acid was redistilled and contained 0.3% acetic anhydride. Ampoules containing the reactants were sealed under nitrogen. The tables contain further information.

Hydrolysis.—Rate studies in 60% acetone were conducted as earlier described.[35] The acetone was freshly distilled from potassium permanganate. Again, ampoules were sealed under nitrogen. Further details may be found in the tables and ref 2.

Product Runs. Acetolysis.—Tosylate solutions (0.025 *M*) were prepared as for the acetolysis rate studies but in larger volume (50 ml). The solutions were heated under nitrogen in a pressure bottle at 95° for 25 hr. The material was added to water (1 l.) and thoroughly extracted with 1:1 ether–pentane. The organic extracts were washed and dried. Removal of solvent left an oil in each case. This oil was analyzed by spectral methods and by glpc to give the product data in Table III. Most glpc work was done on Flexol 8N8 columns, 6 ft × 0.25 in. at 175°. Acetate esters **12**, X = OAc, were characterized by λ 5.75, δ ≅ 2 s (-OCOCH$_3$). Olefins **13** have been described above. Olefins **14** were signified by λ 11, δ ≅ 5 (=CH$_2$). Olefins **15** were best evidenced by δ 5.5 (=CH), an upfield resonance relative to the vinyl proton in **13** (δ 6.3). Proper composition was better obtained prior to glpc because considerable acetate pyrolysis accompanied elution, enriching the vinyl products and decreasing the acetate esters. The olefin materials eluted at half the time of the esters and were easily distinguished. The olefin mixture could subsequently be simplified in composition by hydrogenation. Spectral and glpc data then indicated only the benzocyclenes mentioned above. Saponification of the crude product gave alcohols **12** (X = OH) which were correlated with the hydrolysis study (see below).

(35) J. W. Wilt, C. T. Parsons, C. A. Schneider, D. G. Schultenover, S. J. Wagner, and W. J. Wagner, *J. Org. Chem.*, **33**, 694 (1968).

Hydrolysis.—The product runs were performed upon tosylate solutions (0.030 *M*) made as for the hydrolysis rate studies and as described for acetolysis. Alcohols **12** and the olefin products have been described above and the spectral properties there reported were used to establish their presence in the product. Columns of Reoplex 400, Apiezon L and SE-30 at 175° caused extensive dehydration of **12** upon glpc. A column using Flexol 8N8 allowed less such dehydration, but again proper composition data was better obtained prior to glpc. In the instance of tosylate **5**, $n = 5$, the dihydronaphthalene olefin products were adventitiously oxidized to 2-methylnaphthalene. No olefins **13–15** were observed in this case.

Registry No.—**5**, $n = 4$, 33223-64-2; **5**, $n = 5$, 33223-65-3; **5**, $n = 6$, 33223-66-5; **5**, $n = 7$, 33223-67-5; **6**, $n = 7$, Z = COOCH$_3$, 33223-70-0; **7**, $n = 4$, Z = CN, 33223-68-6; **7**, $n = 7$, Z = CN, 33223-69-7; **7**, $n = 4$, Z = COOCH$_3$, 33223-71-1; **7**, $n = 7$, Z = COOCH$_3$, 33223-72-2; **8**, $n = 4$, 33223-73-3; **8**, $n = 5$, 33223-74-4; **8**, $n = 6$, 25634-94-0; **8**, $n = 7$, 33223-76-6; **10**, $n = 4$, 33223-77-7; **10**, $n = 5$, 33223-78-8; **10**, $n = 6$, 26516-28-9; **10**, $n = 7$, 33223-80-2; **11**, Z = CN, 28769-48-4; **11**, Z = COOCH$_3$, 3070-71-1; **11**, Z = CH$_2$Cl, 32223-83-5; **12**, $n = 4$, X = OH, 32223-84-6; **12**, $n = 5$, X = OH, 33223-85-7; **12**, $n = 6$, X = OH, 33223-86-8; **12**, $n = 7$, X = OH, 33223-87-9; **13**, $n = 7$, 33303-93-4; 1-chloro-2-benzylpropene, 33223-88-0; *cis*-α-benzylacrylic acid, 5669-19-2; 2-methylbenzosuberene, 22851-69-0.

Aryl Participation in the Solvolysis of Some *gem*-Dimethyl-Substituted 4-Aryl-1-alkyl *p*-Bromobenzenesulfonates[1]

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A series of 4-phenyl and 4-anisyl-1-butyl *p*-bromobenzenesulfates with 3,3- and 4,4-dimethyl groups was prepared, and acetolysis and formolysis rates were measured. The *gem*-dimethyl group can appreciably increase the tendency for aryl participation to occur in the solvolysis of these derivatives. Participation by both the 1- and 2(6)-carbon atoms of the aromatic ring is observed depending upon the substituents present. The formolysis of 4-(*m*-anisyl)-4-methyl-1-pentyl *p*-bromobenzenesulfonate produces mainly a mixture of 1,1-dimethyl-7- and 1,1-dimethyl-5-methoxytetralins formed by participation of carbons 2 and 6, respectively, in the solvolysis. With the related *p*-methoxy derivative, formolysis and acetolysis produce an appreciable amount (48% in formolysis) of 1,1-dimethyl-7-methoxytetralin, a rearranged product arising from participation of carbon atom 1 of the *p*-anisyl group producing a spirocationic intermediate which then undergoes a 1:2 shift of the tertiary group in preference to the primary one. In acetolysis, a significant amount (17%) of 1:4 shift of the *p*-anisyl group is also observed. Formolysis rate constants are divided into aryl-assisted and -unassisted fractions and yields of cyclized products were calculated assuming participation resulted in the exclusive formation of cyclized products. Those values were in reasonable agreement with the observed yields.

Participation of remote aryl groups in solvolysis reactions was clearly demonstrated in the previous papers in this series[3,4] with ω-aryl-1-alkyl *p*-bromobenzenesulfonates. Either carbon atom 1 or 2 of the ω-aryl group could assist solvolysis depending upon which was the more susceptible to electrophilic attack and depending upon the distance between the aryl and *p*-bromobenzenesulfonate groups. Participation by either aromatic carbon led exclusively to cyclization. Five- and six-membered rings were preferred. In this paper are reported results on some *gem*-dimethyl substituted aryl-1-alkyl *p*-bromobenzenesulfonates which show the rate-enhancing effect of the *gem*-dimethyl group and the rearrangement of appropriately substituted derivatives during solvolysis.

The compounds prepared and the kinetic data obtained from them are given in Table I. The addition of the 2,2-*gem*-dimethyl group to 2-phenylethyl *p*-bromobenzenesulfonate increases the rate of acetolysis by a factor of about 70,[5] while in the 3-phenyl-1-propyl system the 3,3-*gem*-dimethyl group actually decreases the rate by a factor of 0.7.[3] The *gem*-dimethyl group is apparently sterically inhibiting solvolysis in the last reaction. In the previous study[3,4] addition of methoxyl groups to the aromatic ring enhanced the solvolysis rates when participation was occurring. Since the

(1) Part of the work described in this paper was reported in preliminary form by S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956), and by S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958).

(2) University of Delaware, Newark, Del. 19711.

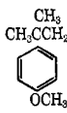
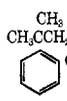
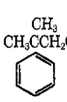
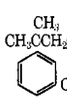
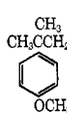
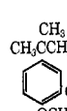
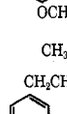
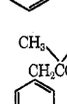
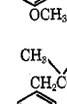
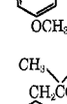
(3) R. Heck and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3105 (1957).

(4) R. Heck and S. Winstein, *ibid.*, **79**, 3114 (1957).

(5) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956).

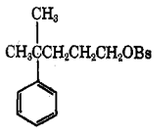
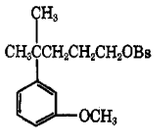
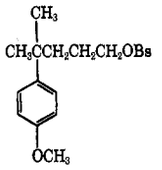
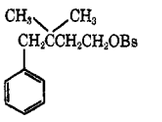
TABLE I

SUMMARY OF SOLVOLYSIS RATE CONSTANTS

Compd	Registry no.	Solvent	Concn, M[a]	Temp, °C	Added salt	$\Delta H^{\ddagger}$, k, sec^{-1}	kcal/mol	$\Delta S^{\ddagger}$, eu
	33214-50-5	HOAc	0.0290	75.00		$(3.04 \pm 0.01) \times 10^{-7}$	24.5	−18.5
		HOAc	0.0268	100.00		$(3.47 \pm 0.05) \times 10^{-6}$		
	33214-51-6	HOAc	0.0269	75.00		$(3.02 \pm 0.09) \times 10^{-7}$		
	33214-52-7[c]							
	33214-53-8	HOAc	0.0282	75.00		$(3.15 \pm 0.03) \times 10^{-7}$		
	33214-54-9[c]							
	33289-90-6	EtOH	0.0274	75.00		$(1.52 \pm 0.04) \times 10^{-4}$ (100)[b]		
	33214-55-0[c]	HOAc	0.0313	50.00		4.5×10^{-5} (31)[b]		
		HOAc	0.0313	75.00		5.6×10^{-4} (34)[b]		
		HOAc	0.0283	75.00	0.0030 M $LiClO_4$	4.6×10^{-4} (42)[b]		
		HOAc	0.0308	75.00	0.0300 M $LiClO_4$	4.2×10^{-5} (92)[b]		
		HOAc	0.0450	75.00	0.0300 M LiOTs	5.2×10^{-4} (25)[b]		
		HOAc	0.0294	75.00	0.0310 M NaOAc	$(5.81 \pm 0.05) \times 10^{-4}$ (93)[b]		
		HOAc	0.0281	50.00	0.0300 M LiOAc	$(4.51 \pm 0.08) \times 10^{-5}$ (91)[b]		
		HOAc	0.0281	75.00	0.0300 M LiOAc	$(6.07 \pm 0.14) \times 14^{-4}$ (90)[b]		
		HCOOH	0.0306	25.00	0.0291 M NaOCHO	$(2.20 \pm 0.05) \times 10^{-4}$ (96)[b]		
	33214-56-1	HOAc	0.02651	75.00		$(1.90 \pm 0.02) \times 10^{-6}$	24.4	−14.9
	33214-57-2[c]	HOAc	0.02670	100.05		$(2.17 \pm 0.03) \times 10^{-5}$		
		HCOOH	0.02921	50.00	0.0315 M NaOCHO	$(4.56 \pm 0.12) \times 10^{-6}$		
		HCOOH	0.02682	75.00	0.0315 M NaOCHO	$(5.93 \pm 0.03) \times 10^{-5}$	22.3	−14.3
	33214-58-3	HCOOH	0.02445	50.00	0.0315 M NaOCHO	$(1.25 \pm 0.01) \times 10^{-5}$		
	33325-79-0[c]	HCOOH	0.02323	75.00	0.0291 M NaOCHO	$(1.58 \pm 0.03) \times 10^{-4}$	22.0	−13.1
	29510-28-9	HOAc	0.02225	75.00		$(2.86 \pm 0.02) \times 10^{-6}$	25.0	−12.4
	26315-95-7[c]	HOAc	0.02225	99.92		$(3.42 \pm 0.03) \times 10^{-5}$		
		HCOOH	0.02527	50.00	0.0315 M NaOCHO	$(9.43 \pm 0.07) \times 10^{-6}$		
		HCOOH	0.02546	75.00	0.0291 M NaOCHO	$(1.24 \pm 0.04) \times 10^{-4}$	23.0	−12.5
	33214-61-8	HCOOH	0.02590	50.0	0.0315 M NaOCHO	$(2.06 \pm 0.12) \times 10^{-5}$		
	33214-62-9[c]	HCOOH	0.02590	75.00	0.0315 M NaOCHO	$(2.54 \pm 0.03) \times 10^{-4}$	21.8	−12.8
	33214-63-0	HOAc	0.02896	75.00		$(2.46 \pm 0.02) \times 10^{-6}$		
	15732-85-1[c]	HCOOH	0.02796	50.00	0.0315 M NaOCHO	$(1.70 \pm 0.04) \times 10^{-5}$		
		HCOOH	0.02640	75.00	0.0291 M NaOCHO	$(2.21 \pm 0.04) \times 10^{-4}$	22.3	−11.7
	33289-91-7	HCOOH	0.02724	50.00	0.0315 M NaOCHO	$(1.03 \pm 0.04) \times 10^{-4}$		
	33214-65-2[c]	HCOOH	0.02580	75.00	0.0315 M NaOCHO	$(1.11 \pm 0.03) \times 10^{-3}$	20.8	−13.3
	33214-66-3	HOAc	0.01850	75.00		$(7.94 \pm 0.52) \times 10^{-6}$		
		HCOOH	0.02504	50.00	0.0291 M NaOCHO	$(4.98 \pm 0.18) \times 10^{-5}$		
		HCOOH	0.02504	75.00	0.0291 M NaOCHO	$(6.43 \pm 0.12) \times 10^{-4}$	22.2	−9.8
	33214-67-4	HCOOH	0.02866	50.0	0.0315 M NaOCHO	$(2.60 \pm 0.04) \times 10^{-6}$		
	33214-68-5[c]	HCOOH	0.02866	75.00	0.0315 M NaOCHO	$(5.20 \pm 0.03) \times 10^{-5}$	26.1	−3.5

[a] Calculated from the infinity titers observed. [b] Per cent of the starting ester which solvolyzed based on the "infinity titer" assuming that the ethanol value (95%) indicated purity of sample. [c] Free alcohol.

TABLE II
SUMMARY OF SOLVOLYSIS PRODUCTS

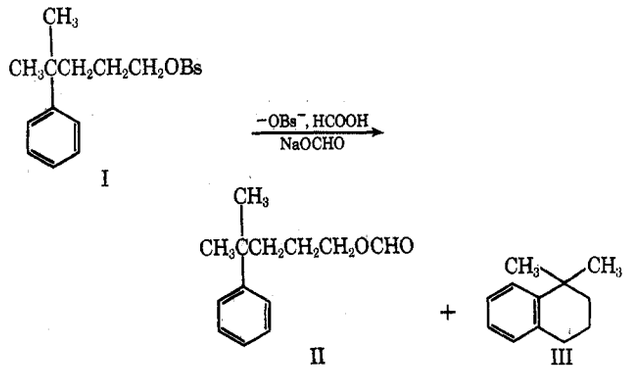
Compd	Solvent	Temp, °C	Total yield, %	Unrearranged products: % Alcohol	Unrearranged products: % Tetralin	Unrearranged products: % Olefin	Rearranged products: % Alcohol	Rearranged products: % Tetralin	Rearranged products: % Olefin
	HOAc	100	94.5	86.5	12.7	0.8			
	HCOOH	75	93.5	61.4	38.6				
	HCOOH	75	87.7	20.8	79.2 {51.5 VI, 27.7 VII}				
	HOAc	100	97.0	57.7	15.5		1.0	9.3	16.5
	HOAc(HOBs)[a]	100	95.0	57.0	15.0			22.0	
	HCOOH	75	86.0	29.0	22.7			48.3	
	HCOOH	75	95.0	5.0	95.0				

[a] HOBs not neutralized in this solvolysis.

m- and *p*-methoxyl derivatives of the 3-methyl-3-phenyl-1-propyl *p*-bromobenzenesulfonate have the same acetolysis rates as the phenyl compound within 5%, participation by either the 1- or 2-aryl carbon atoms in this system must be negligible. The *o*-methoxy derivative, on the other hand, is initially about 5000 times more reactive than the para compound. Only 31% of the expected quantity of sulfonic acid is produced, however, because of concurrent formation of methyl *p*-bromobenzenesulfonate, which is inert under our solvolysis conditions. Similar effects in other *o*-methoxy derivatives have been noted previously and an investigation of salt effects upon this compound demonstrated conclusively that it was another example of a compound showing participation by oxygen of the methoxyl group. A more complete discussion of methoxyl participation has been published elsewhere.[1b,6]

In the 4,4-*gem*-dimethyl-4-aryl-1-butyl derivatives some remote participation becomes detectable from kinetic data. In contrast to the propyl system, where the ω-*gem*-dimethyl group decreased the solvolysis rate of the phenyl derivative, the butyl case showed an increase by a factor of 1.3 in acetic acid and 1.7 in formic acid solvolysis. Here, *m*- and *p*-methoxyl substitution increased the solvolysis rates further; the *m*-methoxyl ω-*gem*-dimethyl compound reacted about 2.7 times faster and the para compound 2.1 times faster than the phenyl derivative in formolysis at 50°.

Convincing evidence that the relatively small rate increases observed in the above compounds were the result of aryl participation was found in an analysis of the formolysis products produced in the three cases. The results are summarized in Table II. Formolysis of 4-methyl-4-phenyl-1-pentyl *p*-bromobenzenesulfonate (I) at 75° produced a mixture of 57.4% 4-methyl-4-phenyl-1-pentyl formate (II, isolated as the alcohol) and 36.1% 1,1-dimethyltetralin (III). Control experiments with the more reactive 4-(*p*-anisyl)-4-methyl-1-pentyl formate show that it does not cyclize under formolysis conditions; therefore, the tetralin must be a product of formolysis, presumably formed from the part of the reaction which was promoted by aryl participation. Whether participation is localized at the 1- or 2-carbon of the phenyl group cannot be determined but more information on this point was obtained from a study of the methoxyl derivatives.

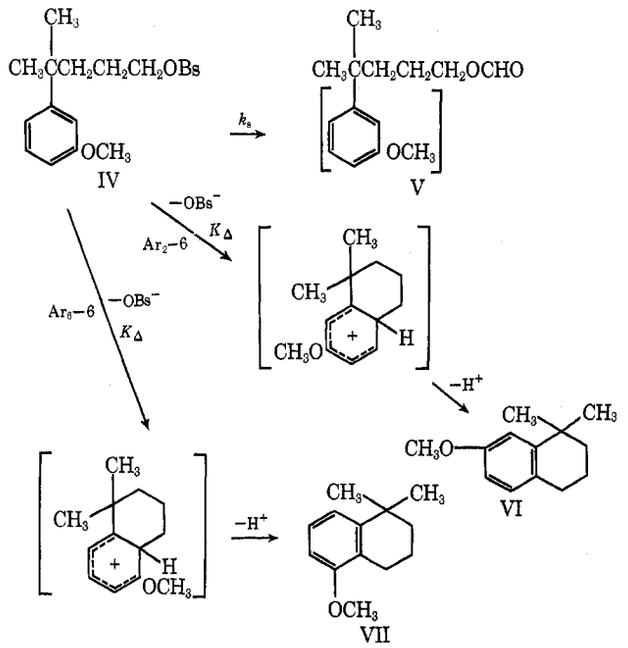


Formolysis of 4-(*m*-anisyl)-4-methyl-1-pentyl *p*-bromobenzenesulfonate (IV) gave 18.2% 4-(*m*-anisyl)-4-methyl-1-pentyl formate (V, isolated as the alcohol) and 69.5% of a mixture of two tetralins, 65% of which was 1,1-dimethyl-7-methoxytetralin (VI) and 35% 1,1-dimethyl-5-methoxytetralin (VII). There could not have been more than 1% of another possible product, 1,1-dimethyl-6-methoxytetralin (X), judging from infrared spectra. Thus, participation appears to be of the Ar_2-6 type[1] and both carbons 2 and 6 take part in the reaction.

The structure of 1,1-dimethyl-5-methoxytetralin was supported by an independent synthesis by the acid-catalyzed cyclization of 5-(*o*-anisyl)-2-methyl-2-pentanol and converison of the tetralin into 4,4-dimethyl-8-hydroxy-1-tetralone. The last compound

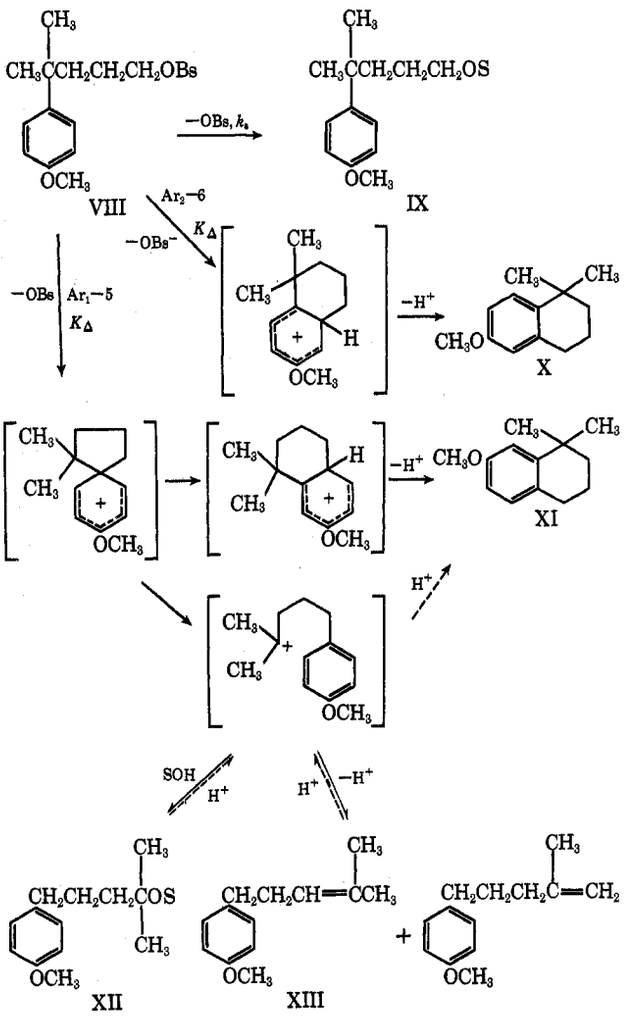
(6) R. Heck, J. Corse, E. Grunwald, and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3278 (1957).

showed the strong intramolecular hydrogen bonding expected from that structure.



The solvolysis of 4-(*p*-anisyl)-4-methyl-1-pentyl *p*-bromobenzenesulfonate (VIII), is more complicated. In formic acid at 75°, a 25% yield of 4-(*p*-anisyl)-4-methyl-1-pentyl formate (IX, S = CHO), isolated as the alcohol, and a 61% yield of a tetralin mixture was obtained. The mixture consisted of 32% 1,1-dimethyl-6-methoxytetralin (X) and 68% 1,1-dimethyl-7-methoxytetralin (XI). The major tetralin product is a rearranged one explicable in terms of an Ar_1-5 intermediate, a spirocarbonium ion, in which the tertiary carbon migrates to the ortho position. The minor tetralin could arise from the Ar_1-5 intermediate also if the primary carbon moved, but it more likely is the result of Ar_2-6 participation, which should still be a competitive reaction. We shall return to the point later.

Another complication of this solvolysis is the possible opening of the spirocationic intermediate to the tertiary carbonium ion which eventually yields the rearranged tetralin. Control experiments showed that under the formolysis conditions the same tertiary carbonium ion formed from the tertiary alcohol, 5-(*p*-anisyl)-2-methyl-2-pentanol (XII, S = H), cyclized exclusively to the "rearranged" tetralin, XI. Information on the spirocarbonium ion opening was obtained by an analysis of acetolysis products (in the presence of a slight excess of lithium acetate), since under basic acetolysis conditions (100°) the tertiary alcohol (XII, S = H) was relatively stable to cyclization and it gave only 6% tetralin along with 33% unrearranged olefin and 58% tertiary acetate ester (XII, S = $COCH_3$). The basic acetolysis of the 4-(*p*-anisyl)-4-methyl-1-pentyl *p*-bromobenzenesulfonate (VIII), at 100° gave 57 ± 1% acetate esters and 40 ± 1% of an olefin–tetralin mixture. The acetate esters consisted of about 98% 4-(*p*-anisyl)-4-methyl-1-pentyl acetate (IX, S = $COCH_3$) (56% of total solvolysis product) and 2 ± 1% of the rearranged tertiary ester, 5-(*p*-anisyl)-2-methyl-2-pentyl acetate (XII, S = $COCH_3$) (1% of total). Quantitative hydrogenation showed the olefin–tetralin mixture to be about 41% olefin (16% of total) presumably the rearranged olefins XIII, since the acetolysis of primary benzenesulfonates generally does not give appreciable amounts of olefinic products. Analyses of the tetralin product showed it to be a mixture of 37 ± 1% 1,1-dimethyl-7-methoxytetralin (XI) (9% of total) and 63 ± 1% 1,1-dimethyl-6-methoxytetralin (X) (15% of total). Acetolysis in the absence of acetate ion gave 57 ± 1% unrearranged acetate ester IX and 38 ± 1% tetralins. The latter product was a mixture of 40 ± 5% of the 6-methoxy isomer X (15% of total) and 60 ± 5% of the 7-methoxy compound XI (22% of total). The olefins and tertiary acetate ester apparently cyclized under the acidic acetolysis conditions, since the sum of the 16% olefin, 9% rearranged tetralin XI, and 1% tertiary acetate from the acetolysis of VIII under basic conditions roughly equals the amount of rearranged tetralin XI formed under acidic acetolysis conditions (22%). Three competing reactions are probably occurring in the basic acetolysis (and formolysis also): an unassisted solvolysis producing unrearranged acetate IX (59% of the reaction); Ar_2-6 type participation producing unrearranged tetralin X (15% of the reaction); Ar_1-5 participation producing rearranged tetralin XI, rearranged acetate XII, and rearranged olefins XIII (26% of the reaction). If this analysis is correct, then the Ar_1-5 intermediate in acetolysis opens to tertiary carbonium ion to the extent of 65%, which is equiva-

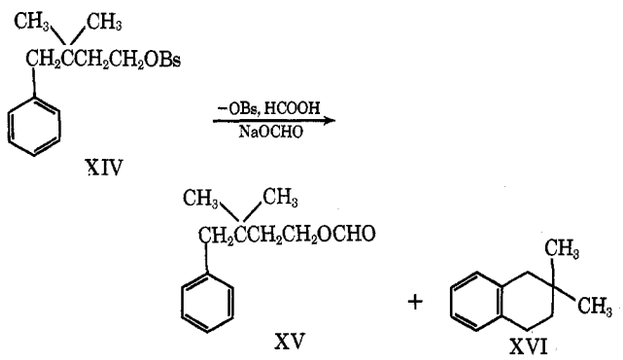


lent to 17% of the total product resulting from a 1:4 shift of the *p*-anisyl group.

For comparison we also investigated the acetolysis products of the parent compound 4-methyl-4-phenyl-1-pentyl *p*-bromobenzenesulfonate (I), under the same basic conditions. Here we obtained 81.5% "unrearranged acetate ester," 1–2% olefin, and 12 ± 1% 1,1-dimethyltetralin. The olefin appeared to be at least 98% unrearranged, suggesting that the participation probably is mainly of the Ar_2-6 type.

The formolysis rate of 4-(3-4-dimethoxyphenyl)-4-methyl-1-pentyl *p*-bromobenzenesulfonate was measured to see if the effects of two methoxyl groups were more than expected on the basis of the monomethoxyl derivatives. A significantly higher rate would suggest a general π-orbital participation rather than a more localized effect on one carbon of the aromatic ring. It is clear that any such effect must be small if it exists since the formolysis rate is only slightly faster than either of the monomethoxy compounds. A more quantitative analysis can be made on the basis of the fractions of the rates resulting from participation. This will be considered below.

The position of the *gem*-dimethyl group on the 4-aryl-1-butyl *p*-bromobenzenesulfonate side chain has a significant effect upon the solvolysis rates. The 3,3-dimethyl-4-phenyl-1-butyl *p*-bromobenzenesulfonate (XIV), reacted 1.3 times faster in acetolysis at 75° and 3.7 times faster in formolysis than the related 4,4-dimethyl compound. The formolysis products from the 3,3-dimethyl compound consisted of 5% 3,3-dimethyl-4-phenyl-1-butyl formate (XV), isolated as the alcohol, and 90% 2,2-dimethyltetralin (XVI). Again Ar_2-6 participation is suspected to be the major mechanism of tetralin formation.



The addition of methoxyl groups to the 3,3-*gem*-dimethyl system caused rate enhancements similar to those in the 4,4-*gem*-dimethyl system. The 3-methoxy derivative is six times and the 4-methoxy derivative is two times more reactive in formolysis at 50° than the 3,3-dimethyl-4-phenyl compound. Clearly Ar_2-6 is more favorable than Ar_1-5 participation.

The final compound in Table I is 2,2-dimethyl-4-phenyl-1-butyl *p*-bromobenzenesulfonate. This compound undergoes formolysis at only half the rate of the 4,4-dimethyl compound. Some Ar_1-5 or Ar_2-6 participation could still be possible here, but the similarity of the rate constant and the entropy of activation (*ca.* 6–10 eu higher than others that show Ar_1-5 or Ar_2-6 participation) to the corresponding values from neopentyl *p*-bromobenzenesulfonate suggest that β-alkyl participation must be the dominant reaction occurring.

The relative reactivities of various 4-aryl-1-butyl derivatives can be assessed more accurately if the rate constants are divided into the component parts resulting from solvent reaction, k_S, and aryl participation, k_Δ.[1] The k_S values of various compounds with the same side chains studied here should be approximately the same, since changes in the aromatic ring are too far away to influence the solvent reaction appreciably. The k_S values are found simply by multiplying the fraction of unrearranged formate ester in the total product by the rate constant measured under the same conditions. The k_Δ values are similarly calculated by multiplying the fraction of tetralin found by the rate constant. Internal consistencies can then be measured and more meaningful comparisons can be made. Measured and calculated k_S and k_Δ values are given in Table III. The k_S values for the first four compounds in the table should have been the same. In the three cases where there were enough data, two agreed very well and the third rather poorly; the k_S of the 4-(*m*-anisyl)-4-methyl-1-pentyl *p*-bromobenzenesulfonate (IV) for formolysis was about 39% too large compared to the compound without the methoxyl group. Some support for the assumption that the k_Δ for 4-methyl-4-phenyl-1-pentyl *p*-bromobenzenesulfonate (I) arises nearly exclusively from Ar_2-6 participation can be obtained by using the value as a k_Δ for the Ar_2-6 part of the reaction of the related *p*-methoxy compound, VIII, and calcualting the yield of the unrearranged tetralin expected (1,1-dimethyl-6-methoxytetralin, X). The calculated value is 18.5% and 22.7% was found. In the 3,4-dimethoxy compound it can be seen that the k_Δ of 21.76×10^{-5} sec^{-1} is only slightly larger than the sum of the k_Δ's of the *m*- and *p*-methoxy derivatives (19.56) and therefore there can be little effect of one methoxyl group upon the other in this reaction.

In both the 4,4- and 3,3-*gem*-dimethyl systems Ar_2-6 ring closure is significantly better than the Ar_1-5 closure. The methoxyl groups in either the meta or para positions, however, are very much less effective in favoring aryl participation in the 4-aryl-1-butyl compounds than they are in the 2-arylethyl system, where factors of 100 are common *vs.* only ~5 in the above samples.

Experimental Section

p-Bromobenzenesulfonates.—These compounds were all prepared by the method described previously.[5]

Kinetic Measurements.—Acetolysis rates[7] and formolysis rates[5] were measured in the usual way.

3-Methyl-3-phenyl-1-butanol.—The reduction of 3-methyl-3-phenylbutyric acid[8,9] with lithium aluminum hydride in ether gave a 93% yield of 3-methyl-3-phenyl-1-butanol, bp 81–82° (0.3 mm), $n^{25}D$ 1.5206 [lit.[10] bp 137–138° (16 mm)].[10]

The *p*-bromobenzenesulfonate had mp 51.5–53.5°. *Anal.* Calcd for $C_{17}H_{19}O_3SBr$: C, 53.27; H, 5.00. Found: C, 53.19; H, 5.14.

3-(4-Acetamidophenyl)-3-methylbutyric Acid.—The acetylation of 244 g of 3-(4-aminophenyl)-3-methylbutyric acid[10] with

(7) S. Winstein, E. Grunwald, and L. Ingraham, *J. Amer. Chem. Soc.*, **70**, 826 (1948).

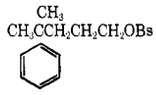
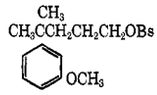
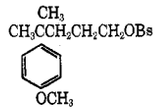
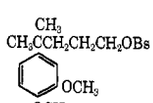
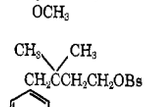
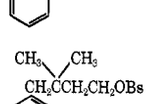
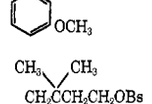
(8) F. Whitmore, C. Weisgerber, and A. Shabica, Jr., *ibid.*, **65**, 1469 (1943).

(9) F. Prout, E. Huang, R. Hartman, and C. Korpics, *ibid.*, **76**, 1911 (1954).

(10) J. Corse and E. Rohrmann, *ibid.*, **70**, 370 (1948).

TABLE III

DISSECTIONS OF RATE CONSTANTS INTO k_S AND k_Δ

Compd	Rel rates HOAc (75°)	Rel rates HCOOH (75°)	HOAc 75.00° 10^6k_S	HOAc 75.00° 10^6k_Δ	HOAc 75.00° k_Δ/k_S	HOAc 75.00° Rel k_Δ	HCOOH 75.00° 10^5k_S	HCOOH 75.00° 10^5k_Δ	HCOOH 75.00° k_Δ/k_S	HCOOH 75.00° Rel k_Δ
	1.0	1.0	1.64[a]	0.26[a]	0.15	1.0	3.64	2.29	0.6	1.0
		2.7					5.05	10.75	2.1	4.7
	1.5	2.1	1.66[a]	1.20[a]	0.72	4.6	3.59	8.81	2.5	3.8
		4.3					(3.64)[b]	(21.76)[b]	6.0	9.5
	1.3	3.7					1.10	21.0	19.1	9.2
		18.7					(1.10)[b]	(110)[b]	100.0	48
	4.2	10.8					(1.10)[b]	(63.2)[b]	57.5	28.

[a] Assuming product composition is the same at 75.00° as was found at 100°. [b] Calculated assuming k_S value is the same as in the compound without the methoxyl group.

155 g of acetic anhydride and 10 g of pyridine at 100° for 1.5 hr gave 263 g of product, mp 138–141°, after crystallization from a mixture of ethyl acetate and pentane. *Anal.* Calcd for $C_3H_{17}O_3N$: C, 66.36; H, 7.28. Found: C, 66.58; H, 7.46.

3-(4-Acetamido-3-nitrophenyl)-3-methylbutyric Acid.—A solution of 30 ml of concentrated nitric acid and 40 ml of concentrated sulfuric acid was added dropwise with stirring to 100 g of 3-(4-acetamidophenyl)-3-methylbutyric acid dissolved in 400 ml of concentrated sulfuric acid. The mixture was kept in an ice bath during the addition, and for 20 min afterward. After stirring for another 1 hr without cooling, the solution was poured onto ice. The product soon crystallized, and it was filtered and crystallized from a mixture of ethyl acetate and petroleum ether (bp 30–60°). The yield of bright yellow needles was 64 g. A small sample was recrystallized again for analysis. The material did not melt sharply, but decomposed at about 150°. *Anal.* Calcd for $C_{13}H_{16}O_5N_2$: C, 55.71; H, 5.75. Found: C, 55.83; H, 5.68.

3-Methyl-3-(3-nitrophenyl)butyric Acid.—3-(4-Acetamido-3-nitrophenyl)-3-methylbutyric acid (56 g) was boiled for 2 hr with a solution of 45 ml of concentrated hydrochloric acid and 90 ml of water. This mixture was treated with 50 ml more concentrated hydrochloric acid and cooled to 0° while a solution of 14.5 g of sodium nitrite in 35 ml of water was added during 1.5 hr. Then 104 ml of 50% hypophosphorus acid, cooled to 0°, was added over a period of 30 min. After standing overnight at 0°, the orange solid was filtered and air dried. The yield was 37 g. A small sample, after two recrystallizations from aqueous methanol, melted at 109–110°. *Anal.* Calcd for $C_{11}H_{13}O_4N$: C, 59.18; H, 5.87. Found: C, 59.20; H, 5.85.

3-(*m*-Anisyl)-3-methylbutyric Acid. Method A.—A solution of 80 g of 3-methyl-3-(3-nitrophenyl)butyric acid in 1200 ml of methanol was hydrogenated at 30 psig using 1 g of platinum oxide as catalyst. After filtering, the methanol was evaporated. A dark oil remained which could be crystallized, with great loss, from a mixture of ether and carbon tetrachloride. *Anal.* Calcd for $C_{11}H_{15}O_2N$: C, 68.37; H, 7.82. Found: C, 67.72; H, 7.32). For the conversion of this compound to 3-(*m*-anisyl)-3-methylbutyric acid, purification was not necessary. The crude dark oil was dissolved in ether and the amino acid was extracted with a solution of 35 g of sulfuric acid in 550 ml of water. The extract was cooled to 0° and diazotized with 27.5 g of sodium nitrite in 50 ml of water. After standing for 10 min at 0°, 5 g of urea was added and the solution was added as rapidly as possible to a refluxing solution of 275 ml of water and 70 ml of concentrated sulfuric acid. After a further 10 min of refluxing, the dark mixture was cooled and extracted twice with ether. The extracts were washed with water and the phenol was extracted from the ether phase with a solution of 30 g of potassium hydroxide in 100 ml of water. The aqueous solution was treated with methyl sulfate at 70–90° and the product from acidification of the basic reaction mixture was recrystallized twice from petroleum ether (bp 60–80°). The red-colored product weighed 5.9 g and was sufficiently pure to be used in the next step. A small sample was distilled under reduced pressure, mp 77–78.5°. *Anal.* Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.75. Found: C, 68.94; H, 7.76.

Method B.—To the Grignard reagent prepared from 75 g of *m*-bromoanisole and 10 g of magnesium in ether, 61 g of isopropylidenecyanoacetic ester was added with stirring. The resulting solution was boiled for 1 hr and poured onto ice and hydrochloric acid. The ether phase was separated and the aqueous phase was extracted again with ether. The combined extracts were washed with water and the solvent was evaporated. The dark residue was boiled for 7 hr with 180 g of potassium hydroxide in 600 ml of ethylene glycol. The cooled solution was diluted with 2 l. of water, and a small amount of a black oil was extracted with three portions of chloroform. On acidification, the aqueous solution precipitated a dark oil which was extracted with two portions of ether. The extracts were washed with water and dried and the solvent was evaporated. The dark oil re-

maining was dissolved in hot hexane and decolorized with Norit. The solution deposited 38 g of crystals on cooling, mp 75–77.5°.

3-(*m*-Anisyl)-3-methyl-1-butanol.—This alcohol, 33 g, bp 135–137° (2.5 mm), n^{25}D 1.5258, was prepared by the reduction of the above acid (38 g) with lithium aluminum hydride. *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.18; H, 9.52.

The alcohol yielded a liquid *p*-bromobenzenesulfonate, n^{25}D 1.5660, which was 97% pure by equivalent weight measurements in acetic acid.

3-(*p*-Anisyl)-3-methylbutyric Acid.—This acid has been prepared by two methods: by the methylation of the hydroxy acid prepared by Corse and Rohrman[10] and by a Friedel–Crafts reaction. Although the Friedel–Crafts reaction gave a poor yield, it was more convenient. A mixture of 220 g of anisole, 540 g of anhydrous aluminum chloride, and 100 g of 3-methylcrotonic acid in 1 l. of tetrachloroethane, was heated to 50–70° for 2 hr. The cooled reaction mixture was poured onto ice and hydrochloric acid. The aqueous phase was extracted with chloroform. The combined organic phases were extracted with water and with 210 g of sodium bicarbonate in 2 l. of water. The bicarbonate solution was extracted with ether and acidified. The liberated acid was extracted with ether. Evaporation of the ether left an oil which was crystallized twice from hexane. There was obtained 23 g of colorless solid, mp 85–87° (lit.[10] mp 89.6–91°).

3-(*p*-Anisyl)-3-methyl-1-butanol.—The above acid was reduced in 79% yield with lithium aluminum hydride. The alcohol had bp 130–133° (2.5 mm), n^{25}D 1.5260. *Anal.* Calcd for $C_{18}H_{21}O_4SBr$: C, 52.30; H, 5.12. Found: C, 52.43; H, 4.86.

3-(*o*-Anisyl)-3-methylbutyric Acid.—A Grignard reagent was prepared in ether solution from 230 g of "*o*-methoxyneophyl chloride"[6] and 24 g of magnesium. The reaction was initiated with methyl iodide and 5–6 hr of refluxing was necessary to complete the reaction. A stream of carbon dioxide was then passed into the solution until the solution became cold. Hydrolysis with acid followed by extraction of acidic product into aqueous bicarbonate solution and reacidification gave the crude acid. Several recrystallizations from hexane gave 14 g of product, mp 70.5–71°. Some of the para isomer, mp 83–85°, crystallized initially from the hexane solution. *Anal.* Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.75. Found: C, 69.35; H, 7.94.

3-(*o*-Anisyl)-3-methyl-1-butanol.—Reduction of 14 g of the above acid with 3 g of lithium aluminum hydride in 300 ml of ether gave, after the usual isolation procedure, 12.5 g of alcohol, bp 109–112° (1.5 mm), n^{25}D 1.5272. *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.96; H, 9.26.

This alcohol gave a viscous liquid *p*-toluenesulfonate which was 91% pure by equivalent weight measurements in formic acid.

1-Bromo-3-methyl-3-phenylbutane.—A cooled mixture of 74 g of 3-methyl-3-phenyl-1-butanol and 36 g of pyridine was treated with 125 g of phosphorus tribromide and heated on a steam bath for 2 hr. After cooling, the mixture was poured onto ice and an orange solid was filtered off and discarded. The filtrate was extracted with ether. The extract was washed with water and a sodium bicarbonate solution. After drying, the ether was evaporated and the bromide was fractionated. The yield of colorless product, bp 125–127° (11 mm), n^{25}D 1.5370, was 59 g. *Anal.* Calcd for $C_{11}H_{15}Br$: C, 58.16; H, 6.66. Found: C, 58.20; H, 6.44.

4-Methyl-4-phenylpentanoic Acid. Method A.—The Grignard reagent was prepared from 34 g of 1-bromo-3-methyl-3-phenylbutane bromide and 3.7 g of magnesium. The reaction was initiated with 1 g of methyl iodide and the reaction mixture was heated with stirring for 1.5 hr. A stream of dry carbon dioxide was bubbled in until the ether became cold. The reaction mixture was treated with cold dilute sulfuric acid and the ether phase was separated and washed with water. The acid product was extracted from the ether with 25 g of sodium carbonate in 200 ml of water. After washing the carbonate extract with ether, it was acidified and the product was extracted with ether. After drying and evaporation of the solvent, an oil was obtained which could be crystallized from pentane at −30°. The yield of acid, mp 29–31°, was 11.5 g. *Anal.* Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.99; H, 8.16.

Method B.—This acid was produced in 40% yield by the Willgerodt reaction from 4-methyl-4-phenyl-2-pentanone as described by Campbell and Cromwell.[11]

(11) R. Campbell and N. Cromwell, *J. Amer. Chem. Soc.*, **77**, 5169 (1955).

4-Methyl-4-phenyl-1-pentanol.—The lithium aluminum hydride reduction of 4-methyl-4-phenylpentanoic acid afforded the alcohol, bp 110–111° (3 mm), n^{25}D 1.5168, in 94% yield. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.84; H, 10.41.

The *p*-bromobenzenesulfonate melted at 38–40°. *Anal.* Calcd for $C_{18}H_{21}O_3SBr$: C, 54.41; H, 5.33. Found: C, 54.46; H, 5.19.

4-(*m*-Anisyl)-4-methylpentanoic Acid.—The crude liquid *p*-bromobenzenesulfonate prepared from 33 g of 3-(*m*-anisyl)-3-methyl-1-butanol was added to a hot mixture of 75 g of potassium cyanide and 1.5 l. of absolute methanol. The mixture was boiled overnight and half of the solvent was distilled off. The remainder of the solution was poured into 4 l. of water. The nitrile which separated was extracted with three portions of ether and the extracts were washed with water. After removing the solvent, the crude nitrile was boiled for 3 hr with a solution of 150 g of potassium hydroxide in 500 ml of ethylene glycol. The cooled reaction mixture was diluted with 3 l. of water and a small amount of oil was extracted with three portions of chloroform. The aqueous phase was then acidified and the crude acid was extracted with two portions of ether. The extracts were washed with water and dried. After the solvent had been evaporated, the oil remaining was crystallized (with seeding) from pentane. The yield of light tan product, mp 47–50°, was 20 g. Another crystallization from pentane gave shiny, colorless needles, mp 48–50°. *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.06; H, 8.21.

4-(*m*-Anisyl)-4-methyl-1-pentanol.—The reduction of 10 g of 4-(*m*-anisyl)-4-methylpentanoic acid with 2 g of lithium aluminum hydride gave 9.35 g of alcohol, bp 145–148° (3 mm), n^{25}D 1.5222. *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.92; H, 9.81.

The *p*-bromobenzenesulfonate was obtained as a colorless, viscous liquid, n^{25}D 1.5588, which was shown to be 88% pure by equivalent weight measurements in acetic and formic acid. Purification of the *p*-bromobenzenesulfonate was achieved by chromatography on alumina. A pentane eluate was discarded and the sulfonate was eluted with 30% benzene–70% pentane. The chromatographed material, though still not crystalline (n^{25}D 1.5228), was shown to be 97 ± 1% pure by an equivalent weight measurement in formic acid.

3-(*p*-Anisyl)-1-bromo-3-methylbutane.—A mixture of 20 g of 3-(*p*-anisyl)-3-methyl-1-butanol and 8 g of pyridine was treated with 28 g of phosphorus tribromide. The hot mixture was stirred for 30 min and poured onto ice. The product was extracted with ether and the extract was washed with water, dried, and distilled. The bromide, bp 126–128° (4 mm), n^{25}D 1.5380, weighed 10 g.

4-(*p*-Anisyl)-4-methylpentanoic Acid. A.—A Grignard reagent was prepared in ether from 6 g of methyl iodide, 2 g of magnesium, and 10 g of 3-*p*-anisyl-1-bromo-3-methylbutane. After refluxing for 2 hr, the mixture was cooled and poured onto an excess of dry carbon dioxide. The mixture was decomposed with cold dilute hydrochloric acid. The ether phase was separated and washed with water and with 100 ml of a 10% sodium bicarbonate solution. Acidification of the bicarbonate extract gave the crude acid. After air-drying, the acid was recrystallized from pentane, giving 1.5 g of product, mp 65.5–67°. *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.17; H, 7.92.

4-Methyl-4-pentanolactone.—Methyl Grignard reagent was prepared from 200 g of methyl iodide and 33.8 g of magnesium in 1 l. of ether and added during 2.5 hr to a well stirred solution of 200 g of ethyl levulinate in 2.5 l. of ether at −80°. After the addition, the mixture was allowed to stand at room temperature overnight. Then 38 ml of concentrated sulfuric acid was diluted with ice and water to 300 ml and added to the reaction mixture. The precipitated solid dissolved slowly and it was necessary to cool the flask to keep the hydrolysis under control. After the solid had dissolved, the ether phase was separated and the aqueous phase was extracted again with ether. The combined extracts were washed with water, aqueous sodium bisulfite, water, and finally with aqueous sodium bicarbonate. After drying, the solvent was removed and the lactone was distilled. The product, bp 50–60° (1.5 mm), n^{25}D 1.4300, weighed 100 g. The material was purified by hydrolysis. For this purpose, 100 g of the crude lactone was boiled for 1 hr with 60 g of sodium hydroxide in 250 ml of water. The cooled solution was extracted twice with ether and acidified carefully with cold

dilute hydrochloric acid. The lactone was extracted with three portions of ether, dried, and distilled. The purified product, bp 87–90° (16 mm), $n^{25}D$ 1.4310, weighed 71.5 g (45%).

4-(*p*-Anisyl)-4-methylpentanoic Acid. Method B.—To a solution of 60 g of anhydrous aluminum chloride in 200 ml of tetrachloroethane, cooled in ice water, was added dropwise with stirring a mixture of 30 g of anisole and 23 g of crude 4-methyl-4-pentanolactone. After the addition the mixture was warmed to 50° for 30 min and poured onto ice and hydrochloric acid. The organic phase was separated and the aqueous solution was extracted with chloroform. The combined organic extracts were washed with water and the acid product was extracted with aqueous sodium bicarbonate. Acidification of the bicarbonate extract gave an oil which soon crystallized. The colorless solid obtained was recrystallized from hexane, giving 2.3 g of material, mp 65–67°.

4-(*p*-Anisyl)-4-methyl-1-pentanol.—The reduction of 5.3 g of 4-(*p*-anisyl)-4-methylpentanoic acid with 1 g of lithium aluminum hydride produced 4.5 g of the alcohol, bp 147–148° (4 mm), $n^{25}D$ 1.5213. *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.74; H, 9.64. The *p*-bromobenzenesulfonate melted at 58–59°. *Anal.* Calcd for $C_{19}H_{23}O_4SBr$: C, 53.40; H, 5.42. Found: C, 53.26; H, 5.34.

3-(3,4-Dimethoxyphenyl)-3-methylbutyric Acid.—A solution of 50 g of 3-methylcrotonic acid and 70 g of veratrole in 500 ml of tetrachloroethane was stirred and cooled in ice while 270 g of powdered anhydrous aluminum chloride was added. The mixture was heated at 50° with stirring for 2 hr. After cooling and pouring onto ice and hydrochloric acid, the organic phase was steam-distilled in the presence of 100 g of sodium bicarbonate in 500 ml of water. After the solvents were removed, the residue was cooled and filtered from some dark tar. The filtrate was acidified and extracted with ether. The extract yielded an oil which was methylated with 80 g of sodium hydroxide in 150 ml of water and 130 g of dimethyl sulfate. The product from the methylation was crystallized from a mixture of benzene and petroleum ether. The light tan crystals obtained weighed 25 g. A small sample, crystallized again, consisted of long, colorless needles, mp 94–94.5°. *Anal.* Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.82; H, 7.87.

3-(3,4-Dimethoxyphenyl)-3-methyl-1-butanol.—A solution of 17 g of 3-(3,4-dimethoxyphenyl)-3-methylbutyric acid in 50 ml of ether was added to 3 g of lithium aluminum hydride in 500 ml of ether and boiled for 8 hr. The alcohol, bp 144–148° (3 mm), $n^{25}D$ 1.5299, weighed 10 g. *Anal.* Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.42; H, 9.08.

1-Bromo-3-(3,4-dimethoxyphenyl)-3-methylbutane.—The *p*-toluenesulfonate was prepared from 10 g of 3-(3,4-dimethoxyphenyl)-3-methyl-1-butanol and 20 g of *p*-toluenesulfonyl chloride by the usual method. The liquid product was dissolved in 400 ml of dry acetone containing 20 g of lithium bromide and the solution was boiled for 3 days. The acetone was removed by distillation and the residue was treated with water. The bromide was extracted with ether and distilled. There was obtained a pale yellow liquid, bp 131–133° (2 mm), $n^{25}D$ 1.5431, weighing 10.2 g. *Anal.* Calcd for $C_{13}H_{19}O_2Br$: C, 54.36; H, 6.67. Found: C, 54.31; H, 6.59.

4-(3,4-Dimethoxyphenyl)-4-methylpentanoic Acid. Method A.—Carbonation of the Grignard reagent prepared from 10 g of 1-bromo-3-(3,4-dimethoxyphenyl)-3-methylbutane with gaseous carbon dioxide yielded a small sodium bicarbonate soluble fraction. This material crystallized after being distilled and standing for 2 months. Once seeds were available, it was recrystallized from a mixture of ether and pentane. The yield was only 0.3 g. A small sample was recrystallized for analysis, mp 41–42°. *Anal.* Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.46; H, 7.47.

Method B.—To 100 ml of tetrachloroethane, cooled with ice and stirred, was added 20 g of anhydrous aluminum chloride followed by a mixture of 12 g of 4-methyl-4-pentanolactone and 25 g of veratrole. After the addition, the solution was stirred at 50° for 1 hr. The resulting solution was cooled and poured onto ice and hydrochloric acid. The aqueous phase was extracted twice with chloroform and the combined organic phases were washed twice with water. The product was extracted with a solution of 15 g of sodium bicarbonate in 200 ml of water in three portions. The bicarbonate extracts were washed twice with chloroform and acidified. The acid was extracted with three portions of chloroform. After drying, the solvent was removed and the acid was distilled. After *ca.* 1 g of unreacted lactone, the acid distilled, bp 170° (0.7 mm). The distillate (1.5 g) was crystallized from ether–pentane twice. There was obtained 0.5 g of acid, mp 42.5–44°. The mother liquors gave an additional 0.5 g of less pure acid, mp 41–42°. *Anal.* Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.67; H, 8.25.

4-(3,4-Dimethoxyphenyl)-4-methyl-1-pentanol.—Heating 1.0 g of the above acid with 0.5 g of lithium aluminum hydride in 200 ml of ether for 24 hr gave, after the usual purification, 0.85 g of alcohol, bp *ca.* 140° (0.8 mm), $n^{25}D$ 1.5259. *Anal.* Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.35; H, 9.45. This alcohol also gave a liquid *p*-bromobenzenesulfonate which was quite pure by equivalent weight measurements in formic acid.

3,3-Dimethyl-4-phenylbutyric Acid.—This material, bp 140–145° (5 mm), $n^{25}D$ 1.5130, was prepared from benzylmagnesium bromide and isopropylidenecyanoacetic ester by the method of Prout, *et al.*[9]

3,3-Dimethyl-4-phenyl-1-butanol.—Reduction of 20 g of the above acid with 4 g of lithium aluminum hydride afforded 17.5 g of the alcohol, bp 112–116° (4 mm), $n^{25}D$ 1.5164. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.05; H, 10.03.

The *p*-bromobenzenesulfonate of this alcohol, mp 29.5–30.5°, was crystallized from a mixture of pentane and ether. *Anal.* Calcd for $C_{18}H_{21}O_3SBr$: C, 54.41; H, 5.33. Found: C, 54.28; H, 5.58.

4-(*m*-Anisyl)-3,3-dimethylbutanoic Acid.—The Grignard reagent was prepared by a high dilution technique from 34 g of *m*-methoxybenzyl bromide,[12] $n^{25}D$ 1.5733, bp 86–88° (2.0 mm). To the stirred Grignard reagent (obtained in 65% yield) was added 18 g of isopropylidenecyanoacetic ester. The solution was stirred and boiled for 2 hr more after the addition was complete. Then cold dilute hydrochloric acid was added with external cooling. The aqueous phase was separated and extracted with ether. The combined ether extracts were washed with water and with aqueous sodium bicarbonate. The solvent was removed and the residue was boiled 15 hours with a solution of 50 g of potassium hydroxide in 200 ml of ethylene glycol. After cooling, the hydrolysis solution was poured into 500 ml of water and extracted twice with ether. Acidification of the aqueous phase liberated the acid. The acid was extracted three times with ether. A considerable amount of material was accidentally lost during the extraction. The combined ether extracts were washed twice with water and dried. Removal of the ether left a dark oil which was distilled, bp 150–155° (1.0 mm), $n^{25}D$ 1.5204, to give a viscous pale yellow oil weighing 7.7 g which could not be induced to crystallize. *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.41; H, 7.98.

4-(*m*-Anisyl)-3,3-dimethyl-1-butanol.—The reduction of 7.5 g of 4-(*m*-anisyl)-3,3-dimethylbutanoic acid with 1.5 g of lithium aluminum hydride in ether gave 6.5 g of the alcohol, bp 125–130° (0.8 mm), $n^{25}D$ 1.5230, as a viscous pale yellow liquid. *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.18; H, 9.60.

The *p*-bromobenzenesulfonate of this alcohol could not be crystallized. The crude ester, $n^{25}D$ 1.5569, was 93% pure by equivalent weight measurements in formic acid.

3,3-Dimethyl-4-(*p*-nitrophenyl)butyric Acid.—3,3-Dimethyl-4-phenylbutyric acid (14 g) was added to 25 ml of fuming nitric acid at −30° over a period of 10 min. The stirred mixture was allowed to warm up to 5° over a period of 3 hr and poured onto ice. After scratching and standing for about 1 hr at 0°, the yellow solid was filtered, washed, dried, and recrystallized from a mixture of ether and pentane and then twice from ether. There was obtained 1.6 g, mp 101–103°. *Anal.* Calcd for $C_{12}H_{15}O_4N$: C, 60.55; H, 6.37. Found: C, 60.91; H, 6.56.

The mother liquors gave 5 g of less pure acid, mp 95–100°, which was suitable for the hydrogenation described below.

4-(*p*-Aminophenyl)-3,3-dimethylbutyric Acid.—A solution of 11.5 g of 3,3-dimethyl-4-(*p*-nitrophenyl)butyric acid in 100 ml of methanol was hydrogenated at 15 psig in the presence of 0.3 g of platinum oxide until no more hydrogen was absorbed (*ca.* 15 min). The resulting hot solution was cooled and filtered through Celite and concentrated to *ca.* 40 ml. After cooling, the crude acid was filtered and recrystallized from methanol. There was obtained 4.5 g of the amino acid, mp 155–157°. *Anal.* Calcd for $C_{12}H_{17}O_2N$: C, 69.53; H, 8.27. Found: C, 69.70; H, 8.19.

(12) R. B. Woodward, *J. Amer. Chem. Soc.*, **62**, 1481 (1940).

3,3-Dimethyl-4-(*p*-hydroxyphenyl)butyric Acid.—A mixture of 4.5 g of the above amino acid and 50 ml of water containing 2 ml of concentrated sulfuric acid was cooled to 0° and treated with a solution of 2.5 g of sodium nitrite in 10 ml of water. The solution was filtered from a small amount of insoluble material, treated with 3 g of urea, and slowly added to 20 ml of boiling water containing 5 ml of sulfuric acid. After 10 min of boiling the mixture was cooled and the product was extracted with two portions of ether. The extracts were washed with water and dried. After removing the ether, a dark oil remained which solidified on scratching. The material was recrystallized from a mixture of carbon tetrachloride and hexane to give 1.6 g of an orange solid, mp 104–106°. The entire crude product was recovered and used in the methylation described below.

4-(*p*-Anisyl)-3,3-dimethylbutyric Acid.—The above crude hydroxy acid was dissolved in a solution of 12 g of sodium hydroxide in 50 ml of water and treated with 15 g of dimethyl sulfate. The reaction mixture was stirred and warmed until the methyl sulfate had reacted. The resulting solution was cooled, washed with ether, and acidified. The precipitated oil was extracted with ether. After washing the extracts with water and drying, the solvent was removed and the residue was crystallized in poor yield from hexane. The product, mp 64–66.5°, however, was still not pure. Since the substance was difficult to purify, the crude product was reduced in the following step.

4-(*p*-Anisyl)-3,3-dimethyl-1-butanol.—The above crude acid was reduced with 1 g of lithium aluminum hydride. The product, bp 137–140° (1.5 mm), $n^{25}D$ 1.5234, weighed 1.8 g. *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.71; H, 9.49.

The *p*-bromobenzenesulfonate of this alcohol was a viscous liquid, $n^{25}D$ 1.5602, which was 84% pure by equivalent weight measurements in acetic and formic acid.

2,2-Dimethyl-4-phenyl-1-butanol.—The reduction of 8.3 g of 3-benzoyl-2,2-dimethylpropionic acid by the Clemmensen method[13] gave 2.6 g of 2,2-dimethyl-4-phenylbutyric acid, mp 92–95°. The latter acid was reduced with 1 g of lithium aluminum hydride in ether by the usual method. The desired alcohol, bp 93–95° (0.8 mm), $n^{25}D$ 1.5109, weighed 2.3 g and had a strong rose-like odor. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.78; H, 10.16.

This alcohol gave a *p*-bromobenzenesulfonate, mp 64–65.5°. *Anal.* Calcd for $C_{18}H_{21}O_3SBr$: C, 54.41; H, 5.33. Found: C, 54.45; H, 5.48.

4,4-Dimethyl-6-methoxy-1-tetralone.—To a solution of 10 g of 4-(*m*-anisyl)-4-methylpentanoic acid in 40 ml of benzene was added 12 g of phosphorus pentachloride in small portions. After standing for 1 hr, the solution was cooled and a cold solution of 8 g of stannic chloride in 20 ml of benzene was added all at once. The solution became green and a viscous green oil separated which soon crystallized. After being cooled and shaken for 15 min, the mixture was poured onto ice and hydrochloric acid. The benzene phase was separated and the aqueous solution was extracted with ether. The extracts were washed twice with cold dilute hydrochloric acid and then with water and aqueous sodium bicarbonate. After drying, the solvent was evaporated and the residue was crystallized from pentane. There was obtained 7.6 g of light tan crystals. Another crystallization from pentane gave a colorless sample, mp 51–53°. *Anal.* Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.20; H, 7.70.

1,1-Dimethyl-7-methoxytetralin.—The above tetralone (7 g) was boiled with 50 g of amalgamated zinc, 25 ml of water, and 55 ml of concentrated hydrochloric acid. The solution was refluxed for 2 days, and 10 ml of concentrated hydrochloric acid was added every 12 hr. The pale yellow product was extracted with two portions of ether and the extracts were washed with water and aqueous sodium bicarbonate. After drying, the extracts were concentrated and distilled over sodium hydride. The product, bp 105–106° (3.5 mm), $n^{25}D$ 1.5291, weighed 4.2 g. *Anal.* Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.20; H, 9.42.

1,2-Dimethyl-7-methoxynaphthalene.—A solution of 0.5 g of 1,1-dimethyl-7-methoxytetralin and 2 g of tetrachloro-1,2-quinone in 5 ml of benzene was refluxed for 20 hr according to the general method reported by Linstead.[14] The reaction mixture was diluted with 25 ml of hexane and chromatographed on 20 g of alumina using hexane as eluent. The first 500 ml of solvent was evaporated and the residue was dissolved in a few milliliters of ether, filtered, and treated with 1 g of picric acid in ether. The solution was concentrated to 40 ml and cooled. The picrate of 1,2-dimethyl-7-methoxynaphthalene crystallized as long orange needles. The product, after recrystallization from methanol, had mp 134.5–135.5° and weighed 0.55 g. *Anal.* Calcd for $C_{19}H_{17}O_8N_3$: C, 54.94; H, 4.13. Found: C, 54.88; H, 4.36.

4,4-Dimethyl-1-tetralone.[11]—The acid chloride was prepared from 100 g of crude 4-phenyl-4-methylpentanoic acid and 90 g of thionyl chloride. The reaction mixture was heated on the steam bath for 30 min and the excess thionyl chloride was distilled under reduced pressure at 100°. The crude acid chloride was then added dropwise to a cold, stirred solution of 80 g of anhydrous powdered aluminum chloride in 450 ml of carbon disulfide. After the addition was complete, the solution was heated to boiling for 10 min and poured onto ice and hydrochloric acid. The organic phase was separated and the aqueous phase was extracted with ether. The combined organic phases were washed with water and with aqueous sodium bicarbonate. The solution was dried and the solvent was distilled. The oil remaining after the removal of the solvent was chromatographed on 1200 g of alumina with pentane. The liquid product obtained, bp 109–110° (3.5 mm), mp 12–13°, $n^{25}D$ 1.5492, weighed 63 g.

4,4-Dimethyl-7-nitro-1-tetralone.—The above tetralone (16 g) was added with stirring to 50 ml of ice cold concentrated sulfuric acid. Then a cold solution of 5 ml of concentrated nitric acid and 10 ml of concentrated sulfuric acid was added with stirring and ice cooling during 5–10 min. The mixture was stirred at 0° for 30 min and then allowed to warm up to room temperature during 30 more min. The reaction mixture was poured onto ice and the pale yellow solid formed was filtered, washed with water, and recrystallized twice from ethanol to give 12.5 g of product, mp 160–161°. *Anal.* Calcd for $C_{12}H_{13}O_3N$: C, 65.74; H, 5.97. Found: C, 65.74; H, 6.08.

4,4-Dimethyl-7-hydroxy-1-tetralone.—A suspension of 36 g of 4,4-dimethyl-7-nitro-1-tetralone in 200 ml of methanol was hydrogenated at 20 psig using 0.2 g of platinum oxide as catalyst. Several hours were required before the uptake of hydrogen stopped. The catalyst was filtered using a filter aid and the filtrate was concentrated on the steam bath under reduced pressure. The amine was obtained as a brown oil which could not be crystallized. This crude amine was treated with a cold solution of 20 ml of concentrated sulfuric acid in 200 ml of water. The amine sulfate immediately crystallized from the solution. The solution was kept at 0° while a saturated aqueous solution of sodium nitrite was added with stirring until there was a positive starch–iodide test, 30 min after the last nitrite addition. A few grams of urea were added and a small insoluble residue was removed by filtration. The cold diazonium salt solution was added as rapidly as possible to a boiling solution of 100 ml of concentrated sulfuric acid and 900 ml of water. The solution was boiled for 1 hr after the addition and cooled. The brown solid so obtained was filtered, air-dried, and recrystallized twice from benzene. The yellow hydroxy tetralone, mp 135–136° weighed 15 g. A colorless sample was obtained by sublimation, mp 135–136°. *Anal.* Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.65; H, 7.39.

4,4-Dimethyl-7-methoxy-1-tetralone.—The above phenol (14.5 g) was dissolved in a solution of 12 g of sodium hydroxide in 50 ml of water and methylated with 30 g of dimethyl sulfate. The product was distilled, bp 120–122° (1.5 mm), and recrystallized twice from pentane, mp 53–54°. *Anal.* Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.45; H, 7.96.

1,1-Dimethyl-6-methoxytetralin.—The Clemmensen reduction of the preceding tetralone (7 g) was carried out at reflux temperature for 48 hr with 50 g of amalgamated zinc, 25 ml of water, 30 ml of toluene, and 55 ml of concentrated hydrochloric acid, adding 10 ml more acid every 12 hr. The tetralin, distilled from sodium hydride, bp 89–91° (1.0 mm), $n^{25}D$ 1.5311, weighed 4.0 g. *Anal.* Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.88; H, 9.71.

1,2-Dimethyl-6-methoxynaphthalene.—The above tetralin (0.5 g) was boiled with 2 g of tetrachloro-1,2-quinone in 5 ml of benzene for 20 hr. The product was isolated by chromatography as in the 1,1-dimethyl-7-methoxytetralin case. Recrystallization of the picrate from absolute ethanol gave 0.05 g of product, mp 131–132°, as orange clusters of needles. The mixture melting point with 1,2-dimethyl-6-methoxynaphthalene

(13) G. Clemo and H. Dickenson, *J. Chem. Soc.*, 256 (1937).

(14) R. Linstead, E. Braude, L. Jackman, and A. Beams, *Chem. Ind. (London)*, 1174 (1954).

picrate (mp 134.5–135.5°) was 114–125°. *Anal.* Calcd for $C_{19}H_{17}O_8N_3$: C, 54.94; H, 4.13. Found: C, 54.39; H, 4.66.

4-*o*-Anisylbutyric Acid.—To a solution of 15 g of sodium metal in 700 ml of dry ethanol was added 100 g of diethyl malonate. Then 100 g of β-*o*-anisylethyl *p*-toluenesulfonate[15] was added. The solution was heated and shaken until the tosylate had dissolved and then boiled overnight. The reaction mixture was cooled and poured into water. After acidification, the product was extracted with three portions of ether. Evaporation of the ether left an oil which was boiled with 140 g of potassium hydroxide in 400 ml of ethylene glycol for 2 hr. After cooling and diluting with water, oily by-products were extracted with two portions of ether and discarded. The clear aqueous solution was acidified with 300 ml of concentrated hydrochloric acid and the organic acid was extracted with three portions of ether. After drying, the solvent was removed and the solid malonic acid so obtained was distilled. The acid lost carbon dioxide at about 190° and the 4-*o*-anisylbutyric acid formed distilled at 155–160° (2.5 mm). The product, 39 g (64%), crystallized on cooling to a colorless solid, mp 39–40.5° (lit.[16] mp 39–39.5°).

The ethyl ester of this acid was prepared by boiling 30 g of the acid with 60 ml of dry ethanol and 0.5 ml of sulfuric acid overnight. The ester, 32 g, bp 115–117° (1.5 mm), $n^{25}D$ 1.5010, was a colorless, nearly odorless liquid. *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.14; H, 8.25.

5-(*o*-Anisyl)-2-methyl-2-pentanol.—To the Grignard reagent prepared from 9 g of magnesium and 52 g of methyl iodide in 500 ml of ether was added dropwise with stirring 40 g of ethyl 4-*o*-anisylbutyrate. After the addition, the solution was boiled for 2 hr and hydrolyzed with saturated aqueous ammonium chloride. The alcohol, bp 108–110° (0.8 mm), $n^{25}D$ 1.5142, was obtained as a colorless, viscous liquid weighing 44.5 g. *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.75; H, 9.86.

1,1-Dimethyl-5-methoxytetralin.—To 50 ml of 85% (by weight) aqueous sulfuric acid, cooled to 0°, was added dropwise with stirring 10 g of 5-(*o*-anisyl)-2-methyl-2-pentanol. The alcohol dissolved at first and then an oil separated. The addition funnel was rinsed with an additional 10 ml of cold 85% sulfuric acid which was added to the main reaction mixture. The pale pink solution was allowed to stir without cooling for 30 min and poured onto ice and water. The tetralin was extracted with three 100-ml portions of pure pentane. The combined extracts were washed with water twice and with aqueous sodium bicarbonate. After drying, the solvent was removed through a short Vigreux column and the colorless product was distilled. The yield of product, bp 90–93° (1.5 mm), $n^{25}D$ 1.5352, was 8.45 g. Three recrystallizations from pentane at −80° and redistillation gave a purer sample, $n^{25}D$ 1.5353, mp 21–22°. *Anal.* Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.24; H, 9.35.

4,4-Dimethyl-8-methoxy-1-tetralone.—A solution of 5 g of 1,1-dimethyl-5-methoxytetralin in 25 ml of acetic acid was cooled to 0° and stirred while a cold solution of 4.2 g of chromic acid in 12 ml of acetic acid and 2 ml of water was added dropwise, according to a method described by Linstead.[14] After the addition (*ca.* 15 min) the solution was stirred at room temperature for 4 hr. The reaction mixture was poured into 500 ml of water extracted four times with pentane. The extracts were washed with water twice and with aqueous sodium bicarbonate. The pentane solution was dried and distilled. Unreacted tetralin, bp 90–100° (1.5 mm), weighing 1 g, distilled first. The ketone, bp 100–135° (1.5 mm), weighed 3 g. Crystallization from hexane gave 1.1 g of ketone, mp 86–87°. A second crystallization gave material of mp 86.5–87.5°. *Anal.* Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.51; H, 7.89.

4,4-Dimethyl-8-hydroxy-1-tetralone.—The preceding methyl ether (1 g) was boiled for 4 hr with 10 ml of 48% aqueous hydrobromic acid and 2 ml of acetic acid. The reaction mixture was poured into cold water and the product was extracted with three portions of ether. The extracts were washed with water and then with cold dilute sodium hydroxide. A precipitate immediately appeared. The greenish solid was filtered, washed well with ether and water, and then treated with cold dilute hydrochloric acid. The oil which separated was extracted with two portions of ether, washed with water, dried, and distilled. The product, 0.4 g, was a pale yellow liquid which readily crystallized on cooling, mp 28–29°. The substance gave a strong violet color with ferric chloride in methanol and a positive carbonyl test with 2,4-dinitrophenylhydrazine in sulfuric acid and ethanol. The infrared spectrum showed a broad band at 3500–2200 cm^{-1} resulting from strong intramolecular hydrogen bonding. *Anal.* Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.76; H, 7.34.

1,2-Dimethyl-5-methoxynaphthalene.—A solution of 0.5 g of 1,1-dimethyl-5-methoxytetralin, 2 g of tetrachloro-1,2-quinone, and 5 ml of benzene was boiled for 20 hr. After cooling and diluting with 25 ml of hexane the products were chromatographed. The naphthalene was eluted with 700 ml of hexane. The product was dissolved in 20 ml of methanol, filtered from an insoluble crystalline material, and treated with 0.4 g of picric acid in 5 ml of methanol. On cooling, the picrate separated as red needles weighing 0.4 g. Recrystallization from methanol gave 0.25 g, mp 143–144°. *Anal.* Calcd for $C_{19}H_{17}O_8N_3$: C, 54.94; H, 4.13. Found: C, 55.16; H, 4.42.

Formolysis Products of 4-Methyl-4-phenyl-1-pentyl *p*-Bromobenzenesulfonate.—A solution of 5.40 g of dry sodium formate in 1 l. of formic acid (0.37% water) was heated to 75° and 27.7 g of the pure *p*-bromobenzenesulfonate was added. The solution was shaken until the sulfonate had dissolved and then kept at 75° for 43 hr. The cooled formolysis solution was poured into 3 l. of water and the products were extracted with five 500-ml portions of pure pentane. The combined extracts were washed with water and aqueous sodium bicarbonate and dried. The pentane was distilled through an 18-in. Vigreux column and the oil remaining was reduced with 2. 5 g of lithium aluminum hydride in 800 ml of ether. The reduced products were chromatographed on 300 g of alumina. The tetralin product was eluted with 1 l. of pentane. Evaporation of the solvent through a short Vigreux column and distillation gave the tetralin, 4.05 g (36.1%), bp 60–62° (1.5 mm), $n^{25}D$ 1.5256. This material did not react with potassium permanganate in acetone and had an infrared spectrum essentially identical with that of authentic 1,1-dimethyltetralin. Dehydrogenation of this tetralin (0.5 g) with 2 g of tetrachloro-1,2-quinone in 5 ml of boiling benzene for 20 hr gave 0.25 g of crude 1,2-dimethylnaphthalene, $n^{25}D$ 1.5616, which in turn gave 0.15 g of picrate, mp 129–131°. The mixture melting point with the authentic material described below was 129–131°.

The dehydrogenation of authentic 1,1-dimethyltetralin (0.5 g) with 2 g of tetrachloro-1,2-quinone as described above gave 0.3 g of crude naphthalene, $n^{25}D$ 1.5654, which also gave only 0.15 g of picrate, mp 129–131°. Thus, in our hands this dehydrogenation gave only a 12% yield of 1,2-dimethylnaphthalene instead of the quantitative yield reported by Linstead.[14]

Elution of the alcohol products of the formolysis was accomplished with 1500 ml of ether. The alcohol, bp 100–105° (1.5 mm), $n^{25}D$ 1.5168, weighed 7.15 g (57.4%). The infrared spectrum of the alcohol was identical with that of authentic 4-methyl-4-phenyl-1-pentanol.

Formolysis Products of 4-(*m*-Anisyl)-4-methyl-1-pentyl *p*-Bromobenzenesulfonate.—To a solution of 1.4 g of sodium formate in 350 ml of formic acid (0.31% water) heated to 75° was added 6.8 g of the liquid *p*-bromobenzenesulfonate (97 ± 1% pure). The solution was mixed well and left at 75° for 15.5 hr. The resulting formolysis solution was poured into 2 l. of water and the products were isolated exactly as in the case of the 4-(*p*-anisyl)-4-methyl-1-pentyl *p*-bromobenzenesulfonate formolysis described above.

The tetralin product, 2.1 g (69.5%), bp 95–100° (1.5 mm), $n^{25}D$ 1.5314 (distilled from sodium hydride under nitrogen), had exactly the same refractive index and infrared spectrum as a mixture of 65% 1,1-dimethyl-7-methoxytetralin and 35% 1,1-dimethyl-5-methoxytetralin. Dehydrogenation of 0.5 g of the tetralin product with 2 g of tetachloro-1,2-quinone as described above gave 0.20 g of the picrate of 1,2-dimethyl-7-methoxynaphthalene, mp 131–133°, mmp 131.5–134°.

The alcohol product from the formolysis was eluted with 1 l. of ether. The product, bp *ca.* 125° (2 mm), $n^{25}D$ 1.5216, weighed 0.60 g (18.2%). The infrared spectrum of this material was nearly identical with the spectrum of pure 4-(*m*-anisyl)-4-methyl-1-pentanol.

Formolysis Products of 4-(*p*-Anisyl)-4-methyl-1-pentyl *p*-Bromobenzenesulfonate.—To a solution of 1.40 g of sodium formate in 330 ml of formic acid (0.33% water), heated to 75°,

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(16) J. Lockett and W. Short, *J. Chem. Soc.*, 789 (1939).

was added 7.0 g of pure *p*-bromobenzenesulfonate. The solution was mixed well and kept at 75° for 16.5 hr and then poured into 2 l. of water. The products were extracted with four 300-ml portions of pure pentane and one of ether. The combined extracts were washed, reduced with 1.5 g of lithium aluminum hydride, and chromatographed as in the above examples. The pentane eluate (600 ml) contained 1.90 g of tetralin. This material, distilled over sodium hydride under nitrogen, had bp 90–92° (1.5 mm), $n^{25}D$ 1.5299. *Anal.* Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.86; H, 9.70. The refractive index and infrared spectrum of this product agreed exactly with those of a mixture of 68% 1,1-dimethyl-7-methoxytetralin and 32% 1,1-dimethyl-6-methoxytetralin. The dehydrogenation of 0.75 g of the tetralin product with 3 g of tetrachloro-1,2-quinone in 7 ml of benzene for 17 hr, as described above, gave 0.40 g of the picrate of 1,2-dimethyl-7-methoxynaphthalene, mp 131–133.5°, mmp 131–134.5°.

The alcohol product from the formolysis, eluted from the alumina with 1.5 l. of ether, weighed 0.85 g (25%) and had bp 130–132° (1.5 mm), $n^{25}D$ 1.5223.

A second formolysis with 1.50 g of sodium formate, 350 ml of formic acid, and 7.3 g of the *p*-bromobenzenesulfonate was carried out exactly as above. The products were 1.90 g of tetralins (58.8%) of $n^{25}D$ 1.5292 and 0.95 g (28.5%) of alcohol, $n^{25}D$ 1.5211. This alcohol fraction had an infrared spectrum essentially identical with the spectrum of pure 4-(*p*-anisyl)-4-methyl-1-pentanol.

Formolysis Products of 3,3-Dimethyl-4-phenyl-1-butyl *p*-Bromobenzenesulfonate.—To a solution of 2.6 g of sodium formate in 750 ml of formic acid (0.37% water) heated to 75° was added 14.0 g of the *p*-bromobenzenesulfonate. The solution was mixed well and left at 75° for 12 hr. It was then poured into 3 l. of water and the products were extracted with five 500-ml portions of pure pentane. The extracts were washed with water and the products were isolated as above. The tetralin product, eluted with 1 l. of pentane, weighed 5.05 g (89.7%) and had bp 109–110° (23 mm), $n^{25}D$ 1.5174. Dehydrogenation of this material (0.5 g) was accomplished with 2 g of tetrachloro-1,2-quinone in 5 ml of purified dioxane by boiling for 20 hr. Isolating the product by chromatography and distillation gave 0.35 g of the crude naphthalene, which yielded 0.15 g of the pure picrate of 1,2-dimethylnaphthalene.

The alcohol from the formolysis, 0.30 g (4.8%), was eluted with 500 ml of ether and 500 ml of methanol, bp *ca.* 110° (3 mm), $n^{25}D$ 1.5160. The infrared spectrum showed the product to be 3,3-dimethyl-4-phenyl-1-butanol.

Ethyl 4-*p*-Anisylbutyrate.—A mixture of 27 g of 4-*p*-anisylbutyric acid,[17,18] 50 ml of absolute ethanol, and 0.1 ml of concentrated sulfuric acid was boiled for 2 hr. There was obtained from this reaction mixture 25.4 g of colorless ester, bp 125–130° (1.5 mm), $n^{25}D$ 1.4994. *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.21; H, 8.06.

5-(*p*-Anisyl)-2-methyl-1-pentanol.—The Grignard reagent was prepared from 40 g of method iodide and 6 g of magnesium in 200 ml of ether. To this was added 25 g of ethyl 4-*p*-anisylbutyrate with stirring. The resulting solution was boiled for 1 hr and cooled while 200 ml of cold saturated aqueous ammonium chloride was added. Isolation gave 20.5 g of the alcohol, bp 120–122° (1.0 mm), $n^{25}D$ 1.5123. *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.54; H, 9.58.

The Reaction of 5-(Anisyl)-2-methyl-2-pentanol with Formic Acid.—A solution of 0.13 g of sodium formate and 2.0 g of the tertiary alcohol in 200 ml of formic acid was heated to 75° for 16 hr. After cooling, the reaction mixture was poured into water and the products were extracted with four portions of pentane. The extracts were washed with water and aqueous bicarbonate and dried. The solvent was distilled and the product was treated with 0.4 g of lithium aluminum hydride. Cold water was added cautiously and the ether solution was separated. The insoluble salts were extracted several times with ether and added to the main ether phase. The combined ether extracts were washed with water and aqueous sodium bicarbonate, dried, and concentrated. The product was chromatographed on 100 g of alumina. Pentane eluted 1.7 g, bp 87–90° (1.5 mm), $n^{25}D$ 1.5299. The infrared spectrum was identical with that of 1,1-dimethyl-7-methoxytetralin. The absence of bands at 1260, 1140, and 835 cm^{-1} limits the amount of the 1,1-dimethyl-6-methoxytetralin possibly present to less than 1%. Dehydrogenation of the product (0.5 g) with 2 g of tetrachloro-1,2-quinone in benzene gave 0.4 g of the picrate of 1,2-dimethyl-7-methoxynaphthalene, mp 130–132°.

Elution of the alumina column with ether gave only a trace (less than 0.1 g) of alcohol.

The Reaction of 5-(*p*-Anisyl)-2-methyl-2-pentanol with Acetic Acid.—A solution of 5.0 g of the alcohol in 100 ml of 0.0310 *M* sodium acetate in dry acetic acid, 500 ml of dry acetic acid, and 3 ml of acetic anhydride was heated at 100.0° for 66 hr. The reaction mixture was cooled, poured into water, and extracted as usual and the products were reduced with 1.0 g of lithium aluminum hydride and chromatographed as in the formic acid reaction described above. The chromatography gave two fractions. The first fraction, eluted with pentane, bp 85–90° (1.5 mm), $n^{25}D$ 1.5122, weighed 1.7 g (37.2%). The second fraction, 2.9 g (58.0%), bp 125–127° (1.5 mm), $n^{25}D$ 1.5123, was eluted with ether. The infrared spectrum was identical with that of pure 5-(*p*-anisyl)-2-methyl-2-pentanol.

A 0.1117-g sample of the first fraction absorbed 14.7 ml of hydrogen at 26° and 750 mm when hydrogenated in acetic acid with 10% Pd/C. A 1.0-g sample of the olefin was also oxidized with 1.5 g of osmium tetroxide and the products were chromatographed. Less than 0.1 g of inert material was eluted with pentane.

Stability of 1,1-Dimethyl-6-methoxytetralin in Formic Acid.—A solution of 0.5 g of the pure tetralin in 50.0 ml of dry formic acid was heated to 75.0° for 17 hr. The solution was cooled and poured into water and the product was extracted with three portions of pentane. The extracts were washed with water and aqueous sodium bicarbonate. The solution was dried and concentrated. Distillation of the product from sodium hydride gave 0.40 g (80%) of a colorless liquid, bp 93° (1.5 mm), $n^{25}D$ 1.5304. The infrared spectrum was identical with that of the starting tetralin. The absence of bands at 1075, 1045, 795, and 700 cm^{-1} indicated that less than 1% of 1,1-dimethyl-7-methoxytetralin could have been present.

The Acetolysis Products of 4-(*p*-Anisyl)-4-methyl-1-pentyl *p*-Bromobenzenesulfonate with Lithium Acetate.—A solution of 10.0 ml of 1.00 *M* lithium acetate in dry acetic acid was added to 1500 ml of dry acetic acid and the resulting solution was heated to 100.0°. Then 9.5 g of the *p*-bromobenzenesulfonate was added. After 1 hr at 100.0°, a titration showed the solution to be 0.0051 *M* in acetate ion, and 5.0 ml of 1.00 *M* lithium acetate was added. In 1.5 hr the solution was 0.0057 *M* in acetate ion and another 5.0 ml of 1 *M* lithium acetate was added. A third portion of 10.0 ml of 1 *M* lithium acetate was added after another 2 hr and 15 min when the solution was 0.0064 *M* in acetate ion. After a total of 56 hr at 100.0°, the solvolysis solution was cooled and poured into water. The products were extracted with five portions of pentane, washed, etc., reduced with 1.5 g of lithium aluminum hydride, and chromatographed on 200 g of alumina exactly as described in the examples above. The first fraction, 1.7 g, bp 85–90° (1.5 mm), $n^{25}D$ 1.5233, was eluted with pentane. The second fraction, 2.65 g, bp 125–130° (1.5 mm), $n^{25}D$ 1.5220, was eluted with ether.

The first fraction reacted slowly with potassium permanganate in acetone. Quantitative hydrogenation of a 0.2221-g sample with 10% Pd/C in acetic acid at 26° and 750 mm required 12.2 ml of hydrogen, hydrogenation being complete in 15 min (41.0% olefin). The infrared spectrum of the olefin mixture showed strong absorption at 825 cm^{-1}, probably indicating trisubstituted olefins. (This band is not present in the possible tetralin products.) The olefins were removed from a 1.00-g sample of the mixture by oxidation with 2 g of osmium tetroxide in ether with a trace of pyridine. Decomposition of the osmic esters with mannitol and aqueous potassium hydroxide gave a mixture of tetralines and glycols. Chromatography on alumina gave 0.65 g (65%) of tetralins, bp 100° (2.5 mm), $n^{25}D$ 1.5300. An infrared analysis of this material showed it to contain 37 ± 1% of 1,1-dimethyl-7-methoxytetralin and 63 ± 1% of 1,1-dimethyl-6-methoxytetralin ($n^{25}D$ 1.5303 calculated).

An infrared analysis of the second chromatographic fraction from the acetolysis products showed it to be 98 ± 1% 4-(*p*-anisyl)-4-methyl-1-pentanol and 2 ± 1% 5-(*p*-anisyl)-2-methyl-2-pentanol.

In the second solvolysis carried out with the same quantity, exactly as above, a 32.0% yield of olefins and tetralins ($n^{25}D$ 1.5229) was obtained and a 60.6% yield of alcohols, $n^{25}D$ 1.5219. The pure tetralins were isolated as above, $n^{25}D$

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(18) L. Gieser and V. Desreux, *ibid.*, **60**, 2255 (1938).

1.5297, and shown by infrared to contain 35 ± 2% of 1,1-dimethyl-7-methoxytetralin and 65 ± 2% of the 6-methoxy isomer. Similarly, the alcohol fraction was shown by infrared to contain 2 ± 1% of 5-(*p*-anisyl)-2-methyl-2-pentanol in 4-*p*-anisyl-4-methyl-1-pentanol.

The Acidic Acetolysis of 4-(*p*-Anisyl)-4-methyl-1-pentyl *p*-Bromobenzenesulfonate.—To 1000 ml of dry acetic acid at 100.0° was added 10.0 g of the bromobenzenesulfonate. After 47 hr at 100.0° the solvolysis solution was poured into water and the products were extracted, reduced, and chromatographed as described above. The first fraction, eluted with pentane, 1.7 g, bp 105–107° (2.5 mm), n^{25}D 1.5288, was pale yellow. The infrared analysis of the mixture indicated it to be 40 ± 5% 1,1-dimethyl-6-methoxytetralin and 60 ± 5% of the 7-methoxy isomer.

The second fraction was eluted with ether. This product, 2.75 g, bp 135–138° (1.5 mm), n^{25}D 1.5227, had an infrared spectrum identical with that of the starting alcohol, 4-(*p*-anisyl)-4-methyl-1-pentanol.

The Acetolysis Products from 4-Methyl-4-phenyl-1-butyl *p*-Bromobenzenesulfonate.—A solution of 15 ml of 1.00 *M* lithium acetate in dry acetic acid and 1500 ml of dry acetic acid was heated to 100.0° and 12.0 g of the bromobenzenesulfonate was added. In 5 hr another 20 ml of 1 *M* lithium acetate in acetic acid was added and after 90 more hr at 100.0° the solvolysis solution was cooled and poured into water. The products were extracted with five portions of pentane and isolated as in the above examples. Pentane elution of the products from alumina gave 0.70 g of hydrocarbons, bp 60° (1.5 mm), n^{25}D 1.5217, and elution with ether gave 4.40 g of alcohols, bp 112–115° (2 mm), n^{25}D 1.5162.

The hydrocarbon fraction reacted slowly with potassium permanganate in acetone. Quantitative hydrogenation of a 0.3121-g sample at 27° and 750 mm in acetic acid with 10% Pd/C took up 4.7 ml of hydrogen. A second sample, 0.2350 g, at 30° and 747 mm, took up 3.2 ml of hydrogen (9.4% and 8.4% olefin, respectively).

The infrared spectrum of the hydrogenated hydrocarbons, n^{25}D 1.5195, was generally very similar to that of 1,1-dimethyltetralin except for a band of medium intensity at 695 cm^{-1} and a small increase in intensity of absorption in the 1075–1300-cm^{-1} region. The 695-cm^{-1} band is present in both possible hydrogenated olefins, 2-methyl-2-phenylpentane and 4-methyl-1-phenylpentane. However, the absence of any appreciable absorption at 740 cm^{-1} indicates that there is less than *ca.* 2% of the second isomer present. A 20% solution of 2-methyl-2-phenylpentane in 1,1-dimethyltetralin will account for the 695-cm^{-1} band but not the 1075–1300 cm^{-1} discrepancy. Considering both the hydrogenation data and the infrared data, the mixture probably contains *ca.* 80% of 1,1-dimethyltetralin, *ca.* 10% of 2-methyl-2-phenylpentane, and *ca.* 10% of some other unknown product.

Registry No.—VI, 33214-69-6; VII, 33214-70-9; X, 33214-69-6; 3-(4-acetamidophenyl)-3-methylbutyric acid, 33214-72-1; 3-(4-acetamido-3-nitrophenyl)-3-methylbutyric acid, 33214-73-2; 3-methyl-3-(3-nitrophenyl)butyric acid, 33214-35-6; 3-(*m*-anisyl)-3-methylbutyric acid, 33214-36-7; 3-(*p*-anisyl)-3-methylbutyric acid, 1136-01-2; 3-(*o*-anisyl)-3-methylbutyric acid, 33214-38-9; 4-(*m*-anisyl)-4-methylpentanoic acid, 33214-39-0; 3-(*p*-anisyl)-1-bromo-3-methylbutane, 33214-40-3; 4-(*p*-anisyl)-4-methylpentanoic acid, 23203-48-7; 4-methyl-4-pentanolacetone, 3123-97-5; 1-bromo-3-methyl-3-phenylbutane, 1197-97-3; 4-methyl-4-phenylpentanoic acid, 4408-55-3; 3-(3,4-dimethoxyphenyl)-3-methylbutyric acid, 33214-44-7; 3-(3,4-dimethoxyphenyl)-3-methyl-1-butanol, 33214-45-8; 1-bromo-3-(3,4-dimethoxyphenyl)-3-methylbutane, 33214-46-9; 4-(3,4-dimethoxyphenyl)-4-methylpentanoic acid, 3754-68-5; 4-(*m*-anisyl)-3,3-dimethylbutanoic acid, 25380-95-4; 4-(*m*-anisyl)-3,3-dimethyl-1-butanol, 33214-48-1, 33214-49-2 (Br); 3,3-dimethyl-4-(*p*-nitrophenyl)butyric acid, 33209-64-2; 4-(*p*-aminophenyl)-3,3-dimethylbutyric acid, 33209-65-3; 4,3-dimethyl-4-(*p*-hydroxyphenyl)butyric acid, 33209-66-4; 4-(*p*-anisyl)-3,3-dimethylbutyric acid, 33209-67-5; 4,4-dimethyl-6-methoxy-1-tetralone, 23203-51-2; 1,2-dimethyl-7-methoxynaphthalene picrate, 33209-69-7; 4,4-dimethyl-1-tetralone, 2979-69-3; 4,4-dimethyl-7-nitro-1-tetralone, 33209-71-1; 4,4-dimethyl-7-hydroxy-1-tetralone, 33209-72-2; 4,4-dimethyl-7-methoxy-1-tetralone, 23203-49-8; 1,2-dimethyl-6-methoxynaphthalene picrate, 33209-74-4; 4-*o*-anisylbutyric acid, 33209-75-5, 33209-76-6 (Et ester); 5-(*o*-anisyl)-2-methyl-2-pentanol, 33209-77-7; 4,4-dimethyl-8-methoxynaphthalene, 33209-78-8; 4,4-dimethyl-8-hydroxy-1-tetralone, 33209-79-9; 1,2-dimethyl-5-methoxynaphthalene picrate, 33209-80-2; ethyl 4-*p*-anisylbuyrate, 4586-89-4; 5-(*p*-anisyl)-2-methyl-1-pentanol, 33209-82-4; 5-(*p*-anisyl)-2-methyl-2-pentanol, 4586-90-7.

Photoaddition Reactions. II.[1] Photoaddition of Dimethyl Acetylenedicarboxylate to Cyclic Ethers

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The photoinitiated free-radical addition of tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, and tetrahydropyran to dimethyl acetylenedicarboxylate is found to give cis and trans 1:1 adducts. The products were isolated and characterized. The reaction has been found to be specific in that the trans adducts predominate over the cis.

Dimethyl acetylenedicarboxylate (DMAD, 2), one of the most versatile acetylenes, has played an important role in organic synthesis because it undergoes a wide variety of thermal cycloaddition and conjugate addition reactions.[4] Very little is, however, known about its photochemical reactions. Photoaddition of 2 to benzene has been reported to give dimethyl cyclooctatetraene-1,2-dicarboxylate,[5,6] and norbornene and pyrrole have been reported to give 1:1 photoadducts with DMAD.[7,8] Recently, the photoaddition of DMAD to two molecules of ethylene has also been re-

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