Intramolecular Nucleophilic Participation. VII. The Role of the *o*-Carbomethoxy Group in the Solvolysis of Ring-Substituted Benzyl Halides and Their α-Methyl Derivatives

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Rate constants (k_s) for the solvolysis of 1-(2- and 4-carbomethoxyphenyl)ethyl bromides in 80 vol. % aqueous dioxane have been determined. In this medium at ordinary temperatures the 2-carbomethoxy derivative hydrolyzes more rapidly than its 4-carbomethoxy isomer. The k_s values have been compared with those for reactions under comparable conditions of structurally related carbomethoxy and dicarbomethoxy derivatives of benzyl and 1-phenylethyl bromides, and the role of the *o*-CO_2CH_3 group as an internal nucleophile in promoting solvolytic reactions of substituted benzyl halides and their α-methyl derivatives has been reevaluated. The contribution of this substituent as a participant in hydrolytic processes appears to increase with changes in structure of the reacting halide in the order *o*-$CH_3OOCC_6H_4CH_2X$ < *o*-$CH_3OOCC_6H_4CH(CH_3)X$ < *o*-$CH_3OOCC_6H_4C(CH_3)_2X$. This series is discussed in terms of the orientation of the bonds to α carbon relative to the ring plane in the activated complexes for hydrolysis of such compounds.

The fact that *o*-carbophenoxybenzhydryl bromide hydrolyzes considerably more rapidly than its *para* isomer has been ascribed to the capacity of the *o*-CO_2R group to participate as a nucleophile in the polar rupture of the carbon–bromine bond.[1] The solvolysis rates of *o*-carbomethoxybenzyl bromide and the *o*-carbomethoxy derivative of phenyldimethylcarbinyl chloride (*t*-cumyl chloride) are somewhat larger than those of their *para* isomers, but the differences in reactivity are not so great as those observed for the substituted benzhydryl halides. It was, therefore, concluded that the ring substituent does not function very effectively as a participant in the reactions of the *o*-carbomethoxy derivatives of either the benzyl or cumyl halide.[1,2] In the case of the reaction of the benzyl halide it is reasoned that, for maximum stabilization of the activated complex, the bonds to carbon at the reaction center must lie in the plane of the aromatic nucleus. This provides for maximum overlap of the ring π electrons with the vacant, or partially vacant, p orbital which develops as halide ion departs. This is a conformation which is not favorable for the involvement of the *ortho* substituent. A similar explanation has been considered in discussing the *t*-cumyl chloride results, and alternatively it has been suggested that an activated complex which is akin to a carbonium ion generated from a tertiary halide might not derive much additional stabilization through electron release by *o*-CO_2CH_3 even if the geometric situation were favorable.[3]

The 1-(2- and 4-carbomethoxyphenyl)ethyl bromides have now been prepared, and their solvolysis rates in 80 vol. % aqueous dioxane have been investigated. The results of a comparative study of the hydrolysis rates of the 1-(2,4- and 2,6-dicarbomethoxyphenyl)ethyl bromides have also become available recently.[4] With this new information at hand it is appropriate to reevaluate the contribution of the carbomethoxy group as a participant in polar reactions of *o*-carbomethoxybenzyl halides and their α-methyl derivatives.

Results and Discussion

Table I is presented to review briefly the relative influences of nonparticipating *ortho* and *para* substituents on the solvolysis rates of benzyl halides and their α-methyl and α,α-dimethyl derivatives. The *ortho*-substituted compounds are less reactive than their *para* isomers, even in those cases in which the opposite order is predicted if only the inductive effects of the substituents are taken into consideration [as, for example, for *o*- and *p*-$CH_3C_6H_4C(CH_3)_2Cl$].[5] The factor which is dominant in controlling the relative reactivities of the pairs of isomers must, therefore, be the steric hindrance provided by the *ortho*-ring substituents to stabilization of the activated complex through solvation and through delocalization of ring π electrons.[6-8]

TABLE I

SOLVOLYSIS RATE CONSTANT RATIOS [k_s (*ortho*)/k_s (*para*)] FOR ISOMERIC MONOSUBSTITUTED BENZYL, 1-PHENYLETHYL, OR *t*-CUMYL HALIDES

Compounds	Solvent	Temp, °C	k_s (*ortho*)/ k_s (*para*)	Ref
o- and *p*-$ClC_6H_4CH_2Cl$	50% aq acetone	50	0.52	*a*
o- and *p*-$CH_3C_6H_4CH_2Cl$	50% aq acetone	50	0.48	*a*
o- and *p*-$CH_3C_6H_4CH(CH_3)Cl$	100% ethanol	34.8	0.41	*b*
o- and *p*-$ClC_6H_4C(CH_3)_2Cl$	90% aq acetone	25	0.026	*c*
o- and *p*-$CH_3C_6H_4C(CH_3)_2Cl$	90% aq acetone	25	0.14	*d*

[a] S. C. J. Olivier, *Rec. Trav. Chim.*, **49**, 697 (1930). [b] See ref 6. [c] H. C. Brown, Y. Okamoto, and G. Ham, *J. Amer. Chem. Soc.*, **79**, 1906 (1957). [d] See ref 5.

In Table II a summary is presented of rate runs which have been made in studying the hydrolysis of the 1-(2- and 4-carbomethoxyphenyl)ethyl bromides, later designated as compounds VII and VIII. In Table III a comparison is made of the solvolysis rate constants of these two compounds in 80 vol. % aqueous dioxane at 70.7° relative to those of 1-phenylethyl bromide and two of its dicarbomethoxy derivatives and with those of benzyl bromide and certain of its mono- and dicarbomethoxy derivatives.

Although no other substituent (*e.g.*, CH_3 or Cl) can

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[1] A. Singh, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, **84**, 1179 (1962).

[2] J. L. Cotter, L. J. Andrews, and R. M. Keefer, *J. Org. Chem.*, **28**, 1917 (1963).

[3] E. A. Jeffery, R. K. Bansal, L. J. Andrews, and R. M. Keefer, *ibid.*, **29**, 3365 (1964).

[4] M. J. Strauss, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, in press.

[5] H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *ibid.*, **79**, 1897 (1957).

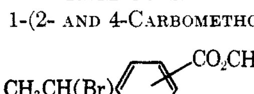
[6] J. C. Charlton and E. D. Hughes, *J. Chem. Soc.*, 850 (1956).

[7] G. Baddeley, J. Chadwick, and H. T. Taylor, *ibid.*, 2405 (1954).

[8] S. Winstein and B. K. Morse, *J. Amer. Chem. Soc.*, **74**, 1133 (1952).

TABLE II

RATE CONSTANTS FOR HYDROLYSIS OF THE 1-(2- AND 4-CARBOMETHOXYPHENYL)ETHYL BROMIDES,



, IN 80% AQUEOUS DIOXANE

Isomer	Range[a] of $[RBr]_i$, mol/l.	Temp, °C	10^5k_s,[b] sec^{-1}
2-CO_2CH_3	0.039–0.075	70.7	12.2 ± 1.0
4-CO_2CH_3	0.026–0.041	70.7	1.59 ± 0.05
2-CO_2CH_3	0.054–0.123	45.4	0.87 ± 0.02
4-CO_2CH_3	0.026–0.060	45.4	0.123 ± 0.01

[a] Three runs at differing initial reactant concentration were made with each isomer at the two temperatures. [b] Activation parameters have been calculated using the rate constants reported at the two temperatures. For the 2-CO_2CH_3 derivative values of $E_a = 22.0 \pm 0.2$ kcal and $\Delta S^{\ddagger} = -13.1 \pm 0.6$ eu have been obtained and for the 4-CO_2CH_3 derivative, $E_a = 21.3 \pm 0.2$ kcal and $\Delta S^{\ddagger} = -18.9 \pm 0.6$ eu.

serve as a totally adequate model for the carbomethoxy group, it is concluded on the basis of the results summarized in Table I that, if *o*-CO_2CH_3 were nonparticipating in reactions of the type under consideration, *p*-carbomethoxy-substituted benzyl and related halides should be more reactive than their *ortho* isomers. Actually the reverse is true, as is revealed in various ways in Table III.

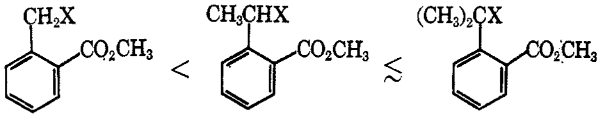
The introduction of a carbomethoxy substituent *para* to the reaction center of benzyl bromide and also of 1-phenylethyl bromide results in diminished reactivity, much more so in the latter case than in the former (*cf.* compounds I and III and VI and VIII). Even if there were no accompanying steric effects, it might normally be anticipated that the rate repression produced by *p*-CO_2CH_3, which is electronic in nature, would be more strongly manifested if the substituents were moved from *para* to *ortho* positions; yet the rate constant for 1-(2-carbomethoxyphenyl)ethyl bromide (VII), though substantially less than that of the parent bromide (VI), is almost eight times that of its *para* isomer (VIII), and *o*-carbomethoxybenzyl bromide (II) hydrolyzes almost four times as readily as its *para* isomer (III) and is even somewhat more reactive than benzyl bromide itself.

The rate-lowering effect of *p*-CO_2CH_3 can also be observed by comparing the relative rate constants of the *o*-carbomethoxy-substituted benzyl and 1-phenylethyl bromides with those of the corresponding 2,4-dicarbomethoxy-substituted bromides. On this basis V is only about one-third as reactive as II, and X about one-fourth as reactive as VII. On the other hand, a slightly enhanced reactivity results when *o*-CO_2CH_3 is introduced as a second substituent in a bromide which is already substituted with *p*-CO_2CH_3 (*cf.* III and V and also VIII and X).

In the case of the hydrolysis of 1-(2,6-dicarbomethoxyphenyl)ethyl bromide (IX) the conditions for forced participation of the two CO_2CH_3 groups which flank the reaction center are ideal.[4] In the activated complex the bonds to the carbon at the reaction center must lie in or near a plane perpendicular to the ring because of the severe steric barrier to the attainment of other conformational arrangements which is created by the *ortho* substituents. This places the p orbital at the α carbon in a highly favorable position to accept electrons from either *o*-CO_2CH_3 group. Compound IX has a k_s value over four times that for its 2,4 isomer (X), while the solvolysis rate constants ratios for the chlorine analogs of IX and X (in which CO_2CH_3 groups are replaced by Cl) is about 0.06;[4] that is, the reactivity ratio of IX to X is about 70 times as large as would be predicted on the basis of the behavior of the dichlorophenylethyl bromides. The fact that the 2,4- and 2,6-dicarbomethoxybenzyl bromides (IV and V) are comparable in reactivity is considered to indicate that there is little, if any, steric opposition to a coplanar orientation of the ring and the bonds to trigonal carbon in the activated complex for hydrolysis of IV. This conclusion can be confirmed by the use of molecular models.

It now seems safe to state without qualification that the hydrolysis of *o*-carbomethoxybenzyl bromide (II) as well as of 1-(2-carbomethoxyphenyl)ethyl bromide (VII) is subject to rate enhancement to some degree through release of electrons in the activation process from CO_2CH_3 to the carbon undergoing positive polarization. This statement should be generally applicable to any of the compounds in Table III which have *o*-carbomethoxy substituents.

The influence of the carbomethoxy group as a participant in the reactions of II and VII is considered to be much less than in the reaction of IX since the *ortho*/*para* isomer rate constant ratios for benzyl and phenylethyl bromides which bear nonparticipating substituents are much larger than the corresponding ratios of the chlorine substituted analogs of IX and X (see Table I). The k_s ratio for the *o*- and *p*-carbomethoxy derivatives of *t*-cumyl chloride[2] is of the order of 2.5:1 in 70% aqueous acetone at 25°. By taking this figure and the appropriate data from Tables I and II into consideration, it has been concluded that the influence of *o*-carbomethoxy as a participant on substrate reactivity in solvolytic processes becomes increasingly more important in the order



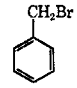
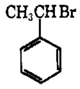
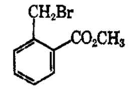
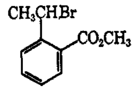
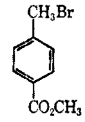
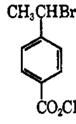
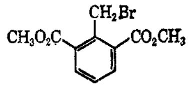
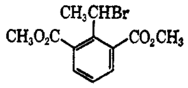
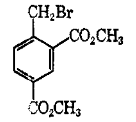
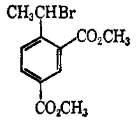
A B C

It seems reasonably safe to say that the hydrolysis of the *t*-cumyl halide derivative is at least as strongly influenced by the *o*-CO_2CH_3 group (functioning as a neighboring nucleophile) as is the reaction of the 1-phenylethyl halide. A more quantitative comparison is not justified because of the difficulties in choosing k_s (*ortho*)/k_s (*para*) ratios (Table II) which would correctly reflect the relative reactivities of the pairs of isomers if *ortho*-substituent participation did not occur and because of differences in reaction conditions employed in studying A, B, and C (*e.g.*, solvent, temperature, and the identity of X).

The above series runs parallel to the relative stability series for the benzyl, 1-phenylethyl, and *t*-cumyl cations. Since these cations are respectively primary, secondary, and tertiary, it seems likely that the importance of bonding interactions between the ring and the reacton center in providing for stabilization of the activated complexes for hydrolysis of the halides in question should diminish in that same order; that is, the energy sacrificed in moving the bonds to trigonal carbon out of the ring plane of the activated complexes should

TABLE III

RELATIVE SOLVOLYSIS RATE CONSTANTS OF CARBOMETHOXY AND DICARBOMETHOXY DERIVATIVES OF BENZYL AND 1-PHENYLETHYL BROMIDES [80 VOL. % AQUEOUS DIOXANE, 70.7°][a]

No.	Compound	Rel reactivity	k_s (*ortho*)/ k_s (*para*)	No.	Compound	Rel reactivity	k_s (*ortho*)/ k_s (*para*
I		1.00		VI		64.5	
II		1.4	3.5	VII		6.9	7.8
III		0.40		VIII		0.89	
IV		0.30	0.55[b]	IX		7.9	4.4[b]
V		0.55		X		1.8	

[a] The k_s values for compounds I, II, and III were calculated from data presented by A. Singh, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, **84**, 1179 (1962); the values for compounds IV, V, IX, and X are from M. J. Strauss, L. J. Andrews, and R. M. Keefer, *ibid.*, in press; and that for VI was calculated from data of A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1602 (1957). [b] The ratio of k_s values for the 2,6- and 2,4-disubstituted compounds.

drop off in this order, and this should be increasingly favorable for the effective release of electrons from the carbomethoxy group to the vacant p orbital of the α carbon. In the case of the *o*-carbomethoxy-substituted *t*-cumyl cation there is no doubt significant steric opposition to the attainment of a coplanar orientation of the ring and the bonds to trigonal carbon.

It is conceivable that, in the reactions of the *o*-carbomethoxy derivatives of the benzyl as well as of the 1-phenylethyl and *t*-cumyl halides, the activated complexes might assume conformations which provide for maximum *ortho*-substituent participation. Under these circumstances the thermodynamic disadvantages of a complete sacrifice of bonding interactions of the reaction center and the ring presumably would be fully offset through involvement of CO_2CH_3. Particularly for the benzyl halide reaction, in which the rate enhancement associated with participation by *o*-CO_2CH_3 is rather subtle, it is considered improbable that the activated complex actually is so structured. Rather it is considered likely that the plane of the trigonal carbon lies in a position somewhere between the ring plane and its perpendicular bisector. Presumably as ring-electron delocalization makes a diminishingly important contribution in providing for stabilization of the activated complex (as the reacting halide changes from primary to secondary to tertiary), the plane of the trigonal carbon shifts progressively toward a position most favorable for involvement of the *ortho* nucleophile. The unusual effectiveness of *o*-$COOC_6H_5$ in promoting the hydrolysis of *o*-carbophenoxybenzhydryl bromide is thought to result because the geometry of the activated complex is favorable for acceptance by the trigonal carbon of electrons both from the unsubstituted ring and from the substituent on the other ring.

Since the process of substituent participation has some of the characteristics of an SN2 reaction, hydrolysis of the tertiary halide (C in the series A–B–C) conceivably might have been found to be less susceptible to the influence of the *ortho* nucleophile than the hydrolysis of the secondary halide (B). Though this does not seem to be the case, it will be recalled in this connection that the *o*-carbophenoxy group is apparently a much less effective participant in the hydrolysis of a substituted 1,1-diphenylethyl halide than of a substituted benzhydryl halide.[3]

From the thermodynamic standpoint the solvolysis rate constant for 1-(2-carbomethoxyphenyl)ethyl bromide (VII) is higher than that for 1-(4-carbomethoxyphenyl)ethyl bromide (VIII) because the activation entropy for reaction of VII is much less negative than that for VIII; the activation energy for VII is actually slightly greater than that for VIII (see Table II). In this instance the entropy loss associated with participation appears to be substantially less than that connected with the incorporation of solvent in the activated complex when the carbomethoxy group is *para* to the reaction center. The fact that *o*-carbomethoxybenzyl bromide hydrolyzes faster than its *para* isomer at normal temperatures is similarly explained.[1] In the case of the carbomethoxy derivatives of *t*-cumyl chloride, however, the *ortho* isomer has the lower activation energy (by about 3 kcal) and more negative entropy of activation (by about 9 eu); these figures apply to reaction in 70% aqueous acetone.[2,9] This reversal is explained on the grounds that the activated complex for solvolysis of the *para*-substituted *t*-cumyl halide is less extensively solvated than that for the corresponding

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(9) Activation entropies in solvolytic processes are frequently considerably less negative for reactions which occur with than for those which take place without neighboring group participation. Such differences in activation energies have been used in a diagnostic sense, as for example in establishing which aryl groups provide anchimeric assistance in the solvolysis of 2-aryl benzenesulfonates; *cf.* S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, **78**, 4803 (1956).

α-phenylethyl halide. The differences in activation parameters for the reactions of the *ortho*- and *para*-substituted *t*-cumyl chlorides are, in fact, directionally like those predicted if the contribution of solvent in providing for stabilization of the activated complex is ignored.

Experimental Section

1-(4-Carbomethoxyphenyl)ethyl Bromide.—A sample of 4-iodo-1-ethylbenzene was prepared by treatment of the diazonium salt of *p*-ethylaniline (K & K Laboratories) with potassium iodide.[10] The Grignard reagent prepared from the iodo compound was carbonated to obtain a crude sample of *p*-ethylbenzoic acid, mp 106–109° (lit.[11] mp 112°). This was converted into its acid chloride by heating with thionyl chloride, and the aroyl halide was esterified with methanol to obtain methyl *p*-ethylbenzoate, bp 80–82° (2 mm) [lit.[11] bp 121–123° (20 mm)]. A mixture of 6.5 g of the ester, 7.2 g of N-bromosuccinimide, and 0.1 g of benzoyl peroxide in 120 ml of carbon tetrachloride was irradiated with ultraviolet light and heated at reflux for 0.5 hr. After removal of the succinimide and the solvent, 1-(4-carbomethoxyphenyl)ethyl bromide was obtained as a pale yellow oil. This was crystallized from ligroin to provide 7.0 g (66% yield) of colorless needles, mp 29° [lit.[11] bp 135–138° (1 mm)]; no melting point has been reported previously.

Anal. Calcd for $C_{10}H_{11}BrO_2$: C, 49.41; H, 4.56; Br, 32.87. Found: C, 49.38; H, 4.58; Br, 32.90.

The nmr spectrum of this material in carbon tetrachloride shows a doublet at τ 8.02 (side chain CH_3), a singlet at 6.70 ($-COOCH_3$), a quartet centered at 4.92 (benzylic H), and two doublets at 2.61 and 2.08 (the aromatic A_2B_2 system).

1-(2-Carbomethoxyphenyl)ethyl Bromide.—The same general procedures which were applied in the synthetic sequence described above were used to convert *o*-ethylaniline (Eastman Organic Chemicals) to 1-ethyl-2-iodobenzene[12] and the iodo compound to *o*-ethylbenzoic acid, mp 62–64° (lit.[13] mp 65–65.5°). The acid was converted by way of the acid chloride to its methyl ester,[14] bp 75° (1 mm). A mixture of 10 g of the methyl *o*-ethylbenzoate, 11.1 g of N-bromosuccinimide, and 0.1 g of benzoyl peroxide in 200 ml of carbon tetrachloride was heated at reflux and irradiated with ultraviolet light for 20 min. After removal of succinimide and the solvent, various unsuccessful attempts were made to induce crystallization of the oily product. It was finally dissolved in ligroin, and the solution was treated with decolorizing carbon. The ligroin was then removed under reduced pressure, leaving 11 g (74% yield) of pale yellow 1-(2-carbomethoxyphenyl)ethyl bromide.

Anal. Calcd for $C_{10}H_{11}BrO_2$: C, 49.41; H, 4.56; Br, 32.87. Found: C, 48.86; H, 3.81; Br, 33.02.

Distillation of this material was not attempted since the structurally similar compounds, *e.g.*, *o*-carbomethoxybenzyl bromide, decompose to give phthalide under such conditions.[1]

Although the product was not analytically pure its nmr spectrum in carbon tetrachloride showed only peaks characteristic of 1-(2-carbomethoxyphenyl)ethyl bromide; these included a doublet at τ 8.34 (side-chain CH_3), a singlet at 6.50 ($-COOCH_3$), a quartet centered at 3.80 (benzylic H), and a multiplet at 2.3–3.3 (aromatic H).

Kinetic Experiments.—The method of purification of the dioxane used in the rate studies has been described previously.[1] In all runs 80 vol. % aqueous dioxane prepared by mixing 20 vol. of water and 80 vol. of purified dioxane at room temperature was used as the solvent. The changes in hydrogen bromide content of the rate mixtures which took place during hydrolysis of the organic bromides were determined by observing the accompanying downfield shifts of the hydroxylic proton nmr peak of the reaction medium. The use of this method in studying the kinetics of hydrolysis of organic halides has been described in detail previously.[4] The rate constants, k_s, which are reported are defined by the equation, $k_s = 2.303/t\ (\log\ [RBr]_i/[RBr]_t)$, in which the subscripts i and *t* relate to initial time and time *t*.

Products of Hydrolysis of the Isomeric 1-(Carbomethoxyphenyl)ethyl Bromides.—A small sample of each of the two bromides was hydrolyzed in aqueous dioxane at 70.7° under conditions comparable to those of the rate runs. The reaction was allowed to proceed for at least 8 half-lives. The solvent was then removed under vacuum at room temperature. The residue was extracted with ether, and the dried extract was concentrated to dryness to obtain the reaction product. The material isolated from the reaction of 1-(2-carbomethoxyphenyl)ethyl bromide was 1-oxo-3-methylphthalan.[15] Because only a small quantity of the liquid product was obtained distillation was not attempted. Its elemental analysis and spectral properties were sufficient to identify it.

Anal. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 73.04; H, 5.33.

The nmr spectrum of the neat liquid showed a doublet at τ 8.78 (side-chain CH_3), a quartet at 4.78 (benzylic H), and a complex multiplet at 2.7 (aromatic H). The infrared spectrum of the liquid showed a strong carbonyl stretch at 1765 cm^{-1}.

Phthalide has been isolated from the products of hydrolysis of *o*-carboxybenzyl bromide,[1] and phthalan derivatives have been obtained from the 2,4- and 2,6-dicarbomethoxybenzyl bromides and the 1-(2,4- and 2,6-dicarbomethoxyphenyl)ethyl bromides.[4] It is not certain whether these are produced directly from the hydrolysis of the bromides or whether they are generated from substituted benzyl alcohols or 1-phenylethanol derivatives which possibly may form as reaction intermediates. This matter has not been further investigated since satisfactory procedures for preparing samples of *o*-carbomethoxybenzyl alcohol and structurally related alcohols have not been discovered.

No pure product could be isolated from the hydrolysis of 1-(4-carbomethoxyphenyl)ethyl bromide. The material recovered was presumably a mixture of 1-(4-carbomethoxyphenyl)ethanol and 1-(4-carboxyphenyl)ethanol. The nmr spectrum of the mixture (in CCl_4) showed a doublet at τ 8.65 (side-chain CH_3), a singlet at 6.23 ($-CO_2CH_3$), a quartet at 5.2 (benzylic H), and two doublets at 2.7 and 2.2 (the A_2B_2 aromatic system). The infrared spectrum of the crude product showed absorption at 3600 cm^{-1} (OH stretch) and a broad carbonyl band at 1700–1725 cm^{-1}.

Registry No.—I, 100-39-0; II, 2417-73-4; III, 2417-72-3; IV, 16281-93-9; V, 16281-94-0; VI, 585-71-7; VII, 16281-95-1; VIII, 16281-97-3; IX, 16281-98-4; X, 16281-99-5.

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