TABLE II

GAS-LIQUID PARTITION CHROMATOGRAPHIC ANALYSES OF NITRATION PRODUCTS OF *cis*- AND *trans*-3-PHENYL-2-PENTENES[a]

Expt no.	1	2	3	4	5
Alkene, %					
trans	3	3	4	96	83
cis	97	97	96	4	17
$AcONO_2$/alkene, max[b]	5	15	5	5	5
erythro, %, obsd[c]	80.5	80.4	77.7	68.9	68.3
erythro, %, cor[d]	87.0	86.8	84.0	74.4	73.8
threo, %, cor	13.0	13.2	16.0	25.6	26.2

[a] All nitrations of 0.003 mole of alkene, run at 0.10° for 5 min. [b] This is the mole ratio of nitric acid to alkene; the ratio of acetyl nitrate to alkene is somewhat lower. [c] Per cent of the total nitro acetates present. [d] Obtained by multiplying the observed percentage of *erythro* by the calibration factor of 1.08.

Nitrations of *cis*- and *trans*-1-Phenylpropenes.—Nitration of samples of *cis*-1-phenylpropene (95% *cis*) and *trans*-1-phenylpropene (96% *trans*) were carried out using 5-min reaction times. The chloroform solutions of the crude products were used for infrared spectroscopy and for glpc analyses. The analyses indicated the presence of only one (and the same) nitro acetate.

Gas-Liquid Partition Chromatographic Analyses of Nitration Products.—Analyses of the chloroform solutions of the nitration products were performed at 170° with a 4 mm i.d. × 4.6 m column packed with 8% silicone oil 550 (Dow Corning) on 60–80 mesh Chromosorb P. The injection port and thermal conductivity cell (detector) temperatures were each about 230°; the bridge current for the detector system was 125 ma, and high amplification was used. Samples taken of the chloroform solutions were usually 200 μl (0.2 ml), or larger if necessary, in cases of low yield of nitration products. Analyses were first carried out on known mixtures. For each nitration three glpc samples were run and the nitro acetate peaks were integrated by cutting out and weighing them. The individual measurements reported in Table II represent the average of the three values, which agreed with good precision.

The glpc analyses of the nitro acetates obtained from *cis*- and *trans*-2-butene[3a] were carried out in a similar manner.

Registry No.—*trans*-2-Phenyl-2-butene, 768-00-3; *cis* isomer of **1**, 767-99-7; acetyl nitrate, 591-09-3; *erythro*-2-acetoxy-3-nitro-2-phenylbutane, 7443-57-4; *erythro*-3-benzamido-2-phenyl-2-butanol, 7431-12-1; *cis*-3-phenyl-2-pentene, 4165-78-0; *erythro*-3-acetamido-2-phenyl-2-butanol, 7443-60-9; *threo*-3-benzamido-2-phenyl-2-butanol, 7443-61-0; *erythro*-3-acetoxy-2-nitro-3-phenylpentane, 7444-76-0; *threo* isomer of **11**, 7444-77-1; *erythro*-2-acetamido-3-phenyl-3-pentanol, 7443-62-1; *threo* isomer of **13**, 7443-63-2; *trans* isomer of **7**, 4165-86-0.

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Leaving Group Effects in Solvolysis Reactions[1a]

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The rate of solvolysis of phenyldimethylcarbinyl *p*-nitrobenzoate and thionbenzoate in ethanol and aqueous ethanol has been determined and compared with the solvolysis of the corresponding chloride. Sensitivity of the solvolysis to the ionizing power of the solvent falls in the order chloride > *p*-nitrobenzoate > thionbenzoate. The products of the solvolysis of the phenyldimethyl derivatives display considerable variation among the leaving groups; the chloride produces 11% 2-phenylpropene and 87% ethyl phenyldimethylcarbinyl ether, while the thionbenzoate produces 85% and 6% of the respective products. The results are interpreted in terms of initial ionization of the substrate to form ion pairs, which may return, dissociate, and give rise to products with the anion influencing the fraction of elimination from the ion pair and the degree of dissociation.

Recently[3] it has become evident that the nature of the leaving group in a limiting solvolysis can effect the product distribution in relatively nondissociating solvents because of the intervention of ion-pair intermediates. For example, the different ratios of olefin products observed in the solvolytic elimination of several 2-phenyl-2-butyl derivatives in acetic acid were interpreted by Cram and Sahyun[3a] as being due to differences in the basicities of the leaving groups, which remain associated with the carbonium ions long enough to affect their fate.

Skell and Hall[3c] reported that the solvolysis of *erythro*- and *threo*-3-deuterio-2-butyl *p*-toluenesulfonate produced olefin by predominately *cis* elimination in nitrobenzene and predominately *trans* elimination in acetamide. These data were interpreted in terms of an intimate association of the leaving group with the carbonium ion with loss of a proton to either the leaving group (*cis* elimination) or the solvent (*trans* elimination.) On the basis of the variation of the products of the thermal decompositions of N,N-dicyclohexylbenzamide *o*-diazonium salts in polar and nonpolar solvents, Cohen and Lipowitz[4] suggested that in solvents of low polarity the formation of carbonium ion pairs play a major role in these reactions. Cocivera and Winstein[3b] have reported an increase in the dependence of the mole fraction of olefin product on the nature of the leaving group in the solvolysis of *t*-butyl and *t*-amyl derivatives with a decrease in solvent dissociating power. With *e.g.*, *t*-butyl chloride, 5% elimination was observed in water at 25° and while in the relatively nondissociating solvent acetic acid, 73% olefin was found at 75°. These results suggested[3b] that large portions of the elimination from *t*-butyl chloride in ethanol and acetic acid involve the counter chloride ion.

The work presented here provides further striking demonstration of the control of product distributions possible by changes in the nature of the counterion

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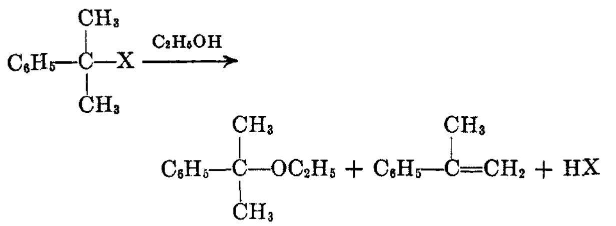
(1) (a) Research was supported by the U. S. Army Research Office (Durham). (b) Alfred P. Sloan Fellow.

(2) The editor wishes to express regret at unusual delays associated with the publication of this work.

(3) (a) D. J. Cram and M. R. Sahyun, *J. Am. Chem. Soc.*, **85**, 1257 (1963); (b) M. Cocivera and S. Winstein, *ibid.*, **85**, 1702 (1963); (c) P. S. Skell and W. L. Hall, *ibid.*, **85**, 2851 (1963).

(4) T. Cohen and J. Lipowitz, *Tetrahedron Letters*, No. 49, 3721 (1964)

in solvolysis reactions. The specific example involves changes in the olefin to ether product ratio resulting from the ethanolysis of phenyldimethylcarbinyl derivatives (eq 1).



$$C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-X \xrightarrow{C_2H_5OH} C_6H_5-\overset{CH_3}{\underset{CH_3}{C}}-OC_2H_5 + C_6H_5-\overset{CH_3}{C}=CH_2 + HX \quad (1)$$

Results

Preparation of Materials and Product Analysis.—Phenyldimethylcarbinyl chloride and *p*-nitrobenzoate were prepared by conventional methods, and phenyldimethylcarbinyl, *p*-methylphenyldimethylcarbinyl, and *p*-trifluoromethylphenyldimethylcarbinyl thionbenzoates were prepared by the action of the sodium salts of the corresponding alcohols[5] on thiobenzoyl chloride.[6]

The ethanolysis of phenyldimethylcarbinyl chloride, trifluoroacetate, and *p*-nitrobenzoate results in the formation of 2-phenylpropene and ethyl phenyldimethylcarbinyl ether. In addition to these products the thionbenzoate also produces 6% phenyldimethylcarbinylthiolbenzoate.

Quantitative product analyses were accomplished by vpc, using internal standards. Solutions used in the determination of the products for these reactions contained *ca.* two to one molar excess of 2,6-lutidine, except for the runs involving the chloride in the presence of excess silver nitrate. The solutions were maintained at the temperatures employed for the kinetic experiments and for times corresponding to *ca.* 10 half-lives of each reaction. The appropriate standards were introduced after the reaction, but before the extraction of products. The applicability of the extraction process was shown by agreement of values for the amount of products weighed into ethanol and the amount determined by vapor phase chromatography after extraction to within ±2% (see the Experimental Section). The results of these product determinations are given in Table I. As summarized in Table I the product ratio varies with the leaving group ranging from 2% 2-phenylpropene from the chloride plus silver nitrate to 85% olefin from the thion ester.

TABLE I

PRODUCTS FROM THE ETHANOLYSIS OF PHENYLDIMETHYLCARBINYL DERIVATIVES[a]

Derivative	Temp, °C	% olefin[b]	% ether[c]	% ester	Total yield, %
Chloride[d]	25	2	96	...	98
Chloride	25.0	11	87	...	98
p-Nitrobenzoate	100.0	53	47	...	100
	100.0	53[e]	49[e]	<1.0[f]	101
	75.0	44	56	...	100
	25.0	30[g]	70[g]	...	100
Thionbenzoate	25.0	85	6	6[h]	97
	25.0	84[i]	5[i]	5.6[f,j]	94

[a] 0.01 *M* with 0.02 *M* 2,6-lutidine added. [b] 2-Phenylpropene. [c] Ethyl phenyldimethylcarbinyl ether. [d] 0.0156 *M* silver nitrate instead of 2,6-lutidine. [e] Contains 0.05 *M* lithium benzoate. [f] Benzoate ester. [g] Calculated from data at higher temperatures. [h] Phenyldimethylcarbinyl thiolbenzoate. [i] Contains 0.054 *M* lithium *p*-methoxythiobenzoate. [j] Less than 1% of the corresponding *p*-methoxythiol ester produced.

The products resulting from the ethanolysis of phenyldimethylcarbinyl *p*-nitrobenzoate at 25° were estimated using the product ratios and rate constants observed at 75 and 100°.

Products of the solvolysis of phenyldimethylcarbinyl thionbenzoate in ethanol at 25° were also determined in the presence of a four to one molar excess of lithium *p*-methoxythiobenzoate over substrate after *ca.* 10 half-lives of the thionbenzoate reaction. The results summarized in Table I indicate that within experimental error 0.05 *M* lithium *p*-methoxythiobenzoate does not change the product distribution. Only a negligible amount (<1%) of phenyldimethylcarbinyl *p*-methoxythiolbenzoate was observed in the vapor phase chromatograph of the products. The stability of the *p*-methoxythiolbenzoate was assumed on the basis of the observed stability of the unsubstituted thiolbenzoate.

In addition, products of the solvolysis of phenyldimethylcarbinyl *p*-nitrobenzoate (0.01 *M*) in ethanol at 75 and 100° were determined in the presence of lithium benzoate (0.05 *M*) after *ca.* 10 half-lives of the *p*-nitrobenzoate reaction. The results presented in Table I indicate that this salt does not effect the ratio of olefin to ether. The presence of a negligible amount (*ca.* 0.5%) of phenyldimethylcarbinyl benzoate was observed under identical conditions as determined by ultraviolet spectrometry (see the Experimental Section). Using a measured rate constant of 1.53×10^{-4} sec^{-1} for the solvolysis of phenyldimethylcarbinyl benzoate determined in ethanol at 100° in the presence of 0.05 *M* lithium benzoate, it may be estimated that *ca.* 43% of the phenyldimethylcarbinyl benzoate if formed from the lithium benzoate would have reacted in the time allowed for the reaction of the *p*-nitrobenzoate in excess lithium benzoate at 100°.

The stabilities of the products of the solvolysis of the phenyldimethylcarbinyl derivatives under the reaction conditions were established by running ethanol solutions, each containing one of the products (0.01 *M*), the appropriate acid (0.01 *M*), and 2,6-lutidine (0.02 *M*) (or silver nitrate, 0.016 *M*), at the appropriate temperature for *ca.* 10 half-lives of the corresponding solvolysis reaction. The average yield of recovered products was 102 ± 2% vpc) of the product initially weighed into each solution.

Kinetics.—The rate of ethanolysis of phenyldimethylcarbinyl chloride was determined by continuous addition of sodium ethoxide solution to the reaction vessel, the rate of addition being such as to maintain constant apparent pH. The integrated first-order rate constants observed for these reactions are given in Table II. The values obtained for the chloride agree well with values reported[7] in the literature. The rates of solvolysis of phenyldimethylcarbinyl *p*-nitrobenzoate at 75 and 100° in ethanol and aqueous ethanol were determined by titration of aliquots with sodium methoxide to a *p*-hydroxyazobenzene end point in acetone. The integrated first-order rate constants observed at 75 and 100° and those calculated for 25° are given in

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(5) S. G. Smith and J. P. Petrovich, *J. Org. Chem.*, **30**, 2882 (1965).

(6) H. Staudinger and J. Siegment, *Helv. Chim. Acta*, **3**, 824 (1920).

(7) Y. Okamoto, T. Inukai, and H. C. Brown, *J. Am. Chem. Soc.*, **80**, 4972 (1958).

TABLE II

REACTION RATE CONSTANTS FOR THE ETHANOLYSIS OF PHENYLDIMETHYLCARBINYL CHLORIDE AS A FUNCTION OF pH AT 25°

[RX], 10^3 *M*	10^4 *k*, sec^{-1}	pH[a]
5.7	3.66 ± 0.03	5.18 ± 0.17
2.7	3.59 ± 0.02	5.30 ± 0.10
2.6	3.62 ± 0.3	7.20 ± 0.20
3.4	3.55 ± 0.01	9.43 ± 0.07

[a] Apparent pH using a glass electrode in ethanol solution. The pH was maintained within the indicated ranges by a pH-Stat.

TABLE III

SUMMARY OF REACTION RATE CONSTANTS FOR THE SOLVOLYSIS OF PHENYLDIMETHYLCARBINYL *p*-NITROBENZOATE

Temp, °C	[RX], 10^2 *M*	% ethanol	ΔH^* [a]	ΔS_{75}^* [b]	10^5 *k*, sec^{-1}
75.0	1.00	100			1.25 ± 0.02
75.0	0.998	100			1.23 ± 0.01
100.0	0.998	100			17.6 ± 0.1
100.0	0.968	100			17.6 ± 0.1
25[c]	1.0	100	26.6	−4.4	0.00147
75.0	0.999	95			3.19 ± 0.02
100.0	0.996	95			39.8 ± 0.2
25[c]	1.0	95	25.2	−6.6	0.00570
75.0	1.01	90			7.16 ± 0.06
100.0	1.00	90			82.9 ± 0.7
25[a]	1.0	90	23.9	−6.2	0.0154
75.0	1.00	80			24.9 ± 0.7
100.0	1.00	80			273 ± 4
25[a]	1.0	80	26.2	−3.9	0.0614

[a] In kcal/mole. [b] Entropy units. [c] Calculated from rate constants observed at 75.0 and 100.0°.

Table III. The rates of solvolysis of phenyldimethylcarbinyl thionbenzoate in ethanol and aqueous ethanol at 25°, of *p*-methylphenyldimethylcarbinyl thionbenzoate in ethanol at 25°, and of *p*-trifluoromethylphenyldimethylcarbinyl thionbenzoate in ethanol at 50 and 75° were determined by measuring the absorbance at 436 mμ as a function of time. The integrated first-order rate constants observed for these reactions are given in Table IV, and a sample run is provided in Table V. In all cases, good first-order kinetics were observed.

Solvent effects on the rates of solvolysis of phenyldimethylcarbinyl derivatives may be judged by the first-order rate constants reported[7] for the solvolysis of the chloride in methanol, ethanol, and 2-propanol at 25°. Plotting log *k* *vs.* *Y* gives an *m* value[8] of *ca.* 1.3. An *m* value[8] of 0.80 was obtained from a plot of log *k* *vs.* *Y* for the solvolysis of the *p*-nitrobenzoate in 100, 95, 90, and 80% aqueous ethanol at 25° using rate constants calculated from those observed at 75 and 100°, from which *m* values of 0.65 and 0.57 arise, respectively. For the solvolysis of the thionbenzoate in 100, 95, 90, and 80% aqueous ethanol an *m* value of 0.54 was obtained from a plot of log *k* *vs.* *Y*. Substituent effects in the ethanolysis of phenyldimethylcarbinyl chloride and thionbenzoate may be judged from the value of −4.67 for ρ (σ) reported[7] for the chloride and values of *ca.* −4.2 (σ) and *ca.* −2.9 (σ^+) for ρ estimated from plots of log *k* *vs.* σ or σ^+ for the *p*-methyl, unsubstituted, and *p*-trifluoromethyl derivatives. Attempts to prepare the *p*-methoxyl derivative have so far been unsuccessful.

Discussion

The data outlined under Results indicate that phenyldimethylcarbinyl chloride, *p*-nitrobenzoate, and thionbenzoate display an apparent sensitivity to solvent-ionizing power which falls in the order chloride, $m = 1.3 > p$-nitrobenzoate, $m = 0.80 >$ thionbenzoate, $m = 0.54$. Substituent effects as measured by ρ (σ^+) also show a similar decrease with chloride, $-4.67 >$ thionbenzoate, −2.9. Quantitative interpretation of these trends is complicated by a lack of knowledge of the amount of ion-pair return with the chloride and *p*-nitrobenzoate. With the thion ester it is likely that return on oxygen is small and the measured rate is close to the ionization rate. The magnitude of the *m* and ρ values are, however, consistent with considerable increase in charge separation between ground and transition states.

The products make it clear that all three derivatives solvolyze by a near-limiting mechanism. With the thion ester, for example, the formation of olefin (85%), ether (6%), and rearranged thiol ester (6%) are most economically accounted for by an ionization process.

The change in the yield of olefin from 2% from the chloride plus silver nitrate to 85% from the thionbenzoate clearly indicates that the anion is involved in a product-determining step. Since addition of lithium benzoate to the *p*-nitrobenzoate solvolysis and lithium *p*-methoxythiobenzoate to the thion ester solvolysis did not result in the incorporation of the added anion, it is unlikely that return from dissociated ions is important. Products may still arise from such species, however.

The data of Cocivera and Winstein[3b] with *t*-butyl halides indicates that dissociation favors substitution while association increases the fraction of olefin. Using this analogy, the silver-assisted ionization tends toward the behavior of a dissociated carbonium ion although the possible interaction[9] of a nitrate ion with a tertiary carbonium ion needs further clarification. The dramatic sensitivity of the fraction of olefin to the nature of the leaving group then reflects the efficiency of various anions in removing a proton within an ion pair or perhaps to direct a solvent molecule to act as a base in competition with dissociation. Experiments designed to provide further information on the details of these transformations are in progress.

Experimental Section

Alcohols.—The phenyldimethylcarbinol employed was a redistilled sample obtained from the Aldrich Chemical Co. The *p*-methyl, bp 82–83° (3 mm), the *p*-trifluoromethyl, mp 39–40°, and *p*-methoxy, bp 113–114°, derivatives were prepared by standard procedures.[10]

Thiobenzoyl chloride was prepared essentially as described by Staudinger.[6]

Phenyldimethylcarbinyl Thionbenzoates.—Phenyldimethylcarbinyl thionbenzoate was prepared from the action of thiobenzoyl chloride on the alcohol under the conditions previously described[5] in 49% yield. Recrystallization of the crude product from pentane at −70° gave the yellow ester, mp 81–82°.

Anal. Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29; S, 12.51. Found: C, 75.10; H, 6.27; S, 12.48.

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(8) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).

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(10) (a) H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *ibid.*, **79**, 1897 (1957); (b) Y. Okamoto, T. Inukai, and H. C. Brown, *ibid.*, **80**, 4969 (1958); (c) A. J. Birch, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 245 (1949).

TABLE IV

SUMMARY OF REACTION RATE CONSTANTS FOR THE SOLVOLYSIS OF PHENYLDIMETHYLCARBINYL THIONBENZOATES

Thionbenzoate	Temp, °C	[RX], 10^2 M	[2,6-Lutidine], 10^2 M	% ethanol	10^5k, sec^{-1}
Phenyldimethylcarbinyl	25.0	0.19	...[a]	100	6.16[b]
	25.0	0.35	...[c]	100	5.97 ± 0.01
	25.0	0.35	...[d]	100	5.73 ± 0.02
	25.0	0.93	2.04	100	6.10 ± 0.05
	25.0	0.95	2.07	100	5.96 ± 0.05
	25.0	1.03	11.2	100	5.98 ± 0.06
	25.0	1.11	10.5	95	10.9[b]
	25.0	1.09	10.2	90	23.9 ± 0.2
	25.0	1.09	10.2	90	23.4 ± 0.3
	25.0	0.96	9.61	80	59.3 ± 0.8
	25.0	0.96	9.61	80	63.6 ± 0.4
	25.0	0.97	1.09	...[e]	11.6 ± 0.1
	25.0	1.02	1.03	...[e]	11.5 ± 0.1
	25.0	0.98	...	...[f]	12.7 ± 0.1
	25.0	0.99	...	...[f]	12.6 ± 0.1
p-Methylphenyldimethylcarbinyl	25.0	0.75	2.08	100	94.2[b]
	25.0	0.92	2.08	100	94.2 ± 0.8
p-Trifluoromethylphenyldimethylcarbinyl	50.0	1.02	2.14	100	2.99 ± 0.10
	50.0	0.97	2.00	100	2.83 ± 0.03
	75.0	1.03	2.08	100	60.3 ± 1.1
	75.0	1.02	2.06	100	63.7 ± 1.4
	75.0	1.01	1.87	100	61.5 ± 0.7
	25[g]	1.0	2.0	100	0.0879

[a] Apparent pH (glass electrode in ethanol) maintained at 9.80 ± 0.05. [b] Obtained by the Guggenheim method. [c] Apparent pH maintained at 9.0 ± 0.4. [d] Apparent pH maintained at 7.55 ± 0.05. [e] Acetic acid. [f] Acetic acid–0.01 M lithium acetate. [g] Calculated from rate constants observed at 50.0 and 75.0°.

TABLE V

REACTION RATE OF 0.00930 M PHENYLDIMETHYLCARBINYL THIONBENZOATE IN ETHANOL AT 25° [a]

Time, 10^{-3} sec	A	Rel % reacn	10^5k, sec^{-1}
...	0.863	0	...
0.90	0.838	4.9	5.60
3.06	0.784	15.5	5.51
4.50	0.747	22.8	5.75
6.30	0.699	32.3	6.17
8.10	0.659	40.1	6.32
11.70	0.606	50.5	6.01
13.50	0.581	55.5	5.08
15.30	0.554	60.8	6.11
26.4	0.456	80.2	6.09
28.2	0.449	81.5	5.95
30.6	0.434	84.3	6.05
78.0	0.356	99.8	
84.0	0.354	100.0	

[a] Weighted least-square rate constant, (6.10 ± 0.05) × 10^{-5} sec^{-1}.

In a similar way[5] 2.0 g of *p*-methylphenyldimethylcarbinol resulted in 3.1 g (82%) of the yellow thion ester, mp 62–63°.

With *p*-trifluoromethylphenyldimethylcarbinol (4.1 g) and thiobenzoyl chloride (3.0 g), 3.5 g (54%) of *p*-trifluoromethylphenyldimethylcarbinyl thionbenzoate was obtained, mp 52–53°. *Anal.* Calcd for $C_{17}H_{15}F_2OS$: C, 62.95; H, 4.66; S, 9.89. Found: C, 62.55; H, 4.71; S, 10.74.

Phenyldimethylcarbinyl Thiolbenzoate.—Phenyldimethylcarbinyl thiolbenzoate was prepared by a modification of the method described by Bordwell.[11] A mixture of 2-phenylpropene (100 g, 0.85 mole), thiourea (65 g, 0.85 mole), and 3 ml of concentrated hydrochloric acid in *ca.* 500 ml of absolute ethanol was refluxed for 2 hr. The solvent was removed at reduced pressure leaving a colorless glass, which was crystallized from ethanol–ethyl acetate to give a white solid, mp 164–166°. This material was added to 200 ml of 10% aqueous sodium hydroxide, the mixture was brought to reflux, cooled, neutralized with concentrated hydrochloric acid, and extracted with three 60-ml portions of ether. After drying and removal of the ether, 24.5 g of crude mercaptan was obtained. The liquid was treated with benzoyl chloride (25.5 g, 0.18 mole) in *ca.* 25 ml of pyridine at 0°. After standing at room temperature for 1.5 hr, the mixture was added to 250 ml of water, and the aqueous solution was extracted with 500 ml of ether. The ether solution was washed with dilute aqueous hydrochloric acid and water and then dried over magnesium sulfate. The ether was removed at reduced pressure leaving a dark brown oil, which was crystallized from methanol to give 16.1 g (6.3% yield) of white phenyldimethylcarbinyl thiolbenzoate, mp 48–49°. The infrared spectrum showed characteristic bands at 1655 (s), 1200 (s), 910 (s), 670 (s), and 690 (s) cm^{-1}. *Anal.* Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29. Found: C, 74.69; H, 6.37.

Lithium *p*-Methoxylthiobenzoate.—Potassium hydroxide (25.8 g, 0.46 mole) dissolved in 95% aqueous ethanol was neutralized to phenolphthalein end point with hydrogen sulfide. To the neutral solution, at 0°, *p*-methoxybenzoyl chloride (39.2 g, 0.23 mole) was slowly added as described by Nobel and Tarbell.[12] After filtration of the mixture, the solvent was removed from the filtrate at reduced pressure leaving crude potassium *p*-methoxythiobenzoate. The crude salt was dissolved in water and neutralized with concentrated hydrochloric acid, and the *p*-methoxythiobenzoic acid was extracted with 500 ml of ether. The ether solution was washed with water, and the solvent was removed at reduced pressure to give a dark brown oil. Distillation of the oil gave 9.0 g (24.8% yield) of light pink *p*-methoxythiobenzoic acid, bp 114° (1 mm), mp 81.5–82.5°. The infrared spectrum showed bands at 2500 (m), 1660 (s), 1600 (s), 1580 (s), 1270 (s), 1220 (s), 1020 (s), and 845 (s), cm^{-1}. The acid (9.0 g, 0.057 mole) was treated with lithium carbonate (2.1 g, 0.028 mole) in 90% aqueous acetone for 24 hr. The solvent was removed at reduced pressure giving 9.8 g (99% yield, 24% over-all yield) of lithium *p*-methoxythiobenzoate, decomposing at *ca.* 230°. The infrared spectrum showed bands at 1600 (s), 1255 (s), 1220 (s), 1160 (s), 960 (s), and 845 (s) cm^{-1}. The equivalent weight of the salt, by electrometric titration of a 0.2182-g sample with 2.25 ml of 0.50 M aqueous hydrochloric acid, was 194 (calcd 174).

Phenyldimethylcarbinyl *p*-Methoxythiolbenzoate.—To a stirred suspension of 90% lithium *p*-methoxythiobenzoate (2.5 g, 0.013 mole) in 15 ml of acetone was added phenyldimethylcarbinyl chloride. The mixture was allowed to stand (with occasional

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[11] F. G. Bordwell, P. E. Sokol, and J. D. Spainhour, *J. Am. Chem. Soc.*, **82**, 2881 (1960).

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stirring) for 24 hr, after which the solvent was removed at reduced pressure, leaving a yellow oil. Distillation and subsequent recrystallization from aqueous ethanol gave 1.0 g (27% yield) of white phenyldimethylcarbinyl *p*-methoxythiolbenzoate, bp 173–174° (0.1 mm), mp 58–59°. The infrared spectrum showed characteristic bands at 1650 (s), 1600 (s), 1260 (s), 1170 (s), 1025 (m), 910 (s), and 700 (m) cm^{-1}. *Anal.* Calcd for $C_{17}H_{18}O_2S$: C, 71.29; H, 6.33; S, 11.20. Found: C, 71.29; H, 6.35; S, 10.70.

Phenyldimethylcarbinyl *p*-Nitrobenzoate.—To a mixture of *p*-nitrobenzoyl chloride (9.0 g, 0.049 mole) and 50 ml of pyridine at 0° was added phenyldimethylcarbinol (6.0 g, 0.044 mole, Aldrich Chemical Co.). The mixture was allowed to stand overnight in a refrigerator and was then added to 500 ml of water to precipitate the product. The filtered solid was washed with dilute aqueous hydrochloric acid and water, and was recrystallized from acetone–pentane to give 12.0 g (95.6% yield) of phenyldimethylcarbinyl *p*-nitrobenzoate, mp 134–135°, λ_{max} 263 mμ (ϵ 1.33 × 10^4) (methylene chloride). The infrared spectrum showed strong bands at 1705, 1510, 1290, 1100, 845, 760, 720, and 690 cm^{-1}. *Anal.* Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30. Found: C, 67.11; H, 5.34.

Ethyl Phenyldimethylcarbinyl Ether.—A solution of 2-phenylpropene (25.0 g, 0.138 mole) and *p*-toluenesulfonic acid (0.5 g, 0.003 mole) in 400 ml of absolute ethanol was refluxed for 3 days. The solution was poured into 2 l. of dilute, aqueous sodium bicarbonate and extracted with five 50-ml portions of methylene chloride. The combined methylene chloride solutions were washed with aqueous sodium bicarbonate and water and dried over magnesium sulfate. After removal of the solvent at reduced pressure, the desired product was separated from unreacted olefin and collected at 170° from two, parallel, 6-ft 20% XF-1150 (silicone nitrile) on Chromosorb columns on a Fischer Prep/Partitioner. The combined collected fractions were distilled to give 6.0 g (26% yield) of ethyl phenyldimethylcarbinyl ether, bp 86–88° (14 mm), λ_{max} *ca.* 220 mμ (ϵ *ca.* 2.5 × 10^3) [lit.[13] bp 48.0–49.5° (2.5 mm)]. This product was shown to be 98.6 ± 1.0% ether by quantitative vapor phase chromoatography of three samples; 2-phenylpropene was the only impurity observed.

2,6-Lutidine.—Eastman Kodak 2,6-lutidine was treated[14] with boron trifluoride and distilled twice collecting the fraction with bp 142–143° (lit.[14] bp 143.4°).

Ethanol and Aqueous Ethanol.—Several batches of ethanol for use as solvent were purified as described by Fieser.[15] The aqueous ethanol solutions were obtained by aliquoting the appropriate volumes of ethanol and distilled deionized water with the same pipet.

Kinetic Procedures. Procedure A.—This procedure was employed to determine reaction rates for the solvolysis of phenyldimethylcarbinyl chloride and thionbenzoate in ethanol at 25° by constant-base-concentration titration of acids fromed in the reactions. The titrations were made using a Polarad Model AT-2A automatic recording titrator equipped with (among other features) a pH-Stat, which controlled the apparent pH to within 0.4–0.1 pH units within a run.

Base was added to the stirred and thermostated reaction mixture by the titrator at the rate required to maintain the indicated pH. Rate constants were calculated from a strip chart recording of the volume of standard base added as of function time.

Procedure B.—This procedure was employed to determine reaction rates of phenyldimethylcarbinyl thionbenzoates in ethanol and aqueous ethanol at 25° by measuring the visible absorption of the esters at 436 mμ on a Perkin-Elmer 202 spectrophotometer. The spectrophotometer was fitted with a thermostated brass cell holder maintained at 25.0 ± 0.02°. Deoxygenated reaction solution at 25° was transferred by pipet into a 1-cm quartz cell previously flushed for 2–3 min with nitrogen, and the cell was capped and quickly placed in the sample side of the cell holder, an empty cell being used in the reference. After 5 min had been allowed for temperature equilibration, the visible spectrum was scanned, the time was recorded, and additional scans were made at appropriate times.

The reaction of *p*-trifluoromethylphenyldimethylcarbinyl thionbenzoate in ethanol at 50 and 75° was run in sealed deoxygenated ampoules thermostated in Carbowax-400 baths maintained at 50.0 ± 0.03° and at 75.0 ± 0.03°. At appropriate times samples were removed from the bath, cooled to room temperature, and analyzed for absorption at 436 mμ with a Beckman DU spectrophotometer at a slit width of 0.02 mm. If the solutions were not deoxygenated, unstable infinity readings were encountered.

Procedure C.—The usual sealed-ampoule technique was employed for the ethanolysis of benzoates and *p*-nitrobenzoates. Aliquots were titrated to a *p*-hydroxyazobenzene end point with 0.01 *M* sodium methoxide.

Product Analysis.—Quantitative product analyses were done by vapor phase chromatography. The calibrations were accomplished by weighing out appropriate amounts of 2-phenylpropene and chlorobenzene, ethyl phenyldimethylcarbinyl ether and chlorobenzene, and phenyldimethylcarbinyl thiolbenzoate and methyl 2-nitro-3-methylbenzoate, dissolving each pair of compounds in methylene chloride.

In a typical experiment 0.1744 g of phenyldimethylcarbinyl chloride and 0.2171 g of 2,6-lutidine were dissolved in ethanol in a 100-ml volumetric flask. The solution was placed in a water bath at 25.0 ± 0.01° for 5 hr (*ca.* 10 half-lives of this reaction). When other solutions were run at higher temperatures, as for the *p*-nitrobenzoate, they were placed in 100- or 200-ml, round-bottom flasks and sealed. To the chloride solution after 5 hr at 25° was added 0.0990 g of chlorobenzene, the resulting solution was poured into 500 ml of water, and immediately extracted with five 25-ml portions of methylene chloride. The combined methylene chloride solutions were washed with dilute, aqueous hydrochloric acid, aqueous sodium bicarbonate, and water, and then dried over magnesium sulfate. The dried methylene chloride solution was concentrated to 10–15 ml in a 100-ml flask at 50–55°, the solvent distilling through a 7-in. column packed with glass helecies. Injections of 0.03–0.10-ml samples were made into a 3 ft 20% XF-1150 (silicon nitrile) on Chromosorb column at 100° in an Aerograph A-90P vapor phase chromatograph. The order of appearance of compounds was chlorobenzene, 2-phenylpropene, and ethyl phenyldimethylcarbinyl ether. The areas of each of the peaks were measured by a Disc Chart Integrator.

The extraction procedure was found to be functional, as demonstrated by an average deviation of ±2% resulting between the weighed amount of compound and the amount found by analysis after the solution was extracted, the determinations being made on two samples each of the olefin and ether and one sample of the thiol ester. All product analyses and product-stability experiments were done by this method of analysis and extraction, with the addition of deoxygenation (as described for kinetic runs) of solutions containing thion ester and thiobenzoic acid. In the analysis of phenyldimethylcarbinyl thiolbenzoate after extraction the sample was injected into a 1-ft 20% XF-1150 (silicon nitrile) on Chromosorb column at 130° in an Aerograph vapor phase chromatograph. After the methyl 2-nitro-3-methylbenzoate came off the column, the temperature of the column was raised to 150°. The peak attributed to thiol ester was identified by collection from the vpc instrument and subsequent comparison with authentic phenyldimethylcarbinyl thiolbenzoate. The collected oil was crystallized from methanol to give a white solid, mp 48–49°, with mmp 47.5–48.5°, and whose infrared spectrum contained all of the major absorptions present in the spectrum of the authentic ester and no additional absorptions.

The products of the solvolysis of phenyldimethylcarbinyl *p*-nitrobenzoate in ethanol at 75 and 100° were determined in the presence of a four to one molar excess of lithium benzoate, prepared from the reaction of stoichiometric amounts of *p*-nitrobenzoic acid and lithium carbonate. In a typical experiment 0.6805 g of phenyldimethylcarbinyl *p*-nitrobenzoate and 0.5230 g of 2,6-lutidine were dissolved in 250 ml of ethanol in a volumetric flask. Two 100-ml portions of the resulting solution were transferred by automatic pipet into two 200-ml, round-bottom flasks, one of which contained 0.6432 g of lithium benzoate. Both flasks were sealed, the lithium benzoate was dissolved with agitation, and the flasks were immersed in a Carbowax-400 bath at 100.0 ± 0.03° for 10 hr (*ca.* 10 half-lives of the reaction of the *p*-nitrobenzoate in ethanol at 100°). The flasks were removed from the bath and cooled, and the solutions were extracted as described previously for other product analysis. The dry methylene chloride solutions were each diluted with methylene chloride to a volume of 250 ml in a volumetric flask. A sample of the

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[14] H. C. Brown, S. Johnson, and H. Podall, *J. Am. Chem. Soc.*, **76**, 5556 (1954).

[15] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1955, p 286.

solution which had contained no lithium benzoate was transferred to a 1-mm, quartz cell and placed on the reference side of a Perkin-Elmer spectrophotometer, while a sample of the other solution was placed in the sample beam. The ultraviolet spectrum was then scanned. It was previously determined by vapor phase chromatography that the products of the solvolysis under these conditions were the same in the presence of the salt as in its absence within ±1%. Consequently, absorptions owing to 2-phenylpropene [$\lambda_{\max}$ 245 mμ (ϵ 1.09 × 10^4)], ethyl phenyldimethylcarbinyl ether [$\lambda_{\max}$ *ca.* 220 mμ (ϵ *ca.* 2.5 × 10^3)], and any phenyldimethylcarbinyl *p*-nitrobenzoate [$\lambda_{\max}$ 263 mμ (ϵ 1.33 × 10^4)] which may have remained were cancelled by the presence of the same amounts of these compounds in the reference sample and thus, the slight absorption (0.038) observed at 230 mμ in the spectrum of the sample which had contained lithium benzoate was due to phenyldimethylcarbinyl benzoate [$\lambda_{\max}$ 230 mμ (ϵ 1.53 × 10^4)]. The addition to the sample solution of an amount of phenyldimethylcarbinyl benzoate corresponding to 0.05% of the *p*-nitrobenzoate reacting to form the benzoate increased the absorption from 0.038 to 0.070, indicating that in the original analysis there was an amount of phenyldimethylcarbinyl benzoate remaining which corresponded to less than 1% of the original amount of the *p*-nitrobenzoate. A rate constant of 1.53 × 10^{-4} sec^{-1} was obtained for the disappearance of phenyldimethylcarbinyl benzoate in ethanol at 100° in the presence of a four to one molar excess of lithium benzoate. From this rate constant it may be calculated that 43% of the phenyldimethylcarbinyl benzoate formed from phenyldimethylcarbinyl *p*-nitrobenzoate and excess lithium benzoate had reacted in 10 hr, the time allowed for the reaction. Thus, less than 1% of the original phenyldimethylcarbinyl *p*-nitrobenzoate had reacted with the four molar excess of lithium benzoate in ethanol at 100°.

The products of the solvolysis of phenyldimethylcarbinyl thionbenzoate in ethanol at 25° were determined in the presence of a four molar excess of lithium *p*-methoxythiobenzoate, prepared as previously described. In this experiment 0.5280 g of phenyldimethylcarbinyl thionbenzoate, 0.4760 g of 2,6-lutidine, and 2.0084 g of 90% lithium *p*-methoxythiobenzoate were dissolved in 200 ml of ethanol in a volumetric flask. The solution was deoxygenated in the usual manner and placed in a water bath at 25.0° ± 0.01° for 24 hr (*ca.* 10 half-lives of the thionbenzoate reaction in ethanol at 25°). Into the resulting solution was dissolved 0.1075 g of chlorobenzene and 0.0990 g of methyl 2-nitro-3-methylbenzoate, this solution was extracted in the usual manner, and the products were analyzed by vapor phase chromatography. The products were the same (±2%) as those observed for the solvolysis of the thionbenzoate in the absence of lithium *p*-methoxythiobenzoate, except for an additional peak in the chromatograph following phenyldimethylcarbinyl thiolbenzoate. A comparison of the integrations of this peak, before and after the addition to the sample solution of an amount of authentic phenyldimethylcarbinyl *p*-methoxythiolbenzoate corresponding to the thion ester forming 1% of *p*-methoxythiol ester, showed that the integration had nearly doubled after the addition of the authentic phenyldimethylcarbinyl *p*-methoxythiolbenzoate. This indicated that less than 1% of the original amount of phenyldimethylcarbinyl thionbenzoate had reacted with the excess lithium *p*-methoxythiobenzoate to form phenyldimethylcarbinyl *p*-methoxythiolbenzoate.

Product Stability Determinations.—In a typical experiment 0.1148 g of 2-phenylpropene, 0.2090 g of 2,6-lutidine, and 5 ml of 0.20 *M* ethanolic hydrochloric acid (prepared by bubbling hydrogen chloride through ethanol) were dissolved in 100 ml of ethanol in a volumetric flask. This solution was then treated as described for product analysis, 0.1051 g of chlorobenzene being added. Analysis showed 0.1138 g (99.1% yield) of 2-phenylpropene present. All products were shown by this method to be stable within a average deviation of ±2.6% under the reaction conditions as described. Commercial *p*-nitrobenzoic acid, thiobenzoic acid, and silver nitrate were employed in the appropriate experiments. In most runs infinity titers were obtained and the first-order rate constants were calculated using a FORTRAN program and an IBM-7094 digital computer. This program calculates the best-fit, least-square line through the points of a plot of ln *Y vs.* time. The points are weighted in proportion to the relative magnitude of *Y* values.

Registry No.—Ethyl phenyldimethylcarbinyl ether, 1712-74-9; phenyldimethylcarbinyl chloride, 934-53-2; phenyldimethylcarbinyl *p*-nitrobenzoate, 7429-06-3; phenyldimethylcarbinyl thionbenzoate, 7429-19-8; *p*-methylphenyl dimethylcarbinyl thiobenzoate, 7429-18-7; *p*-trifluoromethylphenyldimethylcarbinyl thionbenzoate, 7429-15-4; *p*-methylphenyldimethylcarbinol, 1197-01-9; phenyldimethylcarbinyl thiolbenzoate, 7429-01-8; lithium *p*-methoxythiobenzoate, 7429-02-9; *p*-methoxythiobenzoic acid, 6279-44-3; phenyldimethylcarbinyl *p*-methoxythiolbenzoate, 7429-05-2.

The Electron-Impact Fragmentation of 4-Thiapyrone and N-Methyl-4-pyridone

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The mass spectra of 4-thiapyrone (**1**) and N-methyl-4-pyridone (**3**) are analyzed by comparison with the spectra of isotopically substituted derivatives. The doublet shape of the metastable peak associated with the loss of carbon monoxide from the molecular ion is attributed to fragmentation with loss of kinetic energy.

The empirical analysis of the electron-impact fragmentation process of the fundamental functional types has received considerable attention in recent years.[2] Although the structures proposed in such analyses must be regarded as convenient rationales, the utility of these assignments in further structural work has been amply demonstrated. For example, the principal pathways in the fragmentation of 4-pyrone[3] correlate well with the major fragmentation processes in natural products containing this nucleus.[4,5] In order to assess the generality of the fragmentation processes observed with 4-pyrone[3] for similar structure types we have analyzed the mass spectra of 4-thiapyrone (**1**), N-methyl-4-pyridone (**3**), and their isotopically substituted

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[1] (a) Standard Oil of California Fellow, 1964–1965; (b) National Institutes of Health Fellow, 1966–1967.

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[4] (a) R. I. Reed and J. M. Wilson, *J. Chem. Soc.*, 5949 (1963); (b) C. S. Barnes and J. L. Occolowitz, *Australian J. Chem.*, **17**, 975 (1964); (c) M. M. Badawi, M. B. E. Fayez, T. A. Bryce, and R. I. Reed, *Chem. Ind.* (London), 498 (1966).

[5] However, internal consistency in a series and chemical intuition do not establish the validity of a structural assignment. W. H. Pirkle [*J. Am. Chem. Soc.*, **87**, 3022 (1965)] has elegantly shown that the fragment formed by loss of carbon monoxide in the mass spectrum of 2-pyrone is not a cyclic furan ion.