[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LOYOLA UNIVERSITY]

The Anomalous Hunsdiecker Reaction. II. The Scope of the Reaction[1,2]

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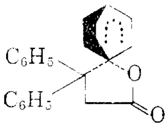
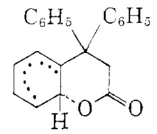
A number of β,β,β-triarylpropionic acids have been prepared and characterized. Their silver salts rearranged under Hunsdiecker reaction conditions to substituted acrylate esters in poor yield (under 20%) but in fair conversion (35–50%). Evidence is presented that these rearrangements proceed *via* a five-membered ring intermediate of the Ar_1-5 type. The effect of competition between phenyl and substituted phenyl groups in the rearrangement was also investigated.

The rearrangement of β,β,β-triphenylpropionic acid under Hunsdiecker reaction conditions was reported earlier from this laboratory.[2] There was found a surprising 53% carbon skeletal rearrangement[3] in addition to a 44% recovery of the original acid and 3% bromodecarboxylation, the normally expected Hunsdiecker reaction.[4] Migration of a phenyl group followed by elimination of the elements of hydrogen bromide yielded phenyl β,β-diphenylacrylate which, in the presence of excess bromine, gave largely its α-bromo derivative. The overall process, a 1,4-phenyl migration, was rationalized as occurring by an intramolecular process involving a five- or six-membered ring intermediate (Ar_1-5 or Ar_2-6 type, respectively[5]) possessing either phenonium ion or free radical characteristics, as shown below without specification as to the electronic nature of each. The earlier work indicated the Ar_1-5 intermediate to be the more likely, primarily from steric considerations. This instance of intramolecular ester formation by rearrangement was the first reported in the literature of the Hunsdiecker reaction, and it was felt of interest to investigate this rearrangement further, particularly to elucidate the ring size of the intermediate, the scope of the reaction, and its conditions.



Ar_1-5



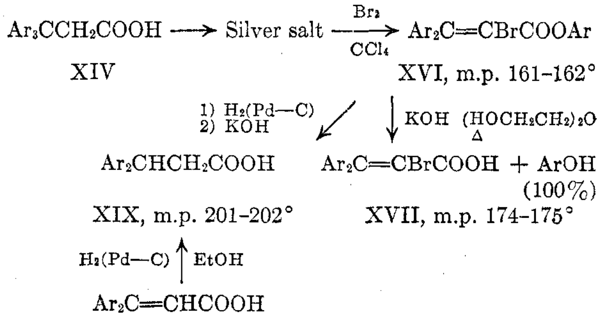
Ar_2-6

RESULTS

The first points, the ring size of the intermediate and the scope of the reaction, were determined by the placement of a substituent on one (or more) of the phenyl groups in the initial acid. Reaction by way of the Ar_1-5 spiro ring would keep the substituent in the same position relative to C-1 in the aromatic ring, while reaction *via* the Ar_2-6 intermediate would in effect isomerize the substituted aromatic ring. The pathway actually involved was easily decided by the isolation and identification of the phenol obtained by saponification of the ester product. The results are given in Table I. Other experiments were performed with the tris-substituted acids I, XIII, XIV, and XV in order to investigate the course of this reaction and the effect thereon of changing the various reaction conditions. The results of these attempts are listed in Table II.

In one reaction series the ester produced was isolated and characterized. The choice of the series using the tris-*p*-*t*-butyl acid (XIV) was occasioned by two considerations. First, a tris-substituted acid was chosen since the ester mixture likely to result would be less complex. Second, an acid that gave a fair yield in the process was chosen. Other than the parent acid I, which had been already investigated only XIV seemed appropriate for this portion of the study.

The rearrangement of XIV gave rise to a single ester (XVI) that was converted by hydrogenation and saponification to β,β-bis(*p*-*t*-butylphenyl)-propionic acid (XIX). The latter material was identical with that obtained by the hydrogenation of authentic β,β-bis(*p*-*t*-butylphenyl)acrylic acid (XVIII).[6] The ester (XVI) was also saponified to the α-bromo acid (XVII).



$$\begin{tikzcd}
\underset{\text{XIV}}{Ar_3CCH_2COOH} \arrow[r] & \text{Silver salt} \arrow[r, "Br_2", "CCl_4"'] & \underset{\text{XVI, m.p. 161-162°}}{Ar_2C{=}CBrCOOAr} \arrow[dl, "1)\ H_2(Pd{-}C)\ 2)\ KOH"'] \arrow[d, "KOH\ (HOCH_2CH_2)_2O\ \Delta"] \\
\underset{\text{XIX, m.p. 201-202°}}{Ar_2CHCH_2COOH} & & \underset{\text{XVII, m.p. 174-175°}}{Ar_2C{=}CBrCOOH + \underset{(100\%)}{ArOH}} \\
\underset{\text{XVIII, m.p., 198-199°}}{Ar_2C{=}CHCOOH} \arrow[u, "H_2(Pd{-}C)\ EtOH"] & &
\end{tikzcd}$$

Ar = *p*-*t*-butylphenyl

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[1] Taken from the doctoral dissertation of James L. Finnerty, S. J., Loyola University, February, 1960.

[2] Paper I, J. W. Wilt and D. D. Oathoudt, *J. Org. Chem.*, **23**, 218 (1958).

[3] Repeated attempts have not duplicated this higher yield; the rearrangement yield seems uniformly 20–23%, the recovered acid 50–70%.

[4] R. G. Johnson and R. K. Ingham, *Chem. Revs.*, **56**, 219 (1956).

[5] R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3105 (1957).

TABLE I

REARRANGEMENT OF MONOSUBSTITUTED β,β,β-TRIARYLPROPIONIC ACIDS (SILVER SALTS)

$X—C_6H_4(C_6H_5)_2CCH_2COOAg$

Code for Acid	X	Decarboxylation,[a] %	Rearrangement,[b] %	Phenol Composition[c]
I	H	3.2	22.0[d]	1.0
II	o-CH_3	5.9	9.5[e]	10.3
III	m-CH_3	2.8	12.4[e]	9.5
IV	p-CH_3	10.7 (5.3)[f]	8.7 (8.0)	1.9
V	p-$(CH_3)_3C$	6.1 (8.9)	7.6 (6.6)	0.64
VI	p-C_6H_5	3.5	[g]	—
VII	(C_4H_3)	Trace (6.8)	[h] (Trace)	—
VIII	p-CH_3O	2.2[i]	[j,k]	—
IX	p-F	2.4	12.3[e]	0.14
X	m-Cl	5.3	13.7[e]	0.55
XI	p-Cl	5.4	11.7[e]	0.29
XII	p-Br	10.4	13.7[d]	0.35

[a] Measured as carbon dioxide evolved (barium carbonate precipitation). An induction period of five to ten minutes was always noticed prior to any gas evolution. [b] Measured as total phenols produced by saponification of reaction product (infrared and v.p.c.). [c] Moles, relative to phenol; found as follows: wt.-% $X—C_6H_4OH$/wt.-% C_6H_5OH × mol. wt. C_6H_5OH/mol. wt. $X—C_6H_4OH$ × 2. [d] Average of two experiments. [e] Average of three experiments. [f] Values in parentheses were obtained when chlorine was used instead of bromine. [g] Bromination of reaction material made analytical techniques invalid. [h] Extensive degradation occurred. α-Naphthyldiphenylcarbinol (m.p. 133–138°) isolated. [i] Hydrogen chloride was evolved, so no barium carbonate was produced. [j] Only isolable product was an acid, m.p. 170–171°, presumably the monobromo derivative of VIII. Neut. equiv. Calcd. for $C_{22}H_{19}BrO_3$, 411. Found: 418. Zeisel test was positive. [k] A dichloro derivative of the initial acid VIII, presumably β-(3,5-dichloro-4-methoxyphenyl)-β,β-diphenylpropionic acid was isolated in 33% yield, m.p. (from alcohol) 207–208°. Neut. equiv. Calcd. for $C_{22}H_{18}Cl_2O_3$, 401. Found: 400, 407. *Anal.* Calcd.: C, 65.86; H, 4.52. Found: C, 65.77; H, 4.59. Only traces of phenols found on saponification of reaction product.

TABLE II

REARRANGEMENT OF TRIS-SUBSTITUTED β,β,β-TRIARYLPROPIONIC ACIDS (SILVER SALTS)

$(X—C_6H_4)_3CCH_2COOAg$

Code of Acid	X	Temp.	Time, Hr.	Solvent, Halogen	CO_2, %	Rearrangement,[a] %
I	H	25°	1 week	CCl_4,Br_2	[b]	21.7
		25–35°	2.5	CCl_4,Br_2	3.2	22.3
		25–70°	2.5	CCl_4,Cl_2	21	6.2
		25°	12	$C_6H_5NO_2,Br_2$	Trace	9.9
		0–25°	6	C_5H_5N,Br_2	7.6	Trace
XIII	p-CH_3	15–45°	0.75	CCl_4,Cl_2	Trace	1–2
XIV	p-$(CH_3)_3C$	25°	12	CCl_4,Br_2	1	21[c]
		77° (Reflux)	1.5	CCl_4,Br_2	13	7[d]
		−12–0°	3.5	CCl_4,Br_2	Trace	8[d]
XV	p-Cl	25°	2	CCl_4,Br_2	5	0

[a] Determined as the polybromo derivative of the phenol obtained from the reaction. [b] Not determined. [c] Based on isolated ester, see Experimental. [d] Based on *p-t*-butylphenol isolated upon saponification.

It is of importance that only *p-t*-butylphenol was isolated from the saponification of XVI as obtained directly from the reaction, *i.e.*, prior to any purification. No trace of isomeric phenols was found.

DISCUSSION

The point most clear from the present study is that *no ortho* shift results from this reaction. The isolation and/or identification of phenols solely with the position of the substituent retained was achieved in every instance where the reaction succeeded. Such a finding eliminates the Ar_2-6 mechanism and affords support for the Ar_1-5 mechanism previously put forward.[2] All attempts to increase aryl migration and the formation of ester were unsuccessful, and these experiments only indicated the reaction limits. While the complexity of these reactions and the low yield of esters obtained do not allow the phenol composition values to be regarded as meaningful "migration aptitudes," certain features seem worthy of mention. The values cover a relatively narrow range grouped about unity (0.1 to 10). Characteristically, radical proc-

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(6) This acid and its methyl ester were graciously supplied by Professor E. C. Kooyman of the University of Leiden, the Netherlands. These compounds were reported by H. Breederveld and E. C. Kooyman, *cf.* footnote *b* to Table VI.

TABLE III

TRIARYLMETHYLMALONIC ESTERS, PARENT AND MONOSUBSTITUTED

$X—C_6H_4(C_6H_5)_2CCH(COOC_2H_5)_2$

X	Yield, %	M.P.		Calcd.		Found	
		Obs.	Lit.	C	H	C	H
H	79	134–135°	132–133°[a]				
o-CH_3	72	112–113°	112–113°[b]				
m-CH_3	83	95–97°	99–100°[c]				
p-CH_3	72	72–73°	74–75°[b]				
p-$(CH_3)_3C$	82	113–114°	107–108°[d]				
p-F	80	123–124°		74.27	5.99	74.16	5.92
m-Cl	80	93–94°		71.47	5.77	71.61	5.94
p-Cl	85	110–111°		71.47	5.77	71.30	5.53
p-Br	78	110–111°		64.86	5.24	65.10	5.32

[a] G. G. Henderson, *J. Chem. Soc.*, **51**, 225 (1887). [b] See Ref. 12a. [c] See Ref. 12b. [d] See Ref. 12c.

TABLE IV

TRIARYLMETHYLMALONIC ESTERS, TRIS-SUBSTITUTED

$(X—C_6H_4)_3CCH(COOC_2H_5)_2$

X	Yield, %	M.P.	Calcd.		Found	
			C	H	C	H
p-CH_3	[a]	94.5–95°	78.35	7.26	78.55	7.11
p-Cl	76	114–115°	61.73	4.58	61.48	4.49

[a] Not determined.

esses show limited selectivity wherever evaluated.[7] In addition, the failure of nitrobenzene and pyridine (polar solvents resistant to ionic substitution) to assist the rearrangement indicated that increased solvent polarity did not facilitate the reaction, as one might expect were this process ionic. On the other hand, the known reactivity of these solvents in radical reactions[8] rationalizes their deleterious effect on this reaction if it be radical, since they could react in some fashion competitively with the rearrangement. While such considerations cast some doubt on our previous suggestion[2] that this reaction is ionic in nature, no compelling evidence was found in this study one way or the other.

The ease of rearrangement of the o-tolyl group in this reaction contrasts with the low migration ability obtained by McNeer[7] for this group in triarylmethyl peroxide decompositions. The difference, we feel, is primarily steric. The Wieland rearrangement is a 1,2-shift and the o-tolyl group usually is poor in such processes,[9] presumably because of steric crowding by the group in the transition state. The opposite situation apparently exists in this process, where the steric strain in the spiro intermediate can be shown by models to be less when the o-tolyl group migrates.[10] Apparently, steric features do not account for the curious values obtained for the m-and p-tolyl groups. p-Tolyl activation in either ionic or radical reactions is considerably greater than m-tolyl and the found values present an anomaly.

EXPERIMENTAL

All melting points were obtained on a calibrated Fisher-Johns block. Infrared spectra were obtained with a Perkin-Elmer model 21 Infrared Spectrophotometer, using a sodium chloride prism. The spectra of all solids were determined in potassium bromide pellets. The spectra of all phenols were determined in carbon disulfide solution.[11] The ultraviolet spectra were from a Beckman model DU instrument, manually operated. The vapor phase chromatograms were obtained with a Perkin-Elmer model 154C Vapor Fractometer with helium as the carrier gas and on a di-2-ethylhexyl sebacate column. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Triarylmethylmalonic esters. These compounds were synthesized by coupling the appropriate triarylmethyl chloride with ethoxymagnesiomalonic ester.[12a,b,c] The latter reagent was prepared from diethyl malonate (240 g., 1.5 moles), magnesium (36.4 g., 1.5 g.-atoms) and absolute ethanol (350 ml.). Since the reaction is highly exothermic, the magnesium and one-third of the malonic ester-ethanol solution were placed in a 1-l. reaction flask equipped with stirrer, condenser and addition funnel. A crystal of iodine and a

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(7) R. M. McNeer, dissertation, University of Chicago (1953). A referee has noted that migration aptitudes in some ionic processes, such as the deamination of β,β-diarylethylamines, are also crowded very close together.

(8) D. R. Augood and G. H. Williams, *Chem. Revs.*, **57**, 123 (1957).

(9) The reaction of o-tolyl Grignard with benzil is such a case, the product obtained resulting from migration of phenyl rather than o-tolyl in a benzilic acid type rearrangement. R. Roger and A. McGregor, *J. Chem. Soc.*, 442 (1934).

(10) See the dissertation of J. L. F., pp. 30–33.

(11) The spectra and v.p.c. data for the appropriate compounds are contained in the dissertation of J.L.F.

(12)(a) G. A. Holmberg, *Acta Acad. Abo. Math. et Phys.*, **16**, 138 pp. (1948). *Cf. Chem. Abstr.*, **45**, 558c (1951). (b) G. A. Holmberg, *Acta Acad. Abo. Math. et Phys.*, **17**, 14 pp. (1950). *Cf. Chem. Abstr.*, **46**, 6114i (1952) (c) G. A. Holmberg, *Acta Acad. Abo. Math. et Phys.*, **18**, 13 pp. (1952). *Cf. Chem. Abstr.*, **49**, 228g (1955).

TABLE V

β,β,β-TRIARYLPROPIONIC ACIDS, PARENT AND MONOSUBSTITUTED

$X—C_6H_4(C_6H_5)_2CCH_2COOH$

			M.P.		Calcd.		Found	
Code	X	Yield, %	Obs.	Lit.	C	H	C	H
I	H	64	180–181°	180°[a]				
II	o-CH_3	81	174–175°	174–175°[b]				
III	m-CH_3	51	117–118°	118–119°[c]				
IV	p-CH_3	80	196–197°	195–196°[b]				
V	p-$(CH_3)_3C$	81	170–171°	165–167°[d]				
VI	p-C_6H_5[e]	31	98°	100–101°[c]				
VII	(C_4H_3)[e]	45	234–235°	236–237°[c]				
VIII	p-CH_3O[e]	66	141–142°[f]	155–156°[c]	79.49	6.07	79.66	6.18
IX	p-F	50	164–165°		78.73	5.35	79.06	5.56
X	m-Cl	31	142–143°		74.88	5.09	75.05	5.02
XI	p-Cl	71	192–193°		74.88	5.09	74.70	5.19
XII	p-Br	78	180–181°		66.16	4.49	66.12	4.39

[a] L. Hellerman, *J. Am. Chem. Soc.*, **49**, 1738 (1927). [b] See Ref. 12a. [c] See Ref. 12b. [d] See Ref. 12c. [e] Prepared from triarylmethyl chloride without isolation of malonic ester intermediate. [f] Presumably a polymorph.

TABLE VI

β,β,β-TRIARYLPROPIONIC ACIDS, TRIS-SUBSTITUTED

$(X—C_6H_4)_3CCH_2COOH$

			M.P.		Calcd.		Found	
Code	X	Yield, %	Obs.	Lit.	C	H	C	H
XIII	p-CH_3	21[a]	233–234°		83.69	7.02	83.45	6.90
XIV	p-$(CH_3)_3C$[b]	58	249–250°	251–253°[b]				
XV	p-Cl	48[c]	192–193°		62.16	3.73	62.22	3.74

[a] Overall yield from triarylmethyl chloride. [b] Prepared by reaction of tris-(p-t-butylphenyl)carbinol with malonic acid in acetic anhydride according to the directions of H. Breederveld and E. C. Kooyman, *Rec. trav. chim.*, **76**, 297 (1957). [c] Yield of crude acid, of which only a part was purified.

few drops of carbon tetrachloride were added, gentle heating was applied until reaction began, and an ice bath was used to moderate the initial hydrogen evolution. Stirring was begun and controlled addition of the remaining malonic ester–ethanol solution was sufficient to maintain reflux. When the magnesium was consumed, the excess ethanol was removed by vacuum distillation and azeotropic distillation with benzene. There remained a solution of the reagent in benzene (425 ml.) which was kept in a graduated cylinder sealed from the atmosphere, under which condition it was stable. In preparing the substituted malonic esters, a benzene solution of the halide was added rapidly to an aliquot of the organomagnesium reagent. The mixture was stirred at reflux for 5 min., then stirred at 25° for 2–3 hr., during which time a variety of color changes occurred, ending in a pale green solution. After hydrolysis with dilute (10%) hydrochloric acid, the benzene layer was separated, washed and dried. Removal of the benzene by vacuum distillation left the ester which was readily crystallized from 95% ethanol. The esters and their properties are listed in Tables III and IV. The infrared spectra of these esters showed a split ester carbonyl in every case except the tris-p-chlorophenyl example. The separation was about 0.05–0.1 μ, with the peaks generally at 5.7–5.8 μ and 5.8–5.9 μ. This splitting is interesting, since malonic ester has normal carbonyl absorption.[13]

β,β,β-Triarylpropionic acids. In the general procedure, a solution, or rapidly stirred emulsion, of the ester, 95% ethanol (7–10 ml./g. ester) and an excess of aqueous potassium hydroxide (50%, 6 moles/mole ester) was refluxed for 5 hr. The solution was concentrated under reduced pressure, and the potassium salt was dissolved in warm water (1 l.). The addition of this solution to dilute (5%), cold hydrochloric acid (10 moles/mole ester) liberated the free acid. Recrystallization was effected from alcohol, although before successful crystallization in some of the preparations, the crude acid required heating to 200° to complete decarboxylation. Thus, acid II was so treated and the resulting plastic material taken up in dilute sodium hydroxide, a small amount of residue was removed by filtration, and upon reprecipitation with acid a readily recrystallized product was obtained. Acid X crystallized slowly and tended to oil out first. Also, the limited solubility of acid IV made a hot wash with alcohol preferable for purification of large quantities. Benzene (with acids III and XI) and benzene-petroleum ether (b.p. 30–60°) (with acid V) were successfully employed in crystallizations. Acid XIV was obtained best by boiling its sodium salt with concentrated hydrochloric acid. The analytical sample of acid XIII was material recovered from the Hunsdiecker reaction, as a persisting trace of potassium salt accompanied the isolation by the above methods. The properties of these acids are given in Tables V and VI.

Silver β,β,β-triarylpropionates. The silver salts were generally prepared by the dropwise addition of an equivalent amount of silver nitrate (10% in distilled water) to a hot, stirred solution of the sodium salt of the acid (1–5% in distilled water, pH adjusted to 7–8 with dilute (1:1) nitric acid). The suspension was stirred for 3–4 hr., protected from light. The white silver salts were filtered, washed with distilled water, and oven-dried at 80° for 48 hr. Ash analyses were performed, but the yield data are not corrected for the slight lack of purity in some of these salts.

Rearrangement of the silver salts. The reaction of the silver salts with bromine was carried out essentially as described earlier.[2] Ordinarily, no attempt was made to separate the esters produced, but rather the esters were saponified directly by refluxing an alcoholic (100 ml.) solution of the esters

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(13) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1954, p. 157.

with aqueous potassium hydroxide (50%, 5 moles/mole of initial silver salt) for 12 hr. In those instances in which chlorine was employed, the gas was bubbled slowly into the reaction mixture from a desk cylinder. These reactions were slower in starting, perhaps due to less intimate contact between reactants. Pertinent data are given in Tables I and II.[14]

Isolation and analysis of the phenols. Three methods were used to obtain the phenols quantitatively from the saponifications. Each method involved removal of the solvent (alcohol) by distillation, acidification of the phenoxides with dilute hydrochloric acid, steam distillation, or codistillation with water of the liberated phenols, and, finally, extraction of the distillate to obtain the carbon disulfide solutions of the phenols for infrared and v.p.c. analysis. No detailed examination of the rest of the saponified material was done, although the residues were soluble in base and gave initial acid (50–70% recovery) upon acidification. The identity of this recovered acid was established in all but a few runs. The distillations were continued in these isolations until negative bromine-water tests were obtained. The aqueous distillation residues were also so checked. The aqueous solutions of the phenols were then saturated with salt and extracted with an organic solvent until the water layer gave a negative bromine water test. In one method, ether was the extractant. The ethereal extract was dried, concentrated, and the ether replaced by carbon disulfide via distillation to 45°. In the other methods, the phenol solution was made alkaline again and redistilled, followed by isolation again as before, in one case by repeated extraction with small volumes of carbon disulfide or, in the other and best method, by day-long continuous extraction. Control experiments on standard solutions of various phenols, using the methods given, indicated isolation yields of better than 98%, well within the limits of accuracy of this work.

Standard mixtures of the phenols expected from each run were prepared and their infrared and v.p.c. characteristics determined. Absorbances (log 1/T) were calculated for a characteristic peak of each phenol in each standard mixture. The ratio of absorbances of the phenols were plotted against the wt.% of the phenols, giving excellent linearity in all cases. The reaction phenol mixture was then examined in the infrared and the ratio of characteristic absorbances determined. From the graph, the percentage composition was readily evaluated. The same standard-width sample cell was used throughout. Vapor phase chromatographic analyses were performed by the ratio of areas method, the peaks being integrated by both planimeter and half-width techniques. The column length was 1 meter, the temperature 180°.

Rearrangement of β,β,β-tris(p-butylphenyl)propionic acid (XIV), *silver salt.* Dry bromine (6.4 g., 0.04 mole) in dried carbon tetrachloride (10 ml.) was added in 1 hr. at 25° to a stirred suspension[15] of the silver salt of XIV (purity 93%, 23 g., 0.04 mole) in carbon tetrachloride (30 ml.), employing a nitrogen sweep as before.[2] After 30 min., a paste resulted. Carbon dioxide evolved was slight (1%). After standing overnight, the reaction was worked up as is customary,[2] giving recovered acid (13.4 g., 71.1%, m.p. 245–247°). A golden semisolid was also obtained which, on trituration with alcohol, gave a white solid (4.5 g., 21%) which was an ester (hydroxamic acid test) containing bromine (Beilstein test). A portion was recrystallized from alcohol, m.p. 161–162°, and subsequent work indicated this material to be *p-t*-butylphenyl α-bromo-β,β-bis(*p-t*-butylphenyl)acrylate (XVI).

Anal. Calcd. for $C_{33}H_{39}BrO_2$: C, 72.39; H, 7.16. Found: C, 72.85; H, 7.03.

The infrared spectrum showed C=O (5.7 μ, strong), C=C (6.05 μ, very weak), and an quartet of peaks in the 11.5–12 μ region, among others. All features of the spectrum were consistent with the proposed structure. The ultraviolet spectrum showed a λ_{max}^{alc} 289 mμ (ε 8920) with λ_{min}^{alc} 282.5 μ (ε 8300). Similar spectra were noted for the compounds obtained in the earlier study.[2]

The remainder of the crude ester was saponified and worked up to give exclusively *p-t*-butylphenol (m.p. and mixture m.p. 98–99°) as the phenolic component. The acid portion was investigated as follows.

α-Bromo-β,β-bis(p-t-butylphenyl)acrylic acid (XVII). XVI (0.45 g., 0.8 mmole, m.p. 161–162°) was saponified at 130–140° for 3–4 min. with potassium hydroxide (0.6 g.) in diethylene glycol (10 ml.). Water (10 ml.) was added to the cooled mixture and the flakes of the potassium salt of XVII collected. Acidification and steam distillation of the filtrate gave *p-t*-butylphenol (0.12 g., 100%, m.p. 98°). Acidification of the potassium salt of XVII gave the acid as a white solid. Two recrystallizations from water-alcohol gave flakes, m.p. 174–175°.

Anal. Calcd. for $C_{23}H_{27}BrO_2$: C, 66.51; H, 6.55. Found: C, 66.71; H, 6.68.

The infrared spectrum was consistent with this structure. The C=O absorption was at 5.95 μ.

β,β-Bis(p-t-butylphenyl)propionic acid (XIX). XVI (0.41 g., 0.75 mmole, m.p. 161–162°) was shaken in a mixture of absolute ethanol (50 ml.), sodium hydroxide (0.5 g.) and palladium on charcoal (10%, 0.5 g.) under 1 atm. of hydrogen for 16 hr. The mixture was neutralized, freed from catalyst, and the ethanol evaporated. Extraction with ether followed. The ester remaining after removal of the ether was saponified as described for ester XVI, giving XIX as a white crystalline solid, m.p. 201–202°.

Anal. Calcd. for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.39; H, 9.03.

The infrared spectrum showed the absence of non-aromatic unsaturation, with C=O (5.8 μ, strong), OH (2.8–3.0 μ, broad), and C—CH_3 (7.3 μ) prominent. Authentic XIX was prepared by the hydrogenation of acid XVIII (palladium on charcoal, 2 atm. hydrogen, 2 hr., quantitative). The acid from this source had a m.p. 201–202° and the mixture melting point of this sample and the material from XVI was undepressed.

β-(p-t-Butylphenyl)-β-phenylacrylic acid. In the course of this work, this acid was synthesized. Since a new intermediate was prepared, the synthesis is recorded briefly at this time. *p-t*-Butylbenzophenone was prepared (75.5%, b.p. 168–170° at 2 mm., lit.[16] b.p. 132–134° at 0.1 mm.). This ketone and ethyl bromoacetate (8.35 g., 0.05 mole) with mossy zinc (3.26 g., 0.05 mole) gave, in a straightforward Reformatsky reaction, ethyl β-hydroxy-β-(*p-t*-butylphenyl)-β-phenylpropionate (flakes, m.p. 84°, 4.3 g., 29%).

Anal. Calcd. for $C_{21}H_{26}O$: C, 77.26; H, 8.03. Found: C, 77.33; H, 8.15.

The infrared spectrum possessed an OH peak at 2.9 μ (sharp, strong). Dehydration and saponification of this ester by the method of Fuson[17] gave the substituted acrylic acid in poor yield (10%, m.p. 171–173°, lit.[18] m.p. 178°).

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[14] For data on the thirty-odd reactions performed, the dissertation of J.L.F. should be consulted.

[15] The silver salts of most of the acids studied were soluble in carbon tetrachloride; the salt of XIV, however, was not.

[16] F. Bergmann and J. Szmuskowicz, *J. Am. Chem. Soc.*, **70**, 2748 (1948).

[17] L. L. Alexander, A. L. Jacoby, and R. C. Fuson, *J. Am. Chem. Soc.*, **57**, 2208 (1935).

[18] F. Bergmann, M. Weizmann, E. Dimant, J. Patai, and J. Szmuskowicz, *J. Am. Chem. Soc.*, **70**, 1612 (1948).