic isotope effect, $k_H/k_D = 2.8 \pm 0.3$, is observed for the radical-producing reaction between ozone and hydroperoxide at −4 °C. The overall Arrhenius parameters are $E_a \simeq 7$ kcal/mol and $\log A \simeq 7$ s^{-1}. We believe that the initial reaction of ozone with hydroperoxide is best formulated as a molecule-assisted homolysis (MAH) reaction. Electron transfer and dipolar insertion mechanisms are eliminated by our data. A series of compounds was studied, and TBH was found to possess a reactivity toward ozone intermediate between that of typical alkanes and alkenes.

Introduction

Reactions in which closed-shell molecules interact to produce free radicals are of considerable theoretical and practical interest.[2-4] In this context, we became fascinated by the reactions of ozone with various organic materials that can lead to radical production even at very low temperatures in the dark. Ozone reacts with olefins to produce radicals under certain conditions[5] and with saturated compounds in processes that often are formulated as involving radicals.[6-8]

We decided to examine the reaction of ozone with hydroperoxides, since the brief communication by Barnard, McSweeny, and Smith[9] suggested that ozone reacts with *tert*-butyl hydroperoxide (TBH) by a molecule-assisted homolysis (MAH) process. Earlier, Bray and Taube[10] had reported a study of the ozone-H_2O_2 reaction and also had proposed a mechanism involving an assisted homolysis. And recently, Bartlett and co-workers[11,12] have used the reaction of ozone with hydroperoxides at temperatures below −50 °C to prepare solutions of trioxides, which they propose are formed by combination of alkoxy and peroxy radicals.

In addition, we are studying the autoxidation of polyunsaturated fatty acids by ozone-air mixtures (at parts per million levels) in an investigation of the mechanisms of ozone-induced lung damage.[13] Fatty acid hydroperoxides are produced in this process; thus, the ozone-lipid hydroperoxide reaction is a possible source of radicals under these autoxidation conditions.

Experimental Section

***tert*-Butyl Hydroperoxide.** Lubrizol (90%) material was fractionally distilled at 20 mm pressure. The main fraction, shown to be 98.6% pure by iodometry, was collected at 40 °C following a forecut containing azeotroped water. *tert*-Butyl hydroperoxide-d_1 was prepared[14] by treating TBH (40 g) in $CDCl_3$ (30 mL) with D_2O (5 × 50 mL). Direct fractional distillation gave a middle cut (15 g) with an active oxygen titer of 98.8% (iodometry). Quantitative IR analysis (O-H stretch, 3530; O-D stretch, 2610 cm^{-1}) indicated about 10% O-H impurity, while quantitative NMR indicated only a trace of O-H proton at 9.1 ppm (ratio of 0.03:9 for methyl proton, indicating 3% proton impurity).

Other Materials. Chloroform (AR grade) was washed with sulfuric acid and then water, dried on $CaCl_2$, and distilled to rid of alcohol stabilizer. Isopropyl alcohol, used as solvent for iodometry, was dried on magnesium sulfate, reluxed with magnesium and iodine, then fractionally distilled.[15] The remaining solvents were found to be greater than 99.98% pure by gas chromatography (GC) and were used directly; if ozone solutions were to be made up in them, they were first pretreated with ozone.[16,17]

Ozonolysis Reactions. Ozonolyses were carried out using a Welsbach T-23 ozonator and appropriate gas-washing apparatus. A high-porosity sintered glass frit was used in reactions carried out at −4 or −24 °C, but a plain tube without a frit was employed to intro-

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