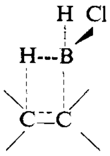
illustrated below, with extensive solvent interaction



and stabilization.

Experimental Section

Preparation of Monochloroborane. Tetrahydrofuran solutions of monochloroborane were prepared by the slow adsorption of gaseous boron trichloride into a borane in tetrahydrofuran solution maintained at −10–0° as described previously.[5]

Dideuteriomonochloroborane was prepared similarly.

Standardization of the Monochloroborane Solutions. An aliquot (2.00 ml) of the solution was hydrolyzed with 10 ml of water at room temperature, the volume of hydrogen evolved being carefully measured. The aqueous solution was transferred to a beaker and titrated to the first end point (neutralization of the hydrochloric acid formed on hydrolysis of the monochloroborane) with standardized 1 *N* sodium hydroxide employing a Beckman research pH meter. Mannitol (approximately 2.5 g) was then added to the solution, and the titration was continued to the end point for the neutralization of boric acid. The analytical data were converted into equivalents of available "hydride," boron, and chloride. When the solution analyzed for less than 98% monochloroborane, calculated amounts of additional boron trichloride or borane in tetrahydrofuran were added and the standardization procedure was repeated. Concentrations of monochloroborane in tetrahydrofuran employed in the kinetic experiments ranged from approximately 0.2 to 1.0 *M*.

Kinetic Measurements. Carefully weighed quantities of the olefin and an inert internal standard (for glpc analytical purposes) were dissolved in 25.0 ml of dry tetrahydrofuran. A 20.0-ml aliquot of this solution was added to 20.0 ml of standardized monochloroborane solution in a thermostated vessel sealed with a rubber septum under a nitrogen atmosphere. Aliquots were periodically removed, by means of a syringe through the rubber septum, and immediately quenched by injection into an excess of methanol. The quenched reaction mixtures were then analyzed by glpc on 10-ft Carbowax 20M columns at appropriate temperatures. The olefin: internal standard area ratios, corrected for response ratio differences, were employed to calculate the second-order rate constants employing the Univac 1107 computer.

Product Analysis. Reaction mixtures of monochloborane and olefin were allowed to proceed to completion under conditions of the kinetic experiments. The reaction mixtures were hydrolyzed by the addition of excess 20% sodium hydroxide and oxidized by the addition of an excess of 30% hydrogen peroxide. The oxidized reaction mixtures were extracted several times with ether. The extract was washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residues were analyzed by glpc on Carbowax 20M columns at appropriate temperatures, the per cent compositions being calculated employing predetermined response ratios.[15]

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(15) Not all of the products from the substituted styrenes were characterized. It was found that the response ratios of substituted α- to β-phenylethanols (H, 4-Me, 4-Cl) did not vary substantially, and thus this response ratio was employed for the analysis of the other systems.

The Reactions of Ambident Anions with an Ambident Electrophile

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Contribution from the Organic Chemistry Department, Research Division, Abbott Laboratories, North Chicago, Illinois. *Received December 29, 1967*

Abstract: It has been found that the reaction of sodiodipivaloylmethane with triphenylmethyl chloride gives nearly 90% yields of the carbon-arylated diketone **6**. Although not isolable, the trityl enol ether **17** is the only other identifiable primary product of this reaction. No evidence for normal C-tritylation or for abnormal O-arylation could be found. The reaction with triphenylmethyl bromide gives increased yields of **17** at the expense of **6**. The arylation reaction is a carbonium ion process. When the trityl halides are replaced by triphenylmethyl fluoroborate, the intermediate cross-conjugated triene **14** can be isolated. Rearrangement of **14** to **6** occurs smoothly, and to some extent intramolecularly, in basic media. The reaction with triphenylcarbonium ion has been extended to 14 other enolate systems. Among those derived from β-diketones, appreciable C-arylation was observable only with the highly hindered dipivaloylmethane. In the β-diester series, however, this reaction is more general. Even diethyl malonate undergoes C-arylation to the extent of 20%, and from two other β-diesters the intermediate trienes **18** and **19** could be isolated. *para* substitution in the trityl system serves to block the arylation reaction completely.

In connection with a spectrophotometric study of enolate ions,[1] the synthesis of several monosubstituted dipivaloylmethanes was undertaken. Alkylation of sodiodipivaloylmethane with benzyl and benzhydryl chlorides gave the expected products **1** and **2** in poor yields (6 and 3%, respectively).

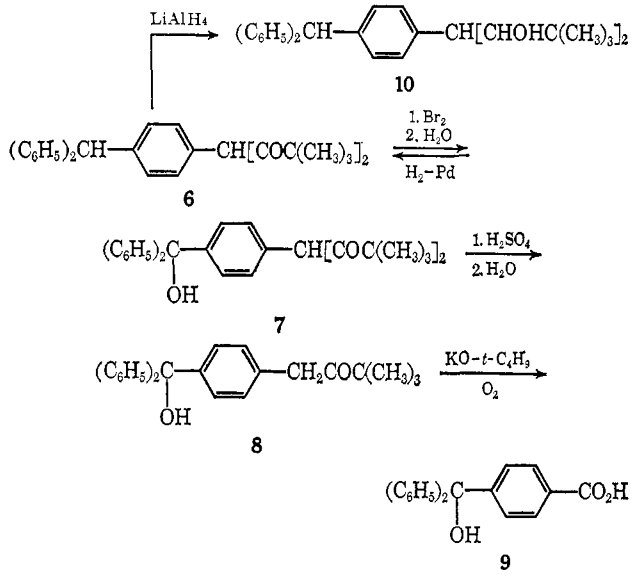
$$RX + Na^+\ \bar{C}H[COC(CH_3)_3]_2 \longrightarrow RCH[COC(CH_3)_3]_2$$

1, $R = C_6H_5CH_2$
2, $R = (C_6H_5)_2CH$
3, $R = (C_6H_5)_3C$
4, $R = (p\text{-}BrC_6H_4)_3C$
5, $R = (p\text{-}CH_3C_6H_4)_3C$

Surprisingly, the bulkiest member of the series, trityl chloride, led to an alkylation product in yields ap-

(1) H. E. Zaugg and A. D. Schaefer, *J. Amer. Chem. Soc.*, **87**, 1857 (1965).

proaching 90%. Its structure, however, was not the expected **3**, but rather **6** resulting from attack of the anion at the *para* position of one of the phenyl rings. Structure **6** was derived from its nmr and mass spectra and from the nmr spectrum of its reduction product **10**, and proved by conversion to the known carboxylic acid **9** by the following sequence.



Bromination of **6** occurred at the trityl carbon atom to give a crude bromide readily hydrolyzable to the carbinol **7** (72% yield),[2–4] which could be reconverted into **6** by catalytic hydrogenolysis. Aqueous quenching of a solution of **7** in concentrated sulfuric acid gave the hydroxy monoketone **8** (88% yield),[5] easily oxidizable under base-catalyzed conditions[6] to the known[7] acid **9**.

It is thus apparent that the behavior of dipivaloylmethane in the tritylation reaction differs markedly from that of the less hindered acetylacetone. Sodioacetylacetone gives the normal alkylation products

$$RX + NaCH(COCH_3)_2 \longrightarrow RCH(COCH_3)_2$$

11, R = $C_6H_5CH_2$
12, R = $(C_6H_5)_2CH$
13, R = $(C_6H_5)_3C$

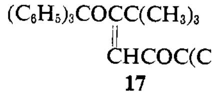
(*i.e.*, **11**, **12**, and **13**) with all three of the arylmethyl chlorides. Although the yield of the normal tritylation product **13** was very low (3.5%), none of the abnormal arylation product corresponding to **6** could be detected in the reaction mixture.

When, however, the three *para* positions of the trityl group are substituted, as in tri(*p*-bromophenyl)methyl chloride, the normal tritylation product **4** was formed even from sodiodipivaloylmethane although in barely isolable yield (1.5%). But more significantly, the abnormal arylation reaction was completely blocked in this instance.

During the course of a study of the effect of varying conditions on the alkylation leading to **6** (see Table I), it was found that, despite completion of the reaction as evidenced by neutral test, the bulk of the product other than **6** was accountable as dipivaloylmethane and triphenylmethanol. This clearly demonstrates the incursion of an oxygen-alkylation process leading to the trityl

Table I. Effect of Conditions on the Reaction of Trityl Halides[a] with Sodiodipivaloylmethane

$(C_6H_5)_3CX + NaCH[COC(CH_3)_3]_2 \longrightarrow$ **6** +


$$\underset{\textbf{17}}{(C_6H_5)_3CO\underset{\underset{CHCOC(CH_3)_3}{\|}}{C}C(CH_3)_3}$$

X	Solvent, ml DMF	C6H6	Other additives or conditions	Yield, % 6[b]	17[c]
Cl	40	0		80	7
Cl	30	10		83	
Cl	20	20		88	11
Cl	15	25		82[d]	
Cl	0	40		64[e]	(25)[f]
Cl	20	20	2.5 hr, 25°	76	12
Cl	20	20	1 hr, 25°, and 1.5 hr, 45°	85	11
Cl	20	20	8 ml of $(C_2H_5)_3N$; 22 hr, 50°	84	11
Cl	20	20	2.3 g of $CH_2[COC(CH_3)_3]_2$	89[g]	5
Cl	20	20	0.0017 g of $CuCl_2$	76[h]	
Cl	20	20	0.0127 g of $CuCl_2$	73[h]	
Br[i]	20	20		47[j]	48[j]
Br[i]	20	20	0.0027 g of $CuCl_2$	47[j]	48[j]
BF_4^- [k]	0	40		72[e]	25[j]

[a] Molar quantities of reactants specified in procedure A were used throughout. Except where otherwise indicated, conditions of time and temperature in procedure A were employed. [b] Except where otherwise indicated, yields of **6** represent isolated product of mp 169–172° or better. [c] With one exception reactions proceeded to neutrality. Since all of the sodiodipivaloylmethane, therefore, must have been consumed, yields of **17** are based on recovered dipivaloylmethane determined by quantitative vpc (see procedure B). [d] Mp 164–172°. [e] Mp 162–168°. [f] Reaction did not proceed to neutrality. Hence, this does not represent the true yield of **17**. [g] Yield based on sodium hydride. [h] Mp 160–166°. [i] Procedure C. [j] By nmr analysis (see procedure C). [k] Freshly prepared salt. See procedure D.

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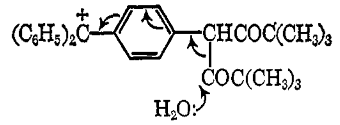
(2) The resistance to bromination at the α-carbon atom of the diketone **6** is clearly a consequence of steric hindrance of its rate of enolization. Comparisons of the nmr spectra (Experimental Section) of acetylacetone *vs.* corresponding dipivaloylmethane derivatives reveal the striking effect of substitution on the *thermodynamics* of enolization of dipivaloylmethane. Whereas benzyl substitution in the less hindered acetylacetone decreases the enol content (in $CDCl_3$ at 30°) only from 80% (in **21**) to 40% (in **11**), the same substitution in dipivaloylmethane effects a reduction from 100% enol (in **26**) to 0% (in **1**). Similar substituent effects on relative acidities also are decidedly more conspicuous in the dipivaloylmethane than in the acetylacetone series.[3] All of these results are in accord with theoretical expectations.[4]

(3) H. E. Zaugg, unpublished work.

(4) G. S. Hammond in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp 442–454. Also compare, D. C. Nonhebel, *J. Chem. Soc., Sect. C*, 1716 (1967). It is interesting to note that, despite preferential bromination at the trityl carbon atom of **6**, the kinetic acidity (D exchange in DMSO) of the trityl hydrogen atom is even lower than that of the α-hydrogen atom. This suggests that what little acidity the α-hydrogen possesses may be entirely carbon acidity (*i.e.*, no kinetically significant enol). We are indebted to Professor Nathan Kornblum for an alternative explanation involving rapid reversible bromination at the α-carbon coupled with slower, but irreversible, bromination at the trityl carbon.

(5) Cleavage of the diketone **7** occurs rapidly. Immediate quenching of its *red* sulfuric acid solution yields only **8** and no **7**. In contrast, similar treatment of the *yellow* solution of the diketone **6** in sulfuric acid results in predominant recovery of **6**. Apparently, the carbonium ion formed from **7** assists the cleavage by a process such as

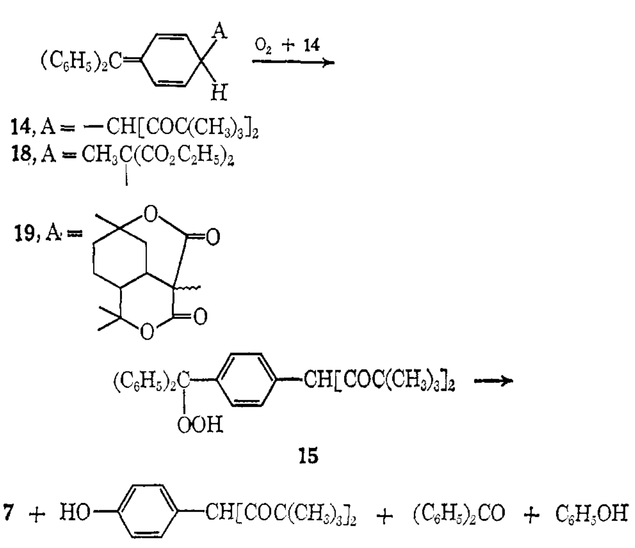


(6) T. J. Wallace and F. A. Baron, *J. Org. Chem.*, **30**, 3520 (1965).

(7) H. Staudinger and K. Clar, *Ber.*, **44**, 1623 (1911).

enol ether **17**.[8] Indeed, when trityl bromide was substituted for the chloride, approximately half of the product was derived from O-alkylation. This led to the question whether any O-substitution also occurred abnormally at a *p*-phenyl position. However, both vpc and tlc analyses of many of the crude reaction products failed to detect the presence of any *p*-hydroxytriphenylmethane. Therefore, although the occurrence of traces of the normal C-alkylation product, trityldipivaloylmethane (**3**), cannot be ruled out, it can be concluded that only two (**6** and **17**) of the several theoretically possible products are formed preferentially in the reaction of the ambident dipivaloylmethide anion with the ambident electrophile, trityl halide. This conclusion, of course, is based on the assumption that any nonaromatic O-alkylated intermediate (*e.g.*, **14**, A = OR) would rearrange to its aromatic isomer before work-up, just as the C-alkylated intermediate does (*vide infra*).

Early in the course of the present work it seemed likely that the arylation reaction leading to **6** proceeds through the intermediate triene **14**. A closely related triene has indeed been isolated by others in the mercuric chloride catalyzed reaction of trityl chloride with dimethylketene dimethyl acetal,[9] and it has been found[10] to undergo ready base-catalyzed proton transfer to the aromatized *para*-substituted triphenylmethane (corresponding to **6**). Preliminary evidence for the intermediacy of **14** in the present work was derivable from the isolation and identification of several by-products from reactions in which special care to exclude air had not been exercised. One of these was the hydroperoxide **15** presumably formed by oxidation of **14**, followed by rearrangement. In addition, the carbinol **7** and the phenol **16** were isolated, and the presence of benzophenone and phenol was demonstrated by vpc and tlc. These four compounds are among the expected[11] reduction and decomposition product of the hydroperoxide **15**.[12]



14, A = $-CH[COC(CH_3)_3]_2$

18, A = $CH_3C(CO_2C_2H_5)_2$

19, A =

15

16

Because of the mechanistic virtuosity of the trityl species[13] several reactions designed to elucidate the mechanism of this arylation reaction were carried out. The possibility of nucleophilic attack by the anion at the trityl halogen atom[14] was ruled out by the fact (Table I) that the presence of excess dipivaloylmethane (**26**) (p$K \sim 11.8$) did not adversely affect the yield of **6**. The possible involvement of trityl radicals was eliminated by the observation that no **6** was formed when a mixture of **26** and its sodium salt was treated with trityl radicals. Addition of cupric chloride to the reaction mixture (Table I) was designed to test the plausible occurrence of a radical-anion mechanism.[15] Although the yield of **6** from trityl chloride was significantly reduced, added salt ($CuCl_2$) had no effect on the yield from the corresponding bromide. This suggested, rather, the occurrence of a common ion rate depression of *ionization* of triphenylmethyl chloride.[16] Stronger evidence implicating the intermediacy of triphenylcarbonium ion was forthcoming from the observation (Table I) that triphenylmethyl fluoroborate[17] (freshly prepared or recrystallized) gave a good yield of **6**.[18] Furthermore, when unpurified fluoroborate was aged for at least 1 week, the reaction with sodiodipivaloylmethane in dimethylformamide solution was largely arrested at the triene stage. Indeed, by careful work-up of the reaction mixture, fair yields of the pure intermediate **14** could be isolated.[19] It showed properties (nmr, uv, instability) characteristic[9,10] of its cyclic cross-conjugated system and could be isomerized by methanolic sodium methoxide to **6** in high yields (83–92%). The use of methanol-O-*d* as solvent verified observations of other workers[10] that a significant part (>30%) of this 1,5-prototropic shift occurs by an intramolecular process.[20]

Using the distinctive spectral characteristics of this triene system, the scope of the arylation process was investigated by extending the reaction with triphenylmethyl fluoroborate to 14 other enolate systems. Examination of the uv and nmr spectra of reaction mixtures provided good estimates of triene yields without product isolation. Results are summarized in Table II. It will be noted that of the seven enolates derived from the β-diketones (**21**–**27**) only the one from dipivaloylmethane (**26**) gave anything more than barely detectable yields of triene. In contrast, only two of the eight anions derived from the β-diesters (**28**–**35**) failed to give

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(8) Although direct spectral evidence for the presence of **17** in crude products was not obtainable because of interference from other constituents, it was possible to show an increase in the quantity of triphenylmethanol resulting from hydrolysis of the crude product.

(9) R. Heck, P. S. Magee, and S. Winstein, *Tetrahedron Lett.*, 2033 (1964).

(10) D. J. Cram, F. Willey, H. P. Fischer, H. M. Relles, and D. A. Scott, *J. Amer. Chem. Soc.*, **88**, 2759 (1966).

(11) M. F. Hawthorne and G. S. Hammond, *ibid.*, **77**, 2549 (1955).

(12) In a control experiment it was found that the triphenylmethane derivative **6** is inert to air oxidation under the conditions of its formation. Hence, **15** could not have been formed from **6**.

(13) J. P. Lorand and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 3294 (1966).

(14) I. J. Borowitz and R. Virkaus, *ibid.*, **85**, 2183 (1963).

(15) R. C. Kerber, G. W. Urry, and N. Kornblum, *ibid.*, **87**, 4520 (1965); N. Kornblum, R. E. Michel, and R. C. Kerber, *ibid.*, **88**, 5660, 5662 (1966); G. A. Russell and W. C. Danen, *ibid.*, **88**, 5663 (1966).

(16) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 623 (1956).

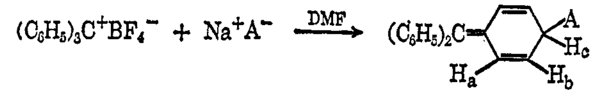
(17) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

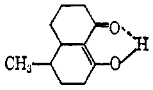
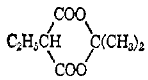
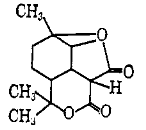
(18) The markedly different results (Table I) of alkylation with trityl bromide as compared to the chloride under otherwise identical conditions show that, even in dimethylformamide solution, the triphenylcarbonium ion is largely associated with its counterion. Compare ref 16, pp 611–612.

(19) Triphenylmethyl fluoroborate is prepared[17] by precipitation from propionic anhydride, last traces of which are impossible to remove merely by washing with dry ether. It seems likely that the aged, unpurified salt contains traces of propionic acid which serves to neutralize residual basic catalysts that promote the rearrangement of **14** to **6**.

(20) Compare also G. Bergson and L. Ohlsson, *Acta Chem. Scand.*, **21**, 1393 (1967), and previous papers.

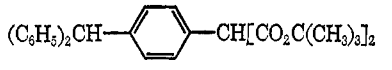
Table II. Spectrophotometric Yields of the Reactions



HA	Yield, %[a]	Uv$_{max}$ (CH$_3$OH), mμ	Chemical shifts,[b] δ, ppm H$_a$	H$_b$	H$_c$
CH$_2$(COCH$_3$)$_2$ **(21)**	<5	280[c]			
(CH$_3$)$_2$CHCH(COCH$_3$)$_2$ **(22)**	5–10	298[c]	*d*	*d*	
CH$_2$(COC$_6$H$_5$)$_2$ **(23)**	<5	345[c,e]			
CH$_3$CH(COC$_6$H$_5$)$_2$ **(24)**	<5	337[c]			
CH$_2$[COCH(CH$_3$)$_2$]$_2$ **(25)**	5–10	290[c]	*d*	*d*	
CH$_2$[COC(CH$_3$)$_3$]$_2$ **(26)**	67–70	310	6.51	5.66	3.99
 **(27)**	<5	297[c]			
CH$_2$(CO$_2$C$_2$H$_5$)$_2$ **(28)**	20	306	6.58	5.82	~4
CH$_3$CH(CO$_2$C$_2$H$_5$)$_2$ **(29)**	43	307	6.60	5.73	~4.1
(CH$_3$)$_2$CHCH(CO$_2$C$_2$H$_5$)$_2$ **(30)**	51	308	6.57	5.90	~4
C$_6$H$_5$CH(CO$_2$C$_2$H$_5$)$_2$ **(31)**	41	308	6.45	5.88	~4.5
(C$_6$H$_5$)$_3$CCH(CO$_2$C$_2$H$_5$)$_2$ **(32)**	<5	282[c]			
CH$_2$[CO$_2$C(CH$_3$)$_3$]$_2$ **(33)**	33	305	6.57	5.87	~3.8
 **(34)**	<5	276[c]			
 **(35)**	73	313	6.72	5.77	4.75

[a] See the Experimental Section for explanation. [b] For all observed spectra except the last one, J_{ab} = 10 Hz, J_{bc} = 4 Hz, and J_{ac} = 2 Hz. In the triene **19**, from **35**, all three absorptions are symmetrical but complex multiplets. [c] A stable uv$_{max}$; also, since no nmr absorption for the triene was detectable, this uv$_{max}$ must be due to starting material or by-product. [d] Detectable only by integration of the nmr spectrum in the 5.5–7.0-ppm range. [e] B. Eistert, F. Weygand, and E. Csendes [*Chem. Ber.*, **84**, 745 (1951)] report uv$_{max}$ (CH$_3$OH) 345 mμ (ε 23,500) for dibenzoylmethane (**23**).

easily measurable yields. Indeed, in two instances (**29** and **35**) the corresponding trienes (**18** and **19**) could be isolated in analytically pure form. When efforts to isolate the triene from di-*t*-butyl malonate anion (*i.e.*, **33**) failed, it was isomerized to **20** which could then be isolated in a yield equivalent to that indicated for triene formation (33%). Similar treatment of the diethyl malonate (**28**) reaction mixture containing only 20% triene, however, led to the normal tritylation product **32** as the only easily isolable substance (37% yield).



$(C_6H_5)_2CH-C_6H_4-CH[CO_2C(CH_3)_3]_2$

20

Attempted extension of the arylation reaction still further to include a *para*-substituted triarylcarbonium ion failed. Thus, treatment of the enolates of dipivaloylmethane (**26**) and of the dilactone **35** with tri-*p*-tolylmethyl fluoroborate gave reaction mixtures containing no spectrally detectable amounts of triene. Work-up of the former reaction led only to the normal tritylation product **5** (16% yield), a result consistent with the previously observed formation of **4** to the apparent exclusion of abnormal arylation product.

Discussion

The ambident reactivity of the trityl species has been known for many years. Recently, Lorand and Bartlett[13] reviewed the literature and showed that either radical or ionic mechanisms can be involved. They concluded that the position of attack on the trityl group is probably controlled by steric factors, so that the bulkier reagents give *para* coupling.[21] The results of the present work summarized in Table II, however, clearly show that electrical as well as steric factors are operative in these ambident *ionic* reactions.

Anions derived from the relatively acidic, highly enolized β-diketones (**21–27**) are generally more prone to undergo O-alkylation than are the weakly acidic, nonenolized diesters (**28–25**, except **34**).[22] Thus, in the diketone series, only when O-alkylation as well as normal C-tritylation are effectively hindered (as in **26**) does the abnormal arylation reaction compete successfully with the other two possibilities. Inspection of space-filling models reveals that for attack of the flattened, propeller-shaped triphenylcarbonium ion parallel to the plane of the enolate ion of **26**, approach to within bonding distance for the normal C-tritylation reaction is prevented by steric interactions between two phenyls and two out-of-plane methyls of the *t*-butyl groups. This "long-range" steric effect is clearly absent for the C-arylation reaction involving attack by the periphery, *i.e.*, a *p*-phenyl position, of the large carbonium ion. In the diester series where O-alkylation is usually less competitive, steric factors are less important. The slightly enhanced triene yield observed in going from diethyl (**20**%) to di-*t*-butyl malonate (33%) reflects a moderate long-range steric effect. The somewhat

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(21) Also compare H. Hoffmann and P. Schellenbeck, *Chem. Ber.*, **99**, 1134 (1966), and H. Lankamp, W. T. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968).

(22) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 174.

larger increments produced by α-substitution in diethyl malonate (*i.e.*, **29**, **30**, **31**) indicate a distinctly, but not dramatically, greater short-range steric effect which can become prohibitive, however, if carried to extreme (*i.e.*, **32**). Models of the anion derived from **35** suggest that long-range effects primarily account for the high yield of triene **19**. (The complex nmr patterns of the vinyl protons in this triene further indicate that these interactions persist even in the arylated product.) When the geometry of the diester anion serves to promote charge delocalization as in the cyclic malonate **34** (pK = 4.5),[1] the arylation reaction again fails to compete.

Experimental Section

Nuclear magnetic resonance spectra were obtained with a Varian Model A-60 instrument using tetramethylsilane as an internal standard unless otherwise indicated. A Perkin-Elmer Model 421 spectrometer was used for the infrared spectra. A Cary Model 11 and a Bausch and Lomb Spectronic 600 (with a Sargent Model SRL recorder) were used for the ultraviolet spectra. Refractive indices were determined with a Zeiss Opton refractometer. Melting points and boiling points are uncorrected.

Materials. The following commercially available (Aldrich or Eastman) compounds were used without further purification: triphenylmethanol, triphenylmethyl chloride, triphenylmethy bromide, diethyl malonate (**28**), diethyl methylmalonate (**29**), dibenzoylmethane (**23**), mp 73–75°, 2,6-dimethyl-3,5-heptanedione (**25**), 99% (vpc), and methanol-O-*d* (Merck Sharp and Dohme of Canada Ltd.). The following were redistilled before use: diethyl phenylmalonate (**31**), bp 167° (16 mm), $n^{25}\mathrm{D}$ 1.4888, 98.5% (vpc), and 2,4-pentanedione (**21**), bp 135° (atm), $n^{25}\mathrm{D}$ 1.4477, nmr ($CDCl_3$), δ 15.1 (s, 0.70, O*H*), 5.53 (s, 0.82, C*H*=C), 3.62 (s, 0.35, $COCH_2CO$), 2.23 (s, 1.04, $COCH_3$), and 2.03 ppm (s, 5.10, enol CH_3); therefore [enol]/[keto] $\cong$ 80/20.

The following compounds were prepared by reported methods: tri-*p*-tolylmethanol,[23] mp 93–95°; 3-isopropyl-2,4-pentanedione (**22**),[24] bp 180° (1 atm), $n^{25}\mathrm{D}$ 1.4275, 99.0% (vpc); 1,1-dibenzoylethane (**24**),[25] mp 83–84°; dipivaloylmethane (**26**),[26] bp 78–80° (12 mm), $n^{25}\mathrm{D}$ 1.4566, 99.9% (vpc), nmr ($CDCl_3$), δ 16.3 (s, 1, O*H*), 5.78 (s, 1, C*H*=C), and 1.18 ppm (s, 18, CCH_3); therefore [enol]/[keto] $\cong$ 100; 3,4,5,6,7,10-hexahydro-8-hydroxy-4-methyl-1(2H)-naphthalenone (**27**),[1] bp 101–102° (1 mm), 97% (vpc); diethyl isopropylmalonate (**30**);[27] bp 96–98° (11 mm), 94% (vpc); diethyl triphenylmethylmalonate (**32**),[28] mp 133–134.5°, nmr ($CDCl_3$), δ 7.28 (m, 15, Ar*H*), 5.33 (s, 1, COC*H*CO), 3.88 (q, 4, J = 7 Hz, OCH_2), and 1.00 ppm (t, 6, J = 7 Hz, CCH_3); di-*t*-butyl malonate (**33**),[29] bp 115° (27 mm), $n^{25.5}\mathrm{D}$ 1.4148; isopropylidene ethylmalonate (**34**),[30] mp 108–109°; *cis*-1(Me),3(H),4(H)-*cis*-3(H),-α(H)-1,8-dihydroxy-3-*p*-menthylmalonic dilactone (**35**),[31] mp 190–191°; 3-benzyl-2,4-pentanedione (**11**),[32] bp 114° (1.8 mm), $n^{25}\mathrm{D}$ 1.5260, purity checked by elemental analysis, uv_{max} (1,2-dimethoxyethane) 288.5 mμ (ϵ 4200, enol form), ir ($CHCl_3$) 1600 (bonded C=O, 1694 (C=O), and 1722 cm^{-1} (C=O), nmr ($CDCl_3$), δ 16.7 (s, 0.26, O*H*), 7.25 (m, 5, Ar*H*), 4.03 (t, 0.62, J = 8 Hz, CH_2CH), 3.67 (s, 0.89, CH_2C=C), 3.15 (d, 1.12, J = 8 Hz, CH_2CH), 2.12 (s, 3.43, $COCH_3$), and 2.07 ppm (s, 2.58, enol CH_3); therefore [enol]/[keto] $\cong$ 40/60; 3-diphenylmethyl-2,4-pentanedione (**12**),[33] mp 114–115°, ir ($CHCl_3$) 1690 (C=O) and 1718 cm^{-1} (C=O), nmr ($CDCl_3$), δ 7.25 (m, 10, Ar*H*), 4.80 (s, 2, Ar_2CH and COC*H*CO), and 2.00 ppm (s, 6, $COCH_3$), nmr (pyridine plus a trace of HCl), δ 5.10 (d, 1, J = 12 Hz, C*H*) and 5.50 ppm (d, 1, J = 12 Hz, C*H*); therefore [enol]/[keto] $\cong$ 0; and 3-triphenylmethyl-2,4-pentanedione (**13**),[1] mp 166–167°, uv_{max} (isooctane) 260 (ϵ 850) and 266 mμ (ϵ 810), ir ($CHCl_3$) 1690 (C=O) and 1728 cm^{-1} (C=O), nmr ($CDCl_3$), δ 7.30 (m, 15, Ar*H*), 5.58 (s, 1, COC*H*CO), and 1.83 ppm (s, 6, $COCH_3$); therefore [enol]/[keto] $\cong$ 0.

4-(*p*-Benzhydrylphenyl)-2,2,6,6-tetramethyl-3,5-heptanedione (6). Procedure A. A 0.65-g sample of sodium hydride (50% dispersion in mineral oil) was washed by centrifugation with three 10-ml portions of Skellysolve B. Using 20 ml of dry dimethylformamide in several portions it was then washed into a 100-ml three-necked flask fitted with a nitrogen inlet, drying tube, thermometer, and dropping funnel. Pure dry nitrogen was passed (5–10 bubbles/sec) through the magnetically stirred suspension for 0.5 hr, then, at room temperature, a solution of 2.30 g (0.0125 mol) of dipivaloylmethane (**26**) in 15 ml of dry benzene was added over a period of 10–15 min during which time the temperature rose to 40°. Nitrogen was passed through the solution for 1 more hr. During this time, the dropping funnel was replaced by a 10-ml cylindrical vial containing 3.90 g (0.014 mol) of solid triphenylmethyl chloride in a nitrogen atmosphere. The vial was attached to the neck of the flask with a short length (6 cm) of Gooch tubing of appropriate diameter. Also a water bath was placed around the reaction flask and warmed to 50°. At the end of 1 hr, the triphenylmethyl chloride was added in one portion (no exothermic reaction was noted), and stirring under nitrogen was continued at 50° for 1 hr and then at 60° for 2 hr. The neutral reaction mixture was poured into cold water (300 ml), extracted with three 200-ml portions of benzene, washed with water, and concentrated to dryness under reduced pressure using a rotating evaporator. The residual solid was triturated with Skellysolve B, filtered, washed with more Skellysolve B, and dried. There was obtained 4.68 g (88%) of fairly pure **6**, mp 169–172°. (From the combined Skellysolve B fractions, 1.13 g of a yellow oil was obtained which was analyzed for dipivaloylmethane according to procedure B). Recrystallization of the solid product from ethanol gave pure **6**, mp 173–174°; on very slow heating, the material softened, resolidified, and melted at 180–181°; recrystallization from benzene gave the dimorphic form, mp 180–181° (no softening at 173°), having the same spectral characteristics as the crystal form: mp 173–174°; uv_{max} (isooctane) 256 (ϵ 1140), 263 (ϵ 1270), 270 (ϵ 1040), and 290 mμ (ϵ 530); ir ($CHCl_3$) 1693 (C=O) and 1725 cm^{-1} (C=O); nmr ($CDCl_3$), δ 7.17 (m, 14, Ar*H*), 5.75 (s, 1, COCHCO), 5.56 (s, 1, Ar_3CH), and 1.12 ppm (s, 18, CCH_3); nmr [$(CD_3)_2SO$], δ 6.05 (s, 1, COC*H*CO) and 5.63 ppm (s, 1, Ar_3CH); with added sodium hydride or potassium *t*-butoxide–*t*-butyl alcohol-O-*d*, the 6.05-ppm peak disappeared (2–6 hr) but the 5.63-ppm peak remained; partial mass spectrum (70 eV) *m/e* [rel intensity, assignment] 426 [60, parent (M)], 427 [20, (M + 1)], 428 [2.4, (M + 2)], 342 [100, $(C_6H_5)_2CHC_6H_4CHCOC(CH_3)_3$], 167 [44, $(C_6H_5)_2CH$], 85 [38, $(CH_3)_3CCO$], 57 [77, $(CH_3)_3C$].

Anal. Calcd for $C_{30}H_{34}O_2$: C, 84.46; H, 8.04; O, 7.50. Found: C, 84.40; H, 7.82; O, 7.70.

Results of varying the conditions of the foregoing reaction are summarized in Table I.

Isolation and Identification of By-Products. During initial experiments leading to the development of optimum conditions for the preparation of **6**, lower temperatures (35–45°) and shorter reaction times were employed and less care was exercised in the exclusion of atmospheric oxygen. Under these conditions lower yields (35–50%) of **6** were obtained together with larger quantities of the Skellysolve B soluble fraction. Thin layer silica gel chromatography using a hexane–dioxane–isobutyl alcohol (96:2:2) system demonstrated the presence of many components in one of these hydrocarbon-soluble fractions. By fractional crystallization using methanol, 95% ethanol, Skellysolve B, and pentane, three of these components, **7**, **15**, and **16**, could be isolated in amounts sufficient only for characterization.

Diphenyl(*p*-dipivaloylmethylphenyl)methyl hydroperoxide (15) showed the following characteristics: prisms from Skellysolve B, mp 139–140°; positive color test for hydroperoxide;[34] ir ($CHCl_3$) 1695 (C=O), 1725 (C=O), 3503 (OH), and 3595 cm^{-1} (OH); nmr ($CDCl_3$), δ 7.30 (m, 14, Ar*H*), 5.75 (s, 1, COC*H*CO), 2.7–2.9 (detectable only by integration before and after D_2O exchange, ~1, OO*H*), and 1.12 ppm (s, 18, CCH_3).

Anal. Calcd for $C_{30}H_{34}O_4$: C, 78.57; H, 7.47; O, 13.96. Found: C, 78.52; H, 7.56; O, 14.12.

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4-(*p*-Hydroxyphenyl)-2,2,6,6-tetramethyl-3,5-heptanedione (16) showed the following characteristics: needles from pentane, mp 162–165°; soluble in hot 10% sodium hydroxide; ir ($CHCl_3$) 1691 (C=O), 1723 (C=O), 3410–3440 (OH), and 3595 cm^{-1} (OH); nmr ($CDCl_3$), δ 7.05 (d, 2, J = 9 Hz, Ar*H*), 6.77 (d, 2, J = 9 Hz, Ar*H*), 6.0–6.3 (detectable only by integration before and after D_2O exchange, ~1, O*H*), 5.70 (s, 1, COC*H*CO), and 1.12 ppm (s, 18, CCH_3).

Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75; O, 17.37. Found: C, 73.83; H, 8.45; O, 17.47.

Diphenyl(*p*-dipivaloylmethylphenyl)methanol (7) showed the following characteristics: mp 159–161°, identical (mixture melting point, microanalysis, ir, and nmr) with the material, mp 163–165°, prepared from **6** by bromination and hydrolysis.

The Skellysolve B soluble fraction also was analyzed using gas–liquid partition chromatography (glpc, three different columns) and thin layer silica gel chromatography (tlc) in combination with many solvent systems. Using known compounds as standards, the presence of the following compounds (in addition to **6**, **7**, and **16**) in the mixture was indicated by both tlc and glpc: phenol, triphenylmethane, triphenylmethanol, and benzophenone. The presence of triphenylmethyl chloride was indicated by glpc, and several spots (and peaks) remained unidentified. However, by using an authentic sample[35] it was established that none of these unidentified materials was *p*-hydroxytriphenylmethane.

Small amounts of these by-products undoubtedly formed even under conditions optimum for the preparation of **6**. For example, in many cases, nmr and tlc analyses indicated the presence of appreciable amounts of the carbinol **7** in reaction residues.

Attempted Air Oxidation of the Diketone 6 under Conditions Approximating Those Present in the Preparation of 6. A solution of 0.65 g of the diketone **6** in 15 ml of dimethylformamide was treated with 0.1 g of sodium hydride and 0.4 g of dipivaloylmethane. The solution was allowed to stand in air at room temperature for 2 days and was then concentrated to dryness under reduced pressure. The residue was treated with water, collected at the filter, and dried. There was obtained 0.60 g (92% recovery) of unchanged diketone **6**. Similar results were obtained when air was passed through the solution for 4 hr. Hence, it appears that the oxidation products **15**, **16**, etc., could not have been formed from **6**.

Quantitative Determination of Dipivaloylmethane by Glpc. Procedure B. The instrument used was an Aerograph Model 1525 equipped with a digital integrator (Model 471). Helium flow rate was 30% of maximum through a 5% SE 30 column (5 ft × 1/8 in.). In preliminary experiments it was found that 3-phenyl-2-benzofuranone[36] gave a well-defined peak far enough removed from those of other components to serve as an internal standard for both dipivaloylmethane and triphenylmethanol. Further preliminary experiments with synthetic mixtures established the necessary response factors of the substances under study. For maximum resolution of the chromatogram it was found necessary to program the column temperature as follows: injection at 115°, 4°/min for 2 min, 20°/min for 6 min, hold for 12 min, 30°/min to maximum of 225°. Results of analyses carried out on many Skellysolve B soluble fractions obtained according to variants of procedure A are summarized in Table I. In most cases, quantitative determinations of triphenylmethanol (corrected for the excess amount of trityl chloride used initially) checked those of dipivaloylmethane.

Alkylation with Triphenylmethyl Bromide. Procedure C. When 4.52 g (0.014 mol) of trityl bromide was substituted for the chloride in procedure A, the reaction proceeded to neutrality and a fraction (3.44 g, mp 135–150°) insoluble, and a liquid fraction (1.80 g) soluble in Skellysolve B were obtained. The nmr spectrum of the solid fraction showed the presence only of the diketone **6** and triphenylmethanol. Integrated areas of the respective peaks established the composition as 68.5% (2.36 g) diketone **6** and 31.5% (1.08 g) triphenylmethanol. The nmr spectrum of the soluble fraction showed the presence of diketone **6**, dipivaloylmethane (**26**), and only a small quantity of triphenylmethanol. This oil (1.80 g) was then warmed on the steam bath with 10 ml of glacial acetic acid containing 2 ml of water and 5 drops of concentrated hydrochloric acid. On standing overnight the clear solution deposited a solid. The mixture was concentrated to dryness under reduced pressure and the semisolid residue was triturated with Skellysolve B. Insoluble material (0.74 g, mp 120–145°) was collected at the filter and dried. Its nmr spectrum showed that it contained 0.14 g of diketone **6** and 0.60 g of triphenylmethanol. The filtrate was concentrated to dryness and the nmr spectrum of the oily residue (0.68 g) showed that it contained 0.25 g of triphenylmethanol, 0.34 g of dipivaloylmethane, and 0.09 g of alkylated diketone, found by tlc to be a mixture of **6** and **7**. The total yield (2.51 g) of diketone **6** was therefore 47% of theory and the total yield (1.93 g) of triphenylmethanol represented a 48% yield of O-alkylated product **17**, after subtracting 0.39 g (0.0015 mol) of carbinol corresponding to the excess amount of bromide used originally [theoretical yield of triphenylmethanol = 3.26 g (0.0125 mol)].

Alkylation with Triphenylmethyl Fluoroborate. Procedure D. When 4.63 g (0.014 mol) of unrecrystallized, freshly prepared (<48 hr) or recrystallized triphenylmethyl fluoroborate[17] was substituted for the chloride in procedure A (0 ml of DMF, 40 ml of C_6H_6), the exothermic reaction (29° → 36°) gave 3.84 g (72%), mp 162–168°, of fairly pure (ir and nmr) diketone **6**. Spectral analysis (ir and nmr) of the residual product showed the presence only of triphenylmethanol and dipivaloylmethane mixed with more of the main product **6**. When samples of the fluoroborate more than 1 week old (even when stored under nitrogen in a desiccator in the dark) were used, either in 100% benzene solution or in 50:50 benzene–dimethylformamide solution, yields of **6** were drastically reduced. Reaction products that were carefully protected from air and moisture contained (nmr) appreciable quantities of the intermediate triene **14**. Reaction mixtures worked up in the usual way showed the presence (ir, nmr, and tlc) of the products (*i.e.*, **7**, **15**, **16**, etc.) derived from **14** by oxidation and cleavage.

3-Triphenylmethyl-2,4-pentanedione (13) from Triphenylmethyl Chloride. When 1.25 g (0.0125 mol) of 2,4-pentanedione was substituted for the dipivaloylmethane in the above procedure for the preparation of the diketone **6**, a brown glassy product (4.1 g) was obtained. Although its nmr spectrum was mainly characteristic of that of pure **13**, it could not be rendered crystalline. After standing with 400 ml of 95% ethanol for 50 days, isoluble material (0.18 g, mp 125–140°) was removed by filtration. The filtrate was concentrated to dryness under reduced pressure and the residue was triturated with 300 ml of Skellysolve B. Crystalline product (0.15 g, mp 151–157°) was collected at the filter and recrystallized from 95% ethanol to give 0.13 g of pure **13**, mp 166–167°, identical (mixture melting point and nmr spectra) with an authentic sample prepared from triphenylmethanol under acid-catalyzed conditions.[1]

Attempted Reaction of Triphenylmethyl with Dipivaloylmethane. Using the procedure and apparatus similar to that described by Hammond, Ravve, and Modic,[37] a solution of triphenylmethyl in 40 ml of benzene was prepared from 7.0 g (0.025 mol) of triphenylmethyl chloride and 11.65 g (0.058 mol, 0.87 ml) of mercury. Using nitrogen pressure, this solution was forced through a plug of glass wool into a solution of 2.30 g (0.025 mol) of dipivaloylmethane in 10 ml of benzene to which 0.0025 mol of sodium hydride (previously washed free from mineral oil) had been added. The mixture was stirred under nitrogen at room temperature in total darkness for 19 hr and then at 60° for 2.5 hr. The reaction mixture was worked up in a manner similar to that described for the preparation of **6**. The Skellysolve B insoluble fraction (3.63 g), mp 178–182°, was shown by its infrared spectrum to be triphenylmethyl peroxide. The Skellysolve B soluble fraction (3.0 g) was mainly unreacted dipivaloylmethane. No **6** could be detected in either fraction (ir and nmr). Similar results were obtained when larger amounts (9.01 mol) of sodium hydride were used.

Diphenyl(*p*-dipivaloylmethylphenyl)methanol (7). To a stirred solution of 8.5 g (0.02 mol) of the diketone **6** in 125 ml of carbon tetrachloride was added dropwise with stirring over a period of 1 hr a solution of 3.2 g (0.02 mol) of bromine in 25 ml of carbon tetrachloride. After about one-third of the bromine was added, hydrogen bromide evolution became noticeable. The mixture was stirred for 4 hr at room temperature and then was allowed to stand over the weekend. The solvent was removed under reduced pressure and the solid residue was recrystallized once from Skellysolve B to give 8.6 g of crude product, mp 144–147°, which contained halogen. Two recrystallizations from a water–isopropyl alcohol mixture gave 6.4 g (72%) of pure **7**: mp 163–165°; ir ($CHCl_3$) 1692 (C=O), 1723 (C=O), and 3597 cm^{-1} (OH); nmr ($CDCl_3$), δ 7.33 (m, 14, Ar*H*), 5.78 (s, 1, COC*H*CO), 2.80 (s, 1, O*H*), and 1.13 ppm (s, 18, CCH_3).

Anal. Calcd for $C_{30}H_{34}O_3$: C, 81.41; H, 7.74; O, 10.85. Found: C, 81.40; H, 8.00; O, 10.91.

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Diphenyl(*p*-pivaloylmethylphenyl)methanol (8). To a solution of 0.855 g (1.93 mmol) of the hydroxy diketone **7** in 5 ml of 1,2-dimethoxyethane was added 11 ml of concentrated sulfuric acid. The red-brown solution was immediately poured into a 100-ml beaker filled with crushed ice. The precipitated product was taken up in ether, washed with water, and dried. Filtration and stripping of the ether gave an oil that solidified upon trituration with pentane. The crude product (0.606 g, 88%, mp 99–102°) was collected at the filter and recrystallized twice from Skellysolve B to give pure **8**: mp 105–106°; ir (CHCl$_3$) 1702 (C=O) and 3600 cm^{-1} (OH); nmr (CDCl$_3$), δ 7.43 (m, 14, Ar*H*), 3.78 (s, 2, C*H*$_2$CO), 2.82 (s, 1, O*H*), and 1.21 ppm (s, 9, CC*H*$_3$).

Anal. Calcd for $C_{25}H_{26}O_2$: C, 83.76; H, 7.32; O, 8.92. Found: C, 84.00; H, 7.51; O, 9.10.

From the pentane filtrate was obtained 0.192 g of liquid residue whose infrared spectrum was qualitatively identical with that of an authentic sample of pivalic acid.

In another experiment, a sample of pure **8**, mp 112–113°, was obtained. This appears to be a dimorphic form. Its infrared spectrum was identical with that of the 100° form and a mixture of the two melted at the higher temperature (112–113°).

When the foregoing procedure was applied to the unhydroxylated diketone **6**, it formed a light yellow solution in concentrated sulfuric acid, and could be recovered in 74% yield upon quenching with ice. Longer contact with sulfuric acid resulted in poorer recovery, presumably because of sulfonation leading to water-soluble products. When **6** was refluxed in ethanolic hydrochloric acid (2 ml of concentrated hydrochloric acid in 25 ml of 95% ethanol) for 18 hr, it could be recovered quantitatively.

In concentrated sulfuric acid, the hydroxy diketone **7** and the hydroxy monoketone **8** gave identical ultraviolet spectra: uv$_{\max}$ 290 (ϵ 1300), 410 (ϵ 34,000, shoulder), and 438 mμ (ϵ 40,000). These spectra were stable for at least 20 hr. The diketone **6**, on the other hand, give a different and quite unstable spectrum in concentrated sulfuric acid: uv$_{\max}$ 232 (ϵ 31,000), 276 (ϵ 3200), 290 (ϵ 2200), 400 (ϵ 220), and 448 mμ (ϵ 290).

***p*-Carboxytriphenylmethanol (9).** Attempts to oxidize the ketone **8** to the corresponding carboxylic acid **9** using several conventional oxidizing agents failed. These included nitric acid (in both water and acetic acid), sodium hypobromite in water, and potassium dichromate in concentrated sulfuric acid. The strong base catalyzed oxygenation procedure reported by Wallace and Baron[6] succeeded.

A stirred solution of 0.708 g (1.98 mmol) of the hydroxy ketone **8** and 0.44 g (3.96 mmol) of potassium *t*-butoxide in 4 ml of hexamethylphosphoramide was treated with a stream of dry oxygen for 3.5 hr. The initial deep red color of the solution changed to amber during this time. The mixture was then poured into 75 ml of water containing excess hydrochloric acid. The precipitated oil was taken up in ether and dried over anhydrous magnesium sulfate. Filtration and removal of the ether by distillation gave an oil that was dissolved in a minimum quantity of methanol and treated with water to the point of turbidity. Crude product (0.53 g, mp 150–180°) slowly crystallized. It was purified by dissolving it in saturated sodium bicarbonate solution, filtering, and reprecipitating with dilute hydrochloric acid. A repetition of this procedure followed by two recrystallizations from aqueous methanol gave 0.305 g of analytically pure **9**: mp 202–204°, identical (mixture melting point and ir spectra) with an authentic specimen, mp 203–204°, prepared according to the method of Staudinger and Clar.[7]

4-(*p*-Benzhydrylphenyl)-2,2,6,6-tetramethyl-3,5-heptanediol (10). To a suspension of 0.15 g (4 mmol) of lithium aluminum hydride in 75 ml of dry ether was added 1.5 g (3.5 mmol) of the diketone **6**. The mixture was stirred and refluxed for 22 hr. To the ice-cooled mixture 1 ml of water was added dropwise with stirring, followed by 1 ml of 50% aqueous sodium hydroxide. The stirred mixture was then refluxed for 0.5 hr, the ether was decanted, and the solid residue was washed several times by decantation with more ether. The combined ether portions were dried over anhydrous magnesium sulfate, filtered to remove the drying agent, and concentrated to dryness. The solid residue (1.5 g, mp 152–160°) was recrystallized three times from dry ethanol to give pure **10** (1.0 g, 66%): mp 179–180°; uv$_{\max}$ (isooctane) 257 (ϵ 960), 263 (ϵ 1140), and 270 mμ (ϵ 910); ir (CCl$_4$) 3518 (OH), 3578 (OH), and 3621 cm^{-1} (OH); nmr (CDCl$_3$), δ 7.17 (m, 14, Ar*H*), 5.57 (s, 1, Ar$_3$C*H*), 3.78 (s, 2, $J < 1$ Hz, C*H*OH), 3.17 (s, 1, $J < 1$ Hz, C*H*CHOH), 3.02 (s, 2, O*H*), and 0.73 ppm (s, 18, CC*H*$_3$).

Anal. Calcd for $C_{30}H_{38}O_2$: C, 83.67; H, 8.90; O, 7.43. Found: C, 83.80; H, 8.81; O, 7.82.

Hydrogenolysis of the Carbinol 7 to the Diketone 6. A solution of 49.6 mg of the carbinol **7** in 20 ml of glacial acetic acid containing one drop of 70% perchloric acid was treated with 25 mg of 5% palladium–charcoal and shaken at room temperature for 24 hr with hydrogen at atmospheric pressure. After removal of the catalyst by filtration, the solution was concentrated to dryness under reduced pressure. The residue was taken up in water, collected at the filter, and dried to give 36 mg (75%) of the diketone **6**, mp 170–172°, identical (mixture melting point, ir, and nmr spectra) with an authentic specimen.

4-Benzyl-2,2,6,6-tetramethyl-3,5-heptanedione (1). To a stirred suspension of 2.7 g (0.06 mol) of sodium hydride (53% dispersion in mineral oil) in 10 ml of 1,2-dimethoxyethane (DME) was added dropwise a solution of 9.5 g (0.0515 mol) of dipivaloylmethane. After stirring and heating the resulting suspension for 3 hr, a solution of 6.5 g (0.0515 mol) of benzyl chloride in 20 ml of DME was added, and stirring and heating were continued for another 18 hr. The solvent was removed under reduced pressure, and the residue was mixed with ice containing 10 ml of dilute (1:4) hydrochloric acid. Insoluble material was taken up in chloroform, washed, and concentrated to dryness. The residue was distilled under reduced pressure and a fraction (3.3 g), bp 107–151° (1.8 mm), partially solidified. Four recrystallizations from Skellysolve B gave 0.8 g (5.7%) of **1**: mp 68–69°; uv$_{\max}$ (isooctane) no enolic absorption; ir (CHCl$_3$) 1679 (C=O) and 1709 cm^{-1} (C=O); nmr (CDCl$_3$), δ 7.25 (s, 5, Ar*H*), 4.78 (t, 1, J = 7 Hz, COC*H*CO), 3.15 (d, 2, J = 7 Hz, ArC*H*$_2$), and 1.10 ppm (s, 18, CC*H*$_3$); therefore [enol]/[keto] $\cong$ 0.

Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55; O, 11.66. Found: C, 78.65; H, 9.68; O, 11.33.

4-Diphenylmethyl-2,2,6,6-tetramethyl-3,5-heptanedione (2). When benzhydryl chloride was substituted for the benzyl chloride in the foregoing procedure, a small quantity of a solid material crystallized from an ethanolic solution of the crude undistilled reaction product. Two recrystallizations of this solid from 95% ethanol gave a 3% yield of pure **2**: mp 201–202°; uv$_{\max}$ (isooctane) no enolic absorption; ir (CHCl$_3$) 1668 (C=O) and 1709 cm^{-1} (C=O); nmr (CDCl$_3$), δ 7.28 (m, 10, Ar*H*), 5.52 (d, 1, J = 12 Hz, COC*H*CO), 4.95 (d, 1, J = 12 Hz, Ar$_2$C*H*), and 0.90 ppm (s, 18, CC*H*$_3$), therefore [enol]/[keto] $\cong$ 0.

Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63; O, 9.13. Found: C, 81.94; H, 8.51; O, 8.83.

4-(*p*,*p*′,*p*′′-Tribromotriphenylmethyl)-2,2,6,6-tetramethyl-3,5-heptanedione (4). Dipivaloylmethane (3.7 g, 0.02 mol) was alkylated in the same way with 5.2 g (0.01 mol) of tri(*p*-bromophenyl)methyl chloride.[38] The 6.7 g of crude oily product thus obtained was taken up in hexane (50 ml) and insoluble material (0.57 g) was removed by filtration. This solid was dissolved in benzene (25 ml) and added to a column packed with Florisil (25 g, 60–100 mesh) in hexane. Elution was conducted first by using a 75% hexane–25% benzene mixture. Four 60-ml fractions were collected in this way, and four more were collected after changing to a 50% hexane–benzene mixture. Solid residues obtained by concentration of fractions 6 and 7 to dryness were combined and recrystallized from 2-butanone to give 0.1 g of the diketone **4**: mp 223–224°; ir (CDCl$_3$ 1687 (C=O) and 1721 cm^{-1} (C=O); nmr (CDCl$_3$), δ 7.35 (d, 6, J = 8.5 Hz, Ar*H*), 7.15 (d, 6, J = 8.5 Hz, Ar*H*), 6.15 (s, 1, COC*H*CO), and 1.07 ppm (s, 18, CC*H*$_3$).

Anal. Calcd for $C_{30}H_{31}Br_3O_2$: C, 54.32; H, 4.71; O, 4.82. Found: C, 54.56; H, 4.76; O, 5.22.

4-[4-(Diphenylmethylene)-2,5-cyclohexadienyl]-2,2,6,6-tetramethyl-3,5-heptanedione (14). A solution of sodiodipivaloylmethane (0.0125 mol) in dimethylformamide (40 ml) was prepared by procedure A. To this magnetically stirred solution at room temperature (under nitrogen) was added in one portion 4.63 g (0.014 mol) of triphenylmethyl fluoroborate (unrecrystallized, and at least 1 week old). After the spontaneous temperature rise (7–9°) was complete, the stirred neutral reaction mixture was concentrated to dryness under vacuum (1 mm) in a water bath (45–50°). The solid residue (under nitrogen) was treated with two 50-ml portions of dry ether (previously gassed with dry nitrogen) which were decanted from insoluble salt (NaBF$_4$) into a 200-ml nitrogen-filled round-bottom flask. The combined extracts were concentrated to about 20 ml by warming (35°) in a water bath under a steady stream of nitrogen blowing over the surface. After cooling at −25° overnight, the ether was decanted from crystallized product which was washed by decantation with two 10-ml portions of cold (−25°)

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[38] G. L. Davies, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 4397 (1956).

deaerated ether. The residue was dried *in vacuo* (1 mm) at room temperature to give 3.66 g (69%) of the crude triene **14**, mp 103–106° (85% pure by uv analysis). Trituration with two 15-ml portions of deaerated ether at room temperature gave 1.7 g of pure **14**: mp 111–114°; uv$_{\max}$ (CH_3OH) 310 mμ (ε 23,800 by extrapolation to zero time of a plot of ε *vs.* time, with ε decreasing about 10%/hr at room temperature); uv$_{\max}$ (isooctane) 313 mμ (ε 24,400); ir ($CHCl_3$) 1680 (C=O) and 1721 cm^{-1} (C=O); nmr ($CDCl_3$), δ 7.17 (m, 10 Ar*H*), 6.51 (q, 2, *J* = 2, 10 Hz, =CC*H*=), 5.66 (q, 2, *J* = 4, 10 Hz, =C*H*CH), 4.73 (d, 1, *J* = 7.0 Hz, COC*H*CO), 3.99 (m, 1, =CHC*H*CH=), and 1.17 ppm (s, 18, CC*H*$_3$).

Anal. Calcd for $C_{30}H_{34}O_2$: C, 84.46; H, 8.04. Found: C, 84.18; H, 7.88.

Diethyl [4-(Diphenylmethylene)-2,5-cyclohexadienyl]methylmalonate (18). Substituting 2.18 g (0.0125 mol) of diethyl methylmalonate (**29**) for the dipivaloylmethane in the foregoing procedure gave a product which was very soluble in cold (−25°) ether. The yellow oil obtained after complete removal of the ether was taken up in 70 ml of pentane, decanted from insoluble material, and cooled (−25°) over a weekend. The rosettes of needles (1.10 g, mp 80–95°) that formed were separated mechanically from oily impurity and recrystallized twice more from cold (−25°) pentane (40 ml) to give 0.50 g (10%) of pure **18**: mp 112–115°; uv$_{\max}$ (CH_3OH) 308 mμ (ε 23,500, decreasing less than 2%/hr at room temperature); ir ($CHCl_3$) 1722 (ester C=O) and 1750 cm^{-1} (shoulder, ester C=O); nmr ($CDCl_3$), δ 7.22 (m, 10, Ar*H*), 6.60 (q, 2, *J* = 2, 10 Hz, =CC*H*=), 5.73 (q, 2, *J* = 4, 10 Hz, =C*H*CH), 4.20 (q, 4, *J* = 7 Hz, OC*H*$_2$), 4.1 (m, 1, =CHC*H*CH=), 1.37 (s, 3, CC*H*$_3$), and 1.25 ppm (t, 6, *J* = 7 Hz, CH$_2$C*H*$_3$).

Anal. Calcd for $C_{27}H_{28}O_4$: C, 77.86; H, 6.78. Found: C, 77.58; H, 6.92.

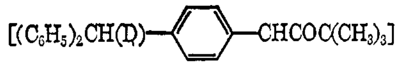
α-[4-(Diphenylmethylene)-2,5-cyclohexadienyl]-*cis*-1(Me),3(H),4(H)-1,8-dihydroxy-3-*p*-menthylmalonic Dilactone (19). Substitution of the dilactone **35** for the dipivaloylmethane in the above procedure for the preparation of **14** gave a solid product insoluble in ether. Using tetrahydrofuran instead of ether to separate the product from inorganic salt gave (after removal of solvent) a 66% yield of crude **19**, mp 150–160°. Two recrystallizations from chloroform–ether gave pure **19**: mp 167–170°; uv$_{\max}$ (CH_3OH) 313 mμ (ε 24,700 by extrapolation to zero time of a plot of ε *vs.* time, with ε decreasing about 10%/hr at room temperature); ir ($CHCl_3$) 1700 (shoulder, C=O) and 1731 cm^{-1} (C=O); nmr ($CDCl_3$), δ 7.32 (m, 10, Ar*H*), 6.72 (m, 2, =CC*H*=), 5.77 (m, 2, =C*H*CH), 4.75 (m, 1, =CHC*H*CH=), and 3.0–1.3 ppm (m, 17, dilactone).

Anal. Calcd for $C_{32}H_{32}O_4$: C, 79.97; H, 6.71. Found: C, 79.56; H, 6.57.

The three trienes **14**, **18**, and **19** could be stored indefinitely under nitrogen at −25° in the dark.

Rearrangement of the Triene 14 to the Triarylmethane 6. A. In CH_3OH. To 5 ml of dry methanol in a 6-ml glass-stoppered vial was added 0.064 g of sodium metal. To the resulting solution of sodium methoxide (0.56 *M*) in an atmosphere of nitrogen was added 0.20 g of the triene **14** (0.094 *M*). The stoppered vial was stirred magnetically at room temperature (~30°) for 4 hr (complete dissolution of reactant and product never took place). After cooling in ice, the product was collected at the filter, washed with 3 ml of cold (0–5°) methanol, and dried to give 0.18 g (90%) of the triarylmethane **6**, mp 179–181°. Ten integrations of the 5.63 (Ar$_3$C*H*) and 6.05 ppm (COC*H*CO) peaks in the nmr gave an average ratio Ar$_3$C*H*/COC*H*CO of 0.98 ± 0.05. This ratio remained unchanged after treating the triarylmethane **6** in 99% CH_3OD for as long as 18 hr under the above conditions.

B. In CH_3OD. Six runs were carried out in which CH_3OD (containing 0.99 atom of deuterium per molecule) was substituted for CH_3OH in the foregoing procedure and in which the amount of triene **14** used varied from 0.07 to 0.65 g. Yields of **6** varied from 83 to 92% and the nmr integration ratios, Ar$_3$C*H*/COC*H*CO, varied from 0.39 to 0.47 (average = 0.43). No trend in the ratio with changes in conditions was apparent. Several deuterated samples of **6** were treated with sodium methoxide in CH_3OH with no significant change in the ratio. Two deuterated samples of **6** containing 41 (sample 1) and 45% (sample 2) Ar$_3$CH by nmr, respectively, were analyzed by the combustion and falling-drop method (by J. Németh, Urbana, Ill.). Results gave 0.40 and 0.44 atom of deuterium corresponding to 60 and 56% Ar$_3$CH for samples 1 and 2, respectively. The same two samples were submitted to both low- (11.5 eV) and high-energy (70 eV) mass spectrometric analysis. Ratios of two pairs of peaks were used as indicators: *m*/*e* 426, 427 (parent) and 342, 343



$[(C_6H_5)_2CH(D)-C_6H_4-CHCOC(CH_3)_3]$

Both relative peak heights (h) of lower resolution spectra and relative peak areas (a) of high-resolution spectra were employed after making appropriate corrections (33.6% of 426 for 427 and 28.0% of 342 for 343) for the M + 1 peak of the nondeuterated species. Results (per cent of Ar$_3$CH) of a number of spectra of sample 1 were as follows: 426/427 (70 eV, h), 34, 35; 426/427 (11.5 eV, h), 34; 426/427 (11.5 eV, a), 34, 35, 32, 33; 342/343 (70 eV, h), 33, 35 (average = 34). Results (% Ar$_3$CH) for sample 2 were: 426/427 (70 eV, h), 31; 426/427 (11.5 eV, a), 32; 342/343 (70 eV, h), 33 (average = 32). Thus, although the mass spectrometry checks neither of the other two methods, it appears to be the most precise of the three. It seems safe to conclude that at least one-third of the rearrangement of **14** to **6** occurs intramolecularly.

Reaction of Diethyl and Di-*t*-butyl Malonates with Triphenylmethyl Fluoroborate. Di-*t*-butyl *p*-Benzhydrylphenylmalonate (20). A solution of sodio di-*t*-butyl malonate (0.0125 mol) in 40 ml of dimethylformamide prepared as in procedure A was treated with "aged" triphenylmethyl fluoroborate (0.014 mol) as described for the preparation of the triene **14**. Nothing could be crystallized from the cold (−25°) ether solution so the solvent was removed. The nmr spectrum of the residual orange oil showed the presence of the cross-conjugated triene system. It was dissolved in 75 ml of *t*-butyl alcohol previously saturated with potassium *t*-butoxide. After standing in the dark, under nitrogen at room temperature for a weekend, the solution was concentrated *in vacuo* to a volume of 20 ml and then poured into water. The precipitated oil was taken up in ether, washed with water, and dried ($MgSO_4$). Filtration followed by removal of the ether by distillation gave an orange oil that partially solidified. Trituration with pentane (10 ml), collection at the filter, and washing with more pentane gave crystals (1.10 g, mp 145–152°) that proved to be impure triphenylmethanol. Evaporation of the pentane from the filtrate gave 1.91 g (33%) of crude ester **20**, mp 108–113°. Three recrystallizations from Skellysolve B gave pure **20**: mp 120–121°; ir ($CHCl_3$) 1716 (ester C=O) and 1735 cm^{-1} (shoulder, C=O); nmr ($CDCl_3$), δ 7.23 (m, 14, Ar*H*), 5.53 (s, 1, Ar$_3$C*H*), 4.43 (s, 1, COC*H*CO), and 1.47 ppm (s, 18, CC*H*$_3$).

Anal. Calcd for $C_{30}H_{34}O_4$: C, 78.57; H, 7.47. Found: C, 78.87; H, 7.72.

When diethyl malonate was substituted for the corresponding *t*-butyl ester in the foregoing procedure (omitting the base-catalyzed rearrangement), the only product isolated in pure form (37% yield) was diethyl triphenylmethylmalonate (**32**), mp 132–134° (from ethanol), identical (mixture melting point, ir, and nmr spectra) with an authentic sample.[28] When the alkylation was carried out using triphenylmethyl chloride in DMF instead of the fluoroborate, **32** was obtained in 39% yield.

Spectrophotometric Determination of Triene Formation. The following procedure for the triene **14** was used to obtain the data of Table II. A solution of sodiodipivaloylmethane (0.00625 mol, from 1.15 g of dipivaloylmethane and 0.325 g of 50% sodium hydride) in 20 ml of dimethylformamide was prepared in the usual manner (procedure A). To this stirred solution (under nitrogen) was added 2.32 g (0.007 mol) of solid triphenylmethyl fluoroborate (aged) in one portion. The temperature rose from 26 to 33° in less than 5 min and became neutral to wet test paper. As soon as the reaction temperature began to decrease, 2 ml of the reaction mixture was pipetted into a 100-ml nitrogen-filled volumetric flask, and made up to volume with dry, deaerated methanol. Then exactly 5 ml of this solution was diluted to 100 ml with methanol in another volumetric flask. This solution (3.125×10^{-4} *M*, based on dipivaloylmethane) was immediately transferred to an 0.1-cm uv cell and the spectrum was scanned between 250 and 400 mμ. The time that elapsed from the addition of the fluoroborate (zero time) to the first uv scan (10–15 min) was noted. Then the scan was repeated three more times at 30-min intervals. In this way the absorbance could be extrapolated back to zero time. In two runs the extrapolated absorbances found (at uv$_{\max}$) were 0.500 and 0.528. Taking ε = 24,000 for the pure triene **14**, these values correspond to triene concentrations of 2.08 and 2.20×10^{-4} *M*, or yields of 67 and 70%, respectively, based on dipivaloylmethane. As a qualitative check on the uv absorption, the reaction mixture was concentrated to dryness *in vacuo* (1 mm), and the residue was separated from inorganic salt by dissolving it in ether. Removal of the ether in the usual way (N_2 and vacuum) gave a crude product which was analyzed by nmr spectroscopy. Relative intensities of the absorption due to the vinyl protons of the triene **14** were roughly proportional to the yield as determined by uv.

Table II summarizes the results of extending the foregoing procedure to other active methylene compounds. All reactions were exothermic (6–9° temperature increase) and proceeded to neutrality in less than 5 min. In some cases (especially the enolizable diketones) extraneous stable uv absorption, presumably from starting materials or enol ethers, interfered with the satisfactory estimation of triene. In these instances, when no nmr evidence for triene was detectable, yields were considered to be less than 5%. In two cases (**22** and **25**) triene nmr absorption could be detected only by integration in the expected range. Yields of 5–10% therefore were assigned to this borderline area. All other yields listed in Table II are based on the uv data, assuming ϵ = 24,000 for all trienes involved in this work.

Tri-*p*-tolylmethyl Fluoroborate. To a stirred solution of 15.12 g (0.05 mol) of tri-*p*-tolylmethanol in 50 ml of acetic anhydride, cooled to 3°, was added dropwise 8 ml (0.068 mol) of 48% fluoroboric acid. The temperature was not allowed to rise above 10°. After addition was complete, 120 ml of cold, dry ether was added to the dark green solution. Solvent was drawn off from the resulting precipitate through a sintered-glass filter tube, and fresh cold ether (50 ml) was added and again drawn off. After two more such washings with ether, the wet residue was partially dried with a stream of dry nitrogen and finally by evacuation (1 mm) for several hours. The yellow-brown product weighed 16.7 g and was used without further purification.

Reaction of Tri-*p*-tolylmethyl Fluoroborate with Sodiodipivaloylmethane. 4-(Tri-*p*-tolylmethyl)-2,2,6,6-tetramethyl-3,5-heptanedione (5). To a stirred solution of 0.00625 mole of sodiodipivaloylmethane (procedure A) in 20 ml of dimethylformamide (under nitrogen) was added 2.60 g (0.007 mol) of the crude tri-*p*-tolylmethyl fluoroborate. The temperature rose from 24 to 30° and the reaction mixture became neutral. Suitable dilution of a 2-ml sample with methanol followed by scanning of the uv spectrum in the 250–400-mμ region showed that less than a 3% yield of a cross-conjugated triene could have formed (assuming uv$_{\max}$ 305–315 mμ with ϵ 24,000). The reaction mixture was poured into water and extracted with ether. Washing with water followed by drying ($MgSO_4$) and removal of the ether by distillation gave a yellow glassy product (2.57 g) which was taken up in pentane (20 ml) and cooled at −25° for several days. Colorless prisms (0.48 g, 16%, mp 154–156°) that formed were removed by filtration and recrystallized from isopropyl alcohol (10 ml) to give pure **5**: mp 156–157°; ir ($CHCl_3$) 1675 (C=O) and 1712 cm^{-1} (C=O); nmr ($CDCl_3$), δ 7.25 (d, 6, J = 8 Hz, Ar*H*), 7.05 (d, 6, J = 8 Hz, Ar*H*), 6.25 (s, 1, COC*H*CO), 2.30 (s, 9, ArC*H*$_3$), and 1.07 ppm (s, 18, CC*H*$_3$).

Anal. Calcd for $C_{33}H_{40}O_2$: C, 84.57; H, 8.60. Found: C, 84.51; H, 8.57.

Application of the foregoing procedure to the dilactone **35** (in place of **26**) resulted in an exothermic (6°) neutralization reaction. However, uv analysis indicated less than 2% triene formation, and no other product could be isolated.

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The *gem* Effect. IV.[1] Activation Parameters Accompanying the Increased Steric Requirements of 3,3′ Substituents in the Solvolysis of Mono-*p*-bromophenyl Glutarates

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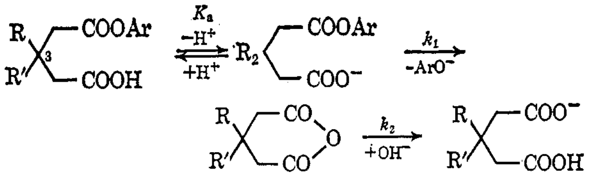
Abstract: The kinetics for the solvolyses of 11 *p*-bromophenyl 3-R- and 3,3′-R,R′-glutarate monoesters with R and R′ groups of differing steric requirements have been studied at several temperatures. The values of $\Delta H^{\ddagger}$ have been found, within experimental error, to be independent of the nature of R and R′ so that steric acceleration is reflected in $T\Delta S^{\ddagger}$. The values of $T\Delta S^{\ddagger}$ are in accord with intramolecular nucleophilic displacement of *p*-bromophenoxide by the carboxyl anion. An explanation is offered for the observed change of mechanism from intramolecular nucleophilic attack when a cyclic anhydride can be formed to intramolecular general base assisted attack of water when the cyclic anhydride cannot be formed.

In previous studies[1] we concluded that substituents in the 3 and 3,3′ positions of mono-*p*-bromophenyl glutarate esters increase the rate of hydrolysis by decreasing the population of extended conformations and thus bring the carboxylate and carbo-*p*-bromophenoxy moieties closer together. No special *gem* effect was noted and the logs of the rate constants for 3-R,3′-R-disubstituted esters were generally calculable from the sum of the log k_1 values for the 3-R- and 3′-R′-monosubstituted esters.



(1)

In the case of phenyl substituents, two different steric parameters were required depending upon whether the second substituent was large or small. This variable steric requirement of the phenyl group has found recent verification in another system.[3] In contrast to the kinetic data, the values of pK_a' for the 3-R- and 3,3′-

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(1) For previous papers in this series see: (a) T. C. Bruice and W. C. Bradbury, *J. Amer. Chem. Soc.*, **87**, 4838 (1965); (b) *ibid.*, **87**, 4846 (1965); (c) *ibid.*, **87**, 4851 (1965).

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(3) S. Sicsic and Z. Welvart, *Chem. Commun.*, 499 (1966).