

Thermal Decomposition of α -Hydroperoxytetrahydrofuran (I).
A. Pyrolysis in the Gas Chromatograph.—A 1- μ l sample of a $4.3 \times 10^{-2} M$ solution of I in THF was injected into a Beckman GC-5 gas chromatograph equipped with a flame ionization detector and a 6 ft \times 0.125 in. Carbowax column on Chromosorb W. The gas chromatogram showed two major peaks for butyrolactone and α -hydroxytetrahydrofuran in a ratio of ca. 1:3.

B. Pyrolysis in a Sealed Tube.—A 5-ml solution of $8.6 \times 10^{-2} M$ I in THF was placed in a glass reaction tube which was connected to a vacuum line. The solution was thoroughly outgassed by conventional freeze-pump-thaw techniques. After a final check for noncondensable gases, the glass reaction tube was isolated by sealing off from the line and then allowed to reach room temperature. The sealed tube was then heated in a furnace at 100° for 30 min. The reaction mixture was analyzed and found to contain III as the only major products.

Photodecomposition of α -Hydroperoxytetrahydrofuran.—A solution of $9.1 \times 10^{-2} M$ I in THF was placed in a 3-ml uv spec-

trophotometric cell. The irradiation procedure used was identical with that described before⁸ except that, instead of bubbling oxygen through the solution, a slow stream of nitrogen was maintained. The products were identified by ir and vpc and the progress of the reaction was followed as described above. For each set of data, five or more experiments were required for the points on the curve for the range of 0 to 65% decomposition of I. The irradiation of I under oxygen was performed and analyzed in a similar manner.

Registry No.—I, 4676-82-8; THF, 109-99-9.

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Electronic Effects in Solvolysis Reactions. III. Solvolysis of Allyl-Substituted Cumyl Derivatives¹

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Synthetic procedures are described for *p*- γ,γ -dimethylallyl-, *p*- α,α -dimethylallyl-, *p*-3-butenyl-, *m*-allyl-, *p*-allyl-, and *p*- γ,γ -dideuterioallylcumyl *p*-nitrobenzoates. The possibility of allylic participation during the solvolysis of these compounds in aqueous mixtures was investigated. Substituent constants (σ^+), skeletal rearrangement studies, and kinetic isotope effect measurements were employed to determine the nature and extent of such participation. These data, coupled with the uniformity of activation parameters and the absence of skeletal isomerizations, suggest that inductive effects by the allylic double bond are the major influence in the solvolytic behavior of these esters.

Much interest and experimental work has centered around the stabilizing influence of cyclopropyl and allyl substituents in solvolytic reactions. Both functional groups provide stabilization for developing carbonium ions and, hence, rate enhancements are frequently observed.³ As a quantitative measure of the electronic effects of the cyclopropyl substituent in carbonium ion reactions, the substituent constant σ^+ was determined from solvolytic studies of substituted cumyl derivatives.⁴⁻⁶ These data indicated that the *p*-cyclopropyl group (relative to other alkyl groups) exhibited an abnormally large (negative) σ^+ value and that the ability of the substituent to supply electron density was conformationally dependent.⁶ It was considered, therefore, of general interest to prepare a number of allyl-substituted cumyl derivatives in order to assess, in more quantitative terms, the stabilizing influence of *m*- and *p*-allyl substituents on developing carbonium ions.

Results

Substituted cumyl *p*-nitrobenzoates were chosen for this investigation and were synthesized, for the most part, by conventional procedures. All esters gave satisfactory elemental analyses.

(1) For part II, see L. B. Jones and S. S. Eng, *Tetrahedron Lett.*, 1431 (1968).

(2) Phillips Petroleum Co. Fellow, 1966-1968.

(3) See, for example, J. D. Roberts, R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, and M. S. Silver, *J. Amer. Chem. Soc.*, **81**, 4390 (1959); J. D. Roberts and K. L. Servis, *ibid.*, **86**, 3773 (1964).

(4) L. B. Jones and V. K. Jones, *Tetrahedron Lett.*, 1493 (1966).

(5) H. C. Brown and J. D. Cleveland, *J. Amer. Chem. Soc.*, **88**, 2051 (1966).

(6) R. C. Hahn, T. F. Corbin, and H. Shechter, *ibid.*, **90**, 3404 (1968).

Water-acetone mixtures were selected as solvolytic media, and rate constants for solvolysis were determined at several temperatures for each of several solvent compositions. Detailed product studies indicated that *p*-nitrobenzoic acid and substituted cumyl alcohols were the only products produced during solvolysis. Under these reaction conditions, isomerization of the double bond in the allyl substituents into conjugation with aromatic ring could not be detected. Similarly, deuterium labeling in the allyl group indicated that carbon skeletal rearrangement did not occur during solvolysis.

Table I summarizes the solvolytic rate data for the substituted cumyl *p*-nitrobenzoates at various temperatures and solvent compositions. In all cases the kinetic runs were followed to at least 70% completion. Agreement between most runs was $\pm 1\%$.

The standard substituents methyl, *t*-butyl, hydrogen, and chlorine were used to obtain Hammett ρ values under each set of conditions. Good linear correlations were observed in each case ($r = 0.994$). At 46.4° in 60% aqueous acetone, the reaction constant (using Brown σ^+ values) was found to be -4.55 , and in 50% aqueous acetone at the same temperature the ρ value was found to be -4.38 . A reaction constant of -4.70 was observed in 50% aqueous acetone at 38.0°. These ρ values were then employed to determine σ^+ values of each allyl and butenyl substituent. These data are tabulated in Table II. Values for several other substituents are included for reference.

Table III lists activation parameters for solvolysis of the allyl-substituted esters. Within experimental error, all of the esters have the same energy of activa-

TABLE I
SOLVOLYSIS RATES OF SUBSTITUTED CUMYL
p-NITROBENZOATES AT VARIOUS TEMPERATURES
AND SOLVENT COMPOSITIONS

Substituent	Solvent compn, w/w	Temp, °C	$k \times 10^4$, sec ⁻¹		
<i>p</i> -Methyl	60% aq acetone	46.4	1.84 ± 0.05		
<i>p</i> -Hydrogen			0.746 ± 0.007		
<i>p</i> -Allyl			7.49 ± 0.06		
<i>p</i> - <i>t</i> -Butyl			11.8 ± 0.2		
<i>p</i> -Chloro			0.220 ± 0.004		
<i>p</i> - γ,γ -Dimethylallyl			11.8 ± 0.1		
<i>m</i> -Allyl			0.858 ± 0.005		
<i>p</i> -3-Butenyl			12.7 ± 0.3		
<i>p</i> -Methyl			50% aq acetone	38.0	61.4 ± 0.2
<i>p</i> -Hydrogen					2.63 ± 0.03
<i>p</i> -Allyl	24.7 ± 0.1				
<i>p</i> - <i>t</i> -Butyl	36.1 ± 0.3				
<i>p</i> - γ,γ -Dimethylallyl	39.0 ± 0.5				
<i>m</i> -Allyl	2.65 ± 0.02				
<i>p</i> -3-Butenyl	38.7 ± 0.3				
<i>p</i> -Methyl	24.6 ± 0.4				
<i>p</i> -Hydrogen	0.879 ± 0.018				
<i>p</i> -Allyl	9.72 ± 0.10				
<i>p</i> - <i>t</i> -Butyl	60% aq acetone	46.4	15.0 ± 0.1		
<i>p</i> - γ,γ -Dimethylallyl			15.4 ± 0.2		
<i>m</i> -Allyl			1.20 ± 0.01		
<i>p</i> -3-Butenyl			15.6 ± 0.2		
<i>p</i> -Allyl			30.0	3.87 ± 0.01	
<i>p</i> - γ,γ -Dimethylallyl			6.15 ± 0.06		
<i>p</i> -3-Butenyl			5.92 ± 0.06		
<i>p</i> -Allyl			8.00 ± 0.08 ^a		
<i>p</i> - γ,γ -Dideuterioallyl			7.97 ± 0.09 ^a		
<i>p</i> - α,α -Dimethylallyl			6.71 ± 0.08 ^a		

^a Determined by V. K. Jones.

TABLE II
SUBSTITUENT CONSTANTS FOR ALLYLIC AND
SEVERAL REFERENCE SUBSTITUENTS

Substituent	σ^+
H	0.00 ^a
<i>p</i> -Ethyl	-0.291 ^b
<i>m</i> -Ethyl	-0.063 ^b
<i>p</i> -Allyl	-0.221 ^c
<i>m</i> -Allyl	-0.023 ^c
<i>p</i> - γ,γ -Dimethylallyl	-0.262 ^c
<i>p</i> -3-Butenyl	-0.262 ^c
<i>p</i> - <i>t</i> -Butyl	-0.256 ^b
<i>p</i> - α,α -Dimethylallyl	-0.212 ^c
<i>p</i> -Cyclopropyl	-0.410 ^d

^a By definition. ^b Y. Okamoto and H. C. Brown, *J. Amer. Chem. Soc.*, **79**, 1913 (1957). ^c Determined in this study. ^d Reference 4.

tion. Data for the *p*-methyl compound is included for comparative purposes. These data are indicative of a common mechanism for reaction of each compound involving ionization in the slow step.

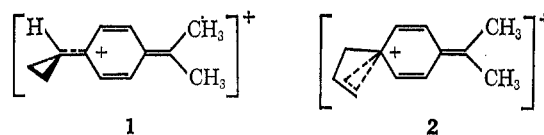
Discussion

The σ^+ relationship defined by Brown and Okamoto⁷ provides a probe for measuring electronic changes in a carbonium ion reaction as a function of substituents suitably located to allow for conjugative interaction. The magnitude of the σ^+ constant for any given substituent is proportional to its ability to interact with a

TABLE III
ACTIVATION PARAMETERS FOR THE SOLVOLYSIS
OF METHYL, ALLYL, AND SUBSTITUTED ALLYL
CUMYL *p*-NITROBENZOATES IN 50% AQUEOUS
ACETONE AT 30.0°

Substituent	E_{act} , kcal/mol	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
<i>p</i> -Methyl	20.2	19.6	-18.2
<i>p</i> -Allyl	21.2	20.6	-20.1
<i>p</i> - γ,γ -Dimethylallyl	20.6	20.0	-19.3
<i>p</i> -3-Butenyl	20.6	20.0	-19.2
<i>m</i> -Allyl	23.1	22.6	-24.4

developing positive charge. It has been demonstrated that the *p*-cyclopropyl group is a more effective electron-donating substituent ($\sigma^+ -0.410^4$) than other alkyl groups, as long as it can assume the required conformation⁵ as in structure 1. It was, therefore, anticipated that *p*-allyl substituents would also exhibit enhanced σ^+ constants, since the groups could interact with the developing positive charge on the *para* carbon of the aromatic ring *via* homoallylic participation 2.⁸



The effect of replacing a terminal methyl group in each alkyl substituent listed in Table II by a vinyl group is to render the unsaturated substituent less electron supplying. Such observations reflect the electron-withdrawing inductive effect of the π cloud of the alkenyl substituents. When the double bond is moved further from the benzene ring (e.g., 3-butenyl), the inductive effect is felt less strongly and the σ^+ value becomes more negative (i.e., the 3-butenyl substituent more effectively stabilizes a positive charge in this system than does the allyl group).

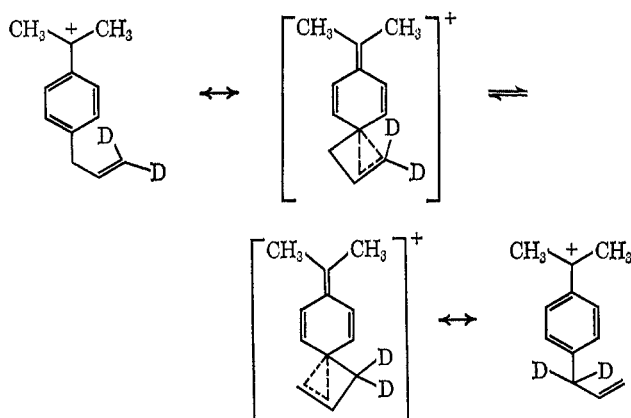
It must be pointed out, however, that the dominant influence of inductive effects in allyl substituents does not necessarily rule out homoallylic participation (resonance interaction). For example, studies of the hydration of divinylbenzenes⁸ demonstrated that a vinyl substituent in a *meta* position was electron withdrawing ($\sigma_m^+ +0.146$) whereas a *p*-vinyl substituent was electron donating ($\sigma_p^+ -0.152$). This large difference ($\sigma_p^+ - \sigma_m^+$) must reflect a significant resonance-donating effect of the double bond even though the combined resonance and inductive effect of the *p*-vinyl group renders it less electron donating than the corresponding saturated group ($\sigma_{p,ethyl}^+ -0.291$). To determine whether a similar situation existed for allyl substituents, two types of studies were carried out. These consisted of kinetic isotope effect measurements and detailed product analyses.

Homoallylic participation of the allyl group could, in principle, lead to carbon skeletal rearrangement. To investigate this possibility *p*- γ,γ -dideuterioallylcumyl *p*-nitrobenzoate was prepared and subjected to solvolytic conditions. Detailed product and nmr studies indicated the complete absence of any rearrangement. Similarly, the kinetic isotope effect for γ,γ -dideuteration

(7) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957); *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(8) Unpublished observations of L. B. Jones and S. S. Eng.

of the *p*-allyl group was determined to be $k_H/k_D = 1.00$. These data are inconsistent with any significant incipient bond formation between the π cloud of the substituent and the aromatic ring.



The most consistent interpretation of these studies is that allyl substituents, in contrast to *p*-cyclopropyl, interact predominantly by an inductive interaction mechanism.

Experimental Section⁹

Materials.—Mallinckrodt AR acetone was refluxed with potassium permanganate until the color persisted and was then distilled. Magnesium turnings and dry ether were both Mallinckrodt AR. The *p*-dibromobenzene, *p*-bromoanisole, *p*-bromotoluene, and bromobenzene were Matheson AR. *p*-Bromochlorobenzene, *t*-butylbenzene, and *p*-chlorobenzyl chloride were obtained from Aldrich Chemical Co. All were used as received. Eastman practical grade allyl bromide was stirred over calcium chloride and distilled before use. Magnesium sulfate was used as the drying agent unless otherwise noted.

***p*-*t*-Butylbromobenzene.**—*t*-Butylbenzene (100 g, 0.745 mol) and 6.1 g of iron filings were placed in a 500-ml round-bottom flask equipped with a magnetic stirrer, thermometer, addition funnel, and condenser fitted with a hydrogen bromide trap. Bromine (131 g, 0.820 mol) was then added dropwise over a 2-hr interval during which time the temperature was maintained at 30°. The solution was then stirred overnight at room temperature. An equal volume of ether was added, and the mixture was extracted with successive portions of sodium bisulfite, sodium bicarbonate, and water. The solution was dried (potassium carbonate), concentrated, and distilled to give 87 g (55%) of *p*-*t*-butylbromobenzene: bp 130–133° (20 mm); n_D^{20} 1.5300 [lit.¹⁰ bp 101–103.5° (11 mm); n_D^{20} 1.5304].

γ,γ -Dimethylallyl Chloride.—The procedure of Uité¹¹ was used. A solution of 477 g (7.0 mol) of isoprene (Eastman White Label) and 100 ml of dry ether was cooled to -70°. Dry hydrogen chloride was then bubbled into the solution until 170 g had been added. The reaction mixture was allowed to stand overnight at Dry Ice temperature. The solution was then neutralized with anhydrous potassium carbonate, dried (calcium chloride), and distilled through a 4-ft Widmer column, yielding 220 g (30%) of γ,γ -dimethylallyl chloride, bp 45–60° (150 mm) [lit.¹² bp 67.2° (167 mm)].

(9) Melting points were determined with a Mel-Temp capillary apparatus and are uncorrected. Nmr spectra were determined in CCl₄ solution with Varian A-80 and HA-100 spectrometers using external and internal tetramethylsilane, respectively, as standards. Infrared spectra were determined with a Perkin-Elmer Model 337 using neat samples between sodium chloride plates. Ultraviolet spectra were obtained on a Cary Model 14 spectrometer. Gas chromatography was performed on a Wilkins Model A-90, P-3 chromatograph. The columns used were a 5-ft 5% FFAP on 60–80 Chromosorb P, and an 8-ft 18% GE SE-30 on base-washed Chromosorb P. Microanalyses were performed by Huffman Laboratories, Inc., Wheatridge, Colo.

(10) J. R. B. Boocock and W. J. Hickinbottom, *J. Chem. Soc.*, 2587 (1961).

(11) A. J. Uité, *ibid.*, 530 (1948).

(12) W. G. Young, S. Winstein, and H. L. Goering, *J. Amer. Chem. Soc.*, **73**, 1968 (1951).

1-(*p*-Chlorophenyl)-3-methyl-2-butene.—The Grignard reagent from 103.0 g (0.54 mol) of *p*-bromochlorobenzene and 13.1 g of magnesium turnings was prepared in 200 ml of dry ether by conventional techniques. The solution was cooled to 0° and 57.0 g (0.54) of γ,γ -dimethylallyl chloride in 100 ml of ether was added over 15 min. A two-phase system gradually developed, and, after 1 hr of stirring, the inorganic salts were granulated by dropwise addition of saturated aqueous ammonium chloride. The slurry was filtered, and the solids were washed with two 100-ml portions of ether. The washings and filtrate were combined, dried, concentrated, and distilled, yielding 40.8 g (42%) of 1-(*p*-chlorophenyl)-3-methyl-2-butene: bp 84–88° (1.5 mm); n_D^{20} 1.5303; nmr (CCl₄) δ 1.54 (d, 6 H, $J = 4$ Hz further split, $J = 1$ Hz, -CH₃), 3.08 (d, 2 H, $J = 8$ Hz, -CH₂-), 4.95–5.37 (t, 1 H, $J = 8$ Hz, further split into multiplet, $J = 1$ Hz, =CH-), 6.93 (M, 4 H, aromatic H).

This reaction, as well as the other coupling reactions to be described, has an induction period of 1–5 min. Care must be taken, therefore, during initial addition of halide to keep the reaction under control and prevent loss of material due to vigorous boiling.

***p*-Bromoallylbenzene.**—The Grignard reagent from 354 g (1.5 mol) of *p*-dibromobenzene and 40 g of magnesium turnings in 900 ml of ether was prepared by conventional techniques. A solution of 200 g (1.65 mol) of allyl bromide in 100 ml of ether was then added. Work-up as above with ammonium chloride followed by distillation of the concentrate yielded 193 g (65%) of *p*-bromoallylbenzene: bp 117–122° (19 mm); n_D^{20} 1.5507 [lit.¹³ bp 95–96° (12 mm); n_D^{20} 1.520]; nmr (CCl₄) δ 3.01 (d, 2 H, $J = 6$ Hz, -CH₂-), 4.63–5.10 (m, 2 H, =CH₂), 5.35–6.20 (m, 1 H, -CH=), 6.50–7.45 (m, 4 H, aromatic H). Vpc analysis (GE SE-30) of the product indicated a 4% contamination of *p*-dibromobenzene.

3-(*p*-Chlorophenyl)-1-butene.—The Grignard reagent from 125 g (0.778 mol) of *p*-chlorobenzyl chloride and 19 g of magnesium turnings in 500 ml of ether was coupled as described above with a solution of 97 g (0.8 mol) of allyl bromide in 100 ml of ether. Distillation yielded 77.6 g (60%) of 3-(*p*-chlorophenyl)-1-butene: bp 59–61° (1.4 mm); n_D^{20} 1.5234; nmr (CCl₄) δ 1.82–2.63 (m, 4 H, -CH₂CH₂-), 4.53 (m, 1 H), 4.75 (m, 1 H), 5.11–5.80 (m, 1 H), 6.47–6.91 (m, 4 H, aromatic H).

***m*-Chloroallylbenzene.**—The Grignard reagent from 100 g (0.68 mol) of *m*-dichlorobenzene and 16.5 g of magnesium turnings in 110 ml of tetrahydrofuran¹⁴ (THF) was coupled as described above with a solution of 84.8 g (0.70 mol) of allyl bromide in 30 ml of THF. Since magnesium halides are somewhat soluble in THF, 500 ml of pentane was added to precipitate them prior to addition of the saturated ammonium chloride solution. Distillation of the concentrate yielded 26 g (25%) of *m*-allylchlorobenzene: bp 60–65° (3 mm); n_D^{20} 1.5321; nmr (CCl₄) δ 2.65 (d, 2 H, $J = 7$ Hz, -CH₂-), 4.27 (m, 1 H), 4.50 (m, 1 H), 4.82–5.42 (m, 1 H), 6.09–6.58 (m, 4 H, aromatic H).

3-(*p*-Chlorophenyl)-3,3-dimethyl-1-butene.¹⁵—*p*-Chlorophenylacetone was prepared from 100 g (0.662 mol) of α -(*p*-chlorophenyl)acetonitrile as described by Overberger and Bilech¹⁶ to give 52 g (0.31 mol, 47%) of material: bp 98.5–102.5° (0.5 mm) [lit.¹⁶ bp 100–101° (3 mm)]; nmr δ 1.9 (s, 3 H, -CH₃), 3.40 (s, 2 H, -CH₂-), and 7.0 (4 H, aromatic H).

To a stirred suspension of 12 g of sodium hydride (15% dispersion in mineral oil) in 120 ml of anhydrous 1,2-dimethoxyethane cooled in ice was added dropwise with stirring over 4 hr a solution of 29.0 g (0.713 mol) of *p*-chlorophenylacetone and 56 g (0.39 mol) of methyl iodide in 20 ml of anhydrous 1,2-dimethoxymethane. The mixture was stirred at room temperature overnight, then poured onto ice, and extracted with ether. The ether layer was dried, concentrated, and distilled to give 28 g (0.143 mol, 82%) of 1-(*p*-chlorophenyl)-1,1-dimethyl-2-propanone: bp 102–104° (1 mm); nmr δ 1.20 (s, 6 H, *gem*-dimethyl), 1.70 (s, 3 H, CH₃), and 6.92 (4 H, aromatic H).

Reduction of 28 g (0.143 mol) of 1-(*p*-chlorophenyl)-1,1-dimethyl-2-propanone with excess lithium aluminum hydride yielded 25 g of the crude alcohol, which was acetylated without further purification with 25 g of acetyl chloride in pyridine to give

(13) K. C. Frisch, *J. Polym. Sci.*, **41**, 359 (1959).

(14) H. E. Ramsden, A. E. Balint, W. R. Whitford, J. J. Walburn, and R. J. Cserr, *J. Org. Chem.*, **22**, 1202 (1957).

(15) Synthesized by Vera K. Jones.

(16) C. G. Overberger and H. Bilech, *J. Amer. Chem. Soc.*, **73**, 4880 (1951).

TABLE IV
 PHYSICAL CONSTANTS AND STARTING HALIDES OF *para*-SUBSTITUTED 2-PHENYL-2-PROPANOLS

Substituted 2-phenyl-2-propanols	Registry no.	Parent compd	Mp, °C	Bp, °C (mm)	n_D^{20}
<i>p</i> -Hydrogen	617-94-7	Bromobenzene		60-65 (4.0)	1.5102
<i>p</i> -Methyl	1197-01-9	<i>p</i> -Bromotoluene		76-78 (2.0)	1.5128
<i>p-t</i> -Butyl	23853-82-9	<i>p</i> -Bromo- <i>t</i> -butylbenzene	76-78		
<i>p</i> -Methoxy	7428-99-1	<i>p</i> -Bromoanisole		85-90 (0.5)	1.5263
<i>p</i> -Allyl	22975-61-7	<i>p</i> -Bromoallylbenzene		70-75 (0.2)	1.5217
<i>p</i> -Chloro	1989-25-9	<i>p</i> -Bromochlorobenzene	42-43	98-103 (4.0)	1.5339
<i>p</i> - γ,γ -Dimethylallyl	23853-86-3	<i>p</i> - γ,γ -Dimethylallylchlorobenzene		85-95 (0.5)	1.5247
<i>m</i> -Allyl	23853-87-4	<i>m</i> -Allylchlorobenzene		74-77 (3.0)	1.5186
<i>p</i> -3-Butenyl	23853-88-5	<i>p</i> -3-Butenylbromobenzene		104-107 (0.45)	1.5184

 TABLE V
 MELTING POINTS, ABSORPTION MAXIMA, AND CHEMICAL ANALYSES OF CUMYL *p*-NITROBENZOATES

<i>para</i> substituent	Registry no.	Mp, °C	λ_{max} (log ϵ)	% C Calcd	% C Found	% H Calcd	% H Found
Hydrogen	7429-06-3	132.5-133.5	259 (3.102)				
<i>p</i> -Methyl	23852-75-7	105-107	259 (3.105)				
<i>p</i> -Methoxyl	23852-76-8	88-91					
<i>p-t</i> -Butyl	23852-77-9	114-116	260 (3.114)				
<i>p</i> -Chloro	23852-78-0	133-134.5	259 (3.108)				
<i>p</i> -Allyl	23852-79-1	45.4-46.1	260 (3.109)	70.14	70.04	5.89	5.91
<i>m</i> -Allyl	23852-80-4	66-67	260 (3.110)	70.14	69.94	5.89	5.83
<i>p</i> -3-Butenyl	23852-81-5	69-69.5	260 (3.107)	70.78	70.63	6.24	6.22
<i>p</i> - γ,γ -Dimethylallyl	23852-82-6	71.0-71.8	258 (3.102)	71.37	71.53	6.56	6.65

25 g (0.1 mol, 80%) of the corresponding acetate: bp 126-128° (1.2 mm); nmr δ 1.02 (d, 2 H, $J = 8$ Hz, $-\text{CH}_3$), 13.8 (s, 6 H, *gem*-dimethyl), 2.02 (s, 3 H, $-\text{COCH}_3$), 5.22 (q, 1 H, $J = 8$ Hz), and 7.48 (s, 4 H, aromatic H); ir 1735 cm^{-1} (ester C=O).

Pyrolysis of 24 g of the acetate at 450-500° gave 11.5 g (0.64 mol, 64%) of a colorless liquid: bp 60-65° (0.6 mm); nmr δ 1.32 (s, 6 H, *gem*-dimethyl), 4.8-6.3 (m, 3 H, olefinic H), and 7.30 (s, 4 H, aromatic); ir 3065 cm^{-1} (olefinic CH) and no absorption at 1700-1750 cm^{-1} .

2-Phenyl-2-propanol.—The Grignard reagent from 157.0 g (1.0 mol) of bromobenzene and 24.3 g of magnesium in 500 ml of ether was prepared by conventional techniques. A solution of 58 g (1.0 mol) of acetone in 100 ml of ether was added with cooling. After a short period of stirring, the alkoxide salts were destroyed by adding a saturated ammonium chloride solution until a heavy granular precipitate formed. The solution was filtered, the salts were washed with two 100-ml portions of ether, and the washings and filtrate were combined, dried, and concentrated. Distillation of the residual oil from potassium carbonate in base-washed glassware yielded 67 g (50%) of 2-phenyl-2-propanol, bp 60-65° (4 mm).

The same general procedure was employed in the synthesis of the other substituted phenyldimethylcarbinols. THF was used as the solvent to prepare the arylmagnesium chlorides.

Table IV lists the starting aryl compound as well as the physical constants of these alcohols. Nmr spectra of all the alcohols were consistent with structure and, where available, the physical constants were in agreement with literature values.¹⁷

Conversion of Alcohols to *p*-Nitrobenzoates.—Although minor variations were used from alcohol to alcohol, the following procedure for 2-(*p*-chlorophenyl)-2-propyl *p*-nitrobenzoate is a typical example. Hereafter the alcohol portion of the esters will be named according to the cumyl system.

A solution of 17.0 g (0.1 mol) of *p*-chlorocumyl alcohol in 100 ml of dry pyridine was cooled to 0° and 18.6 g (0.1 mol) of *p*-nitrobenzoyl chloride (freshly recrystallized from CCl_4) was added in portions. After stirring for 24 hr at 0°, the solution was poured into a cold mixture of 200 ml of 3 *N* hydrochloric acid and 200 ml of pentane. The solution was filtered, the organic layer of the filtrate was separated, and the aqueous layer was extracted with two 100-ml portions of pentane. The pentane solutions were combined and washed with successive 100-ml portions of cold 3 *N* hydrochloric acid, saturated sodium bicar-

bonate, and water. Drying and concentrating yielded an oil which was crystallized by trituration with cold pentane. Recrystallization from hexane yielded 18.1 g (57%) of *p*-chlorocumyl *p*-nitrobenzoate: mp 133-134.5°; λ_{max} ($\text{C}_2\text{H}_5\text{OH}$) 259 nm (log ϵ 3.108); nmr (CCl_4) 2.08 (s, 6 H, *gem*-dimethyl), 7.44 (s, 4 H, cumyl ring aromatic H), 8.39 (s, 4 H, *p*-nitrobenzoyl H).

Table V lists melting points and uv absorbances for all esters synthesized and elemental analyses of the olefinic esters employed in this study. The nmr spectrum of each ester was similar to that reported above for *p*-chlorocumyl *p*-nitrobenzoate.

3-(*p*-Chlorophenyl)-1,1-dideuterio-1-propene.—Diethyl *p*-chlorobenzylmalonate was prepared by the procedure described by Barnes and Gordon¹⁸ from 105 g (0.656 mol) of diethyl malonate, 34 g (0.5 mol) of sodium ethoxide, and 80.5 g (0.5 mol) of *p*-chlorobenzyl chloride in a yield of 70 g (0.246 mol, 49%), bp 145-150° (0.8 mm). Hydrolysis of 67 g (0.236 mol) of diethyl *p*-chlorobenzylmalonate by the procedure described¹⁸ with 180 ml of concentrated hydrochloric acid and 12 ml of acetic acid yielded 33 g of β -4-chloropropionic acid, mp 118-119° (lit.¹⁹ mp 120-122°). Esterification of 54 g (0.292 mol) of the acid by conversion to the acid chloride followed by reaction with ethanol yielded 45 g (0.21 mol, 72%) of ethyl β -4-chlorophenylpropionate, bp 110-112° (0.7 mm) [lit.²⁰ bp 99° (0.4 mm)].

A mixture of 4.3 g (0.099 mol) of lithium aluminum deuteride in 200 ml of ether was cooled to 0°, and a solution of 42 g (0.198 mol) of ethyl *p*-chlorophenylpropionate in 125 ml of ether was added dropwise with stirring and cooling. After addition, the mixture was stirred for 15 min; then consecutively and dropwise were added 4.2 g of water, 4.2 g of a 15% aqueous solution of sodium hydroxide, and 12.6 g of water. The mixture was stirred for 30 min. The solid was filtered and washed with ether. The ether layers were combined and dried over potassium carbonate, and volatile materials were removed by distillation on a steam bath, followed by heating the residue to 100° at 0.8-mm pressure.

The crude alcohol was dissolved in 140 ml of anhydrous pyridine and cooled to 0°; 22.5 g (0.287 mol) of acetyl chloride was added dropwise with stirring. After a short period the mixture was extracted with 150 ml of ether. The ether layer was washed with portions of cold 10% hydrochloric acid until the washings were acidic and then with saturated sodium bicarbonate solution. The organic layer was dried and concentrated on a steam bath. Residual traces of solvent were removed under vacuum

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(0.9 mm) at 50° to give 38.5 g of crude 3-(*p*-chlorophenyl)-1,1-dideuteriopropionyl acetate.

The crude acetate was pyrolyzed at 600°. Distillation of the pyrolysate yielded 18.7 g (0.121 mol, 61% based on ethyl *p*-chlorophenylpropionate) of 3-(*p*-chlorophenyl)-1,1-dideuterio-1-propene, bp 46–50° (1.4 mm). Gas chromatography²¹ showed the material to be 90% pure: nmr δ 2.73 (d, 6 H, $J = 7$ Hz), 5.15–5.50 (2 H, olefinic H), and 6.25–6.80 (4.5 H, aromatic H).

p-(γ,γ -Dideuterioallyl)cumyl *p*-Nitrobenzoate.¹⁵—The Grignard reagent prepared from 5.0 g (0.038 mol) of 3-(*p*-chlorophenyl)-1,1-dideuterio-1-propene and 1.2 g (0.049 g-atom) of magnesium in 9 g of anhydrous tetrahydrofuran was allowed to react with excess acetone to give 3.2 g of material, bp 105–115° (1.5 mm). Gas chromatography²² of the material showed ca. 85% one peak which had retention time identical with that observed upon chromatography of the nondeuterated analog. Ir spectra of distilled material showed strong OH absorption. Ir spectra of material collected by gas chromatography showed no OH absorption; *i.e.*, dehydration had occurred upon gas chromatography. Mass spectral analysis of the deuterated and nondeuterated olefins obtained by gas chromatography of the deuterated and nondeuterated alcohols showed the following composition for the deuterated analog: 0.9% d_0 , 4.9% d_1 , 92% d_2 , 0.7% d_3 , 1.3% d_4 .

Reaction of 3.2 g (0.018 mol) of the alcohol with 5.0 g (0.027 mol) of *p*-nitrobenzoyl chloride in 15 ml of pyridine yielded after normal work-up and recrystallization from pentane 2.66 g (0.0081 mol, 45%) of material, mp 38–39°. Two recrystallizations from pentane and drying under vacuum yielded material having mp 43.5–44° (cor) which was used for the kinetic measurements; nmr δ 3.30 (d, 2 H, $J = 7$ Hz), 5.7–6.0 (1 H, olefinic H), 7.0–7.34 (4 H, aromatic H), and 8.15 (4 H, aromatic H). No absorption was observed at 5 ppm where the nondeuterated derivative shows 2 H absorption.

Kinetic Procedure.—The desired amount of ester was dissolved in a preweighed quantity of acetone in a 100-ml volumetric flask, and the required weight of distilled, carbonate-free water was then added with shaking. The flask was placed in a thermostated bath and allowed to equilibrate for 15 min. In those cases where the half-life was less than 30 min, the solvents were preequilibrated at the bath temperature before mixing. At appropriate time intervals, 9-ml samples were removed and quenched with 10 ml of acetone at 0°, and the free *p*-nitrobenzoic

(21) A column packed with DC 710 on Gas-Chrom Q was employed.

(22) A column packed with Carbowax 20M on base-washed Chromosorb P was employed.

acid was titrated with approximately 0.02 *N* sodium hydroxide using bromthymol blue as indicator. Infinity titers were taken after at least ten times the estimated half-life. Temperatures in all cases were controlled to at least $\pm 0.03^\circ$.

Product Studies.—A solution of 0.307 g of *p*-allylcumyl *p*-nitrobenzoate in 100 ml of 50% w/w aqueous acetone was allowed to stand for 2 weeks at room temperature. After removing the acetone under reduced pressure, the aqueous residue was made basic with sodium bicarbonate, and the resultant solution was extracted with three 20-ml portions of ether. The extracts were combined, washed once with water, dried, and concentrated. The small quantity of residual oil which remained (ca. 50 μ l) was distilled in a Hickman still. Capillary nmr spectra (Varian HA-100 spectrometer) of the distillate proved to be identical with that of *p*-allylcumyl alcohol. The infrared spectrum and retention times of the material upon vapor phase chromatography using GE SE-30 and FFAP liquid phases were identical with that of *p*-allylcumyl alcohol. No other components were detectable in the distillate. The pot residue had a melting point of 235–240°, undepressed on mixture with an authentic sample of *p*-nitrobenzoic acid.

In similar experiments, *p*- γ,γ -dimethylallyl-, *m*-allyl-, *p*-3-butenyl-, *p*- α,α -dimethylallyl-, and *p*- γ,γ -dideuterioallylcumyl *p*-nitrobenzoates were solvolyzed in an identical manner. Isolation of the product alcohols again proved rearrangement had not occurred by virtue of nmr, infrared, and gas chromatographic comparisons with authentic samples.

Registry No.—1-(*p*-Chlorophenyl)-3-methyl-2-butene, 23853-76-1; *p*-bromoallylbenzene, 2294-43-1; 3-(*p*-chlorophenyl)-1-butene, 23853-78-3; *m*-allylchlorobenzene, 3840-17-3; 3-(*p*-chlorophenyl)-3,3-dimethyl-1-butene, 1-(*p*-chlorophenyl)-1,1-dimethyl-2-propanone, 16703-39-2; 1-(*p*-chlorophenyl)-1,1-dimethyl-2-propanol (acetate), 23890-37-1; 3-(*p*-chlorophenyl)-1,1-dideuterio-1-propene, 23852-83-7; *p*-(γ,γ -dideuterioallyl)-cumyl *p*-nitrobenzoate, 23852-84-8.

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Photochemical Transformations of Small-Ring Carbonyl Compounds. XXVI. Ground-State and Photochemical Reactions in the Thiacyclobutane Series^{1,2}

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Reaction of α -bromomethylchalcone with sodium hydrosulfide gives 3-phenyl-4-benzoyl-1,2-dithiolane (3), 2,4-diphenyl-5-benzoyl-1,3-dithiane (4), and 2-phenyl-3,5-dibenzoylthiane (5). Oxidation of dithiolane 3 with peracid affords 3-phenyl-4-benzoyl-1,2-dithiolane 2,2-dioxide (7), which was thermolyzed in dilute solution to give *trans*-2-phenyl-3-benzoylthietane (2). When thiosulfonate 7 was pyrolyzed in the neat, a mixture of *trans*- α -methylchalcone and 3-phenyl-4-benzoyl-1,2-dithiolane (3) was obtained. Irradiation of either dithiolane 3, thiosulfonate 7, or thiacyclobutane 2 afforded a mixture of *cis*- and *trans*-benzalacetophenone. The low bond dissociation energy of the C–S bond appears to be the major factor responsible for the photolytic cleavage of these sulfur heterocycles.

Phenomena regarding excited states of small-ring nitrogen ketones have received considerable attention

during the past few years.⁴ Interest in these compounds has been aroused in part by theoretical studies and in part by the unusual rearrangements that occur upon irradiation.^{5,6} The general types of phototrans-

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