Anal. Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 93.30; H, 6.91.

From these results we concluded that the fraction consisted perhaps of a mixture of 1,2,3,4,1′,2′,3′,4′- (or 1,2,3,4,5′,6′,7′,8′) - octahydro - 2,2′ - binaphthyl and 1,2,3,4-tetrahydro-2,2′-binaphthyl in nearly equal quantities.

Summary

1. The Friedel–Crafts reaction of 1,4-dibromo-2-butene with benzene yielded tetralin as well as 2-phenyl-1,2,3,4-tetrahydronaphthalene.
2. 1,4-Dihydronaphthalene was found to change into naphthalene and tetralin in the presence of aluminum chloride.
3. An analogous reaction was observed also in the case of 1,2-dihydronaphthalene.

KYÔTO, JAPAN RECEIVED APRIL 29, 1947

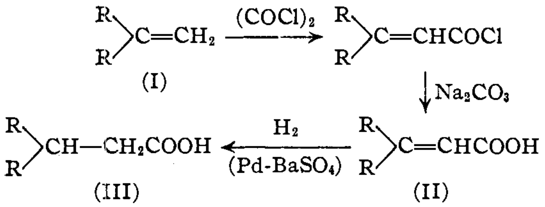
CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE AND THE DEPARTMENT OF ORGANIC CHEMISTRY OF THE HEBREW UNIVERSITY, JERUSALEM]

β,β-Diarylacrylic Acids.[1] I. Synthesis and Properties of Symmetrical and Unsymmetrical β,β-Diarylacrylic Acids.

BY FELIX BERGMANN, MOSHE WEIZMANN, ELCHANAN DIMANT,[1] JOSEF PATAI[1] AND JACOB SZMUSKOWICZ

The reaction of 1,1-diphenylethylene with oxalyl chloride to form β,β-diphenylacrylyl chloride was discovered by Kharasch and co-workers.[2] As part of a program on the investigation of diarylethylenes, we have applied this reaction to a series of symmetrically and unsymmetrically substituted diphenylethylenes (I).

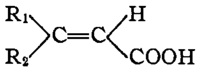
The reaction was found to be a general one; by the use of excess oxalyl chloride (3 to 5 moles) and subsequent hydrolysis of the acid chloride produced, nearly quantitative yields of β,β-diarylacrylic acids (II) were obtained. The application of the reaction to a group of symmetrical and unsymmetrical 1,1-diarylethylenes is summarized in Tables I and II. The corresponding β,β-diarylpropionic acids (III) were easily accessible by catalytic hydrogenation of the acrylic acids (Table III).

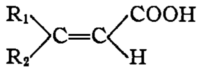


The speed of reaction was markedly influenced by the substituents present in the phenyl groups. 1,1-Di-(*p*-anisyl)-ethylene (I,3) reacted completely at room temperature within a half hour, 1,1-diphenylethylene (I,1) had to be refluxed with oxalyl chloride for about two hours, and 1,1-di-(*p*-bromophenyl)-ethylene (I,6) required about eighteen hours for completion of the reaction. The susceptibility of dianisylethylene to substitution by the —COCl group was so great that phosgene in boiling benzene converted it to the dianisylacrylic acid.

The electronic influence of the substituents also influenced the uncatalyzed decarboxylation of the diarylacrylic acids: while the β,β-diphenylacrylic acid (II,1) was stable at 200° and suffered only very slow decarboxylation at 250°, the β,β-di-(*p*-anisyl)-acrylic acid (II,3) was slowly decarboxylated by boiling a solution of it in acetic acid or even by boiling its aqueous suspension. The β-phenyl-β-*p*-anisylacrylic acid was intermediate in stability; carbon dioxide was eliminated from it at about 200°. These results give an explanation of the observation of Bergmann and Bondi[3] that dianisylethylene does not yield a phosphinic acid with phosphorus pentachloride.

When unsymmetrical 1,1-diarylethylenes were refluxed with oxalyl chloride and the mixture hydrolyzed, the two possible isomers (IIα and IIβ) were obtained in most cases.


(IIα)


(IIβ)

The use of a large excess of the chloride produced this mixture in good yields, but unavoidable losses during the laborious separation procedures permitted only an approximate estimate of the relative proportion of the two isomers (Table II).

1-Phenyl-1-(*p*-fluorophenyl)-ethylene (I,8) gave rise to a single form of β-phenyl-β-(*p*-fluorophenyl)-acrylic acid (II,8) in nearly quantitative yield; 1-(*p*-tolyl)-1-(*p*-fluorophenyl)-ethylene (I, 11) likewise yielded only one form of the corresponding acid (II,11). On the other hand, the *p*-chloro and *p*-bromo derivatives (II,9 and II,10) were obtained as nearly equimolar, sharply melting mixtures of the two isomers. Resolution of each mixture into the individual isomers showed that the individual melting points lay close to each other and were both higher than that of the mixture.

---

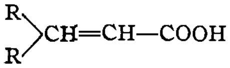
[1] Part of theses submitted to the Hebrew University, Jerusalem 1947, by Elchanan Dimant and Josef Patai.

[2] Kharasch, Kane and Brown, THIS JOURNAL, **64**, 333 (1942).

[3] E. Bergmann and Bondi, *Ber.*, **63**, 1158 (1930); *ibid.*, **64**, 1455 (1931); *cf.* also Kosolapoff and Huber, THIS JOURNAL, **68**, 2540 (1946).

TABLE I

SYMMETRICAL β,β-DIARYLACRYLIC ACIDS (II)



$\begin{matrix}\mathrm{R}\\ \mathrm{R}\end{matrix}\!\!>\!\mathrm{CH{=}CH{-}COOH}$

No.	R	Ratio ethylene to oxalyl chloride	Reaction period, hrs.	Yield, %	Melting point, °C.	Recrystallized from	Crystal form	Formula	Composition, % Calcd. C	Composition, % Calcd. H	Composition, % Found C	Composition, % Found H
1	Phenyl[a]	1:5	2	95[b]	167	Acetic acid	....	....	..	..	..	...
2	*p*-Tolyl[c]	1:3	5	80	174[d]	Benzene–petr. ether	Flat needles	$C_{17}H_{16}O_2$	81.0	6.35	81.2	6.5
3	*p*-Anisyl[e]	1:3	0.5	75	142	Benzene	Flat prisms	$C_{17}H_{16}O_4$	71.8	5.6	71.9	5.6
4	*p*-Fluorophenyl	1:3	3	70	147	Benzene–petr. ether	Rhombic plates	$C_{15}H_{10}F_2O_2$	69.2	3.8	69.0	4.1
5	*p*-Chlorophenyl	1:5	12	55	175	Benzene–petr. ether	Prismatic rods	$C_{15}H_{10}Cl_2O_2$	61.4	3.4	61.7	3.6
6	*p*-Bromophenyl	1:5	18	35	190–191	Dil. ethanol	Needles	$C_{15}H_{10}Br_2O_2$	47.1	2.6	47.0	2.9
7	α-Naphthyl	1:10	4	75	218	Dil. acetic acid	Plates	$C_{23}H_{16}O_2$	85.2	4.9	85.1	4.7

[a] The anisidide of this acid, prepared from the acid chloride and two equivalents of *p*-anisidine in ether solution, crystallized in white needles, m. p. 163°. *Anal.* Calcd. for $C_{22}H_{19}NO_2$: C, 80.2; H, 5.8; N, 4.3. Found: C, 80.1; H, 6.0; N, 4.5. [b] Kharasch (ref. 2) obtained a 50% yield from equimolar proportions of the two reactants. [c] The anisidide, prepared as above, crystallized from methanol in colorless needles, m. p. 153°. *Anal.* Calcd. for $C_{24}H_{23}NO_2$: N, 3.9. Found: N, 4.0. [d] Bergmann, Hoffmann and Meyer, *J. prakt. Chem.*, **135**, 245 (1932), reported a melting point of 168–170°. [e] The melting point of the acid (142°) was almost identical with that of 1,1-di-(*p*-anisyl)-ethylene (141–142°), Linnel and Shaikmahamud, *Quart. J. Pharm. Pharmacol.*, **14**, 64 (1941); *C. A.*, **35**, 6252 (1941). A mixture of the ethylene and the corresponding acid was depressed to 115–120°. Keeping the acid at its melting point converted it to the ethylene.

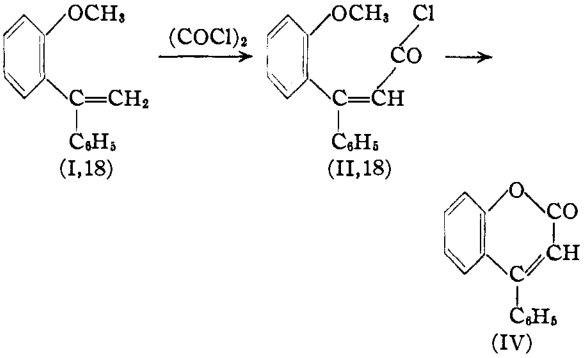
Except for 1-phenyl-1-(*p*-tert-butylphenyl)-ethylene (I,15), the *p*-alkyldiphenylethylenes produced both forms of the acids (II,12; II,13 and II,14). One of the *t*-butyl isomers, m. p. 178°, was isolated in pure form as needles. What may have been the second isomer, recognized by its rod-like crystals, could not be purified satisfactorily because it changed to the first isomer during recrystallization. No decision was made whether the two forms represented dimorphic modifications or whether one of the isomers was unstable.

The β-phenyl-β-(*p*-tolyl)-acrylic acid (II,12) has been described by v. Braun,[4] who prepared it by a Reformatsky reaction and reported the melting point as 140°. This is the melting point which we observed for an equimolar mixture of the two isomers (m. p. 172° and 159°) and constitutes clear evidence that the Reformatsky reaction may yield an isomeric mixture.

The question of formation of isomeric acids in Reformatsky's reaction cannot yet be answered satisfactorily. In the way the reaction is carried out by Natelson and Gottfried,[5] an ester of substituted β-chloropropionic acid is always the intermediate. An analogous intermediate, *i. e.*, the chloride of a substituted β-chloropropionic acid, could be formed in the oxalyl chloride reaction if addition to the double bond were the primary step. There is, however, another possibility, *viz.*, that the COCl— group directly substitutes hydrogen at the terminal carbon atom of a diarylethylene. The basic assumption for further work on the mechanism of these two reactions must, therefore, be that identical results point to identical reactions mechanisms, whereas a difference in the reaction products would indicate a different course for Kharasch's reaction.

1-Phenyl-1-(*p*-anisyl)-ethylene (I,17) yielded a mixture of isomeric acids which were both obtained in pure form. However, the lower-melting form appeared to be unstable and to pass into the higher-melting acid upon prolonged heating in organic solvents. In general, *para* substituents with a very strong mesomeric effect, such as methoxyl or fluorine, brought about a fast reaction and favored the formation of one isomer over the other.

β-Phenyl-β-(*o*-anisyl)-acrylic acid (II,18) was isolated in small yield; however, if the reaction time was doubled, 4-phenylcoumarin (IV) was produced in about 60% yield. The reaction, in this case, paralleled exactly the observations of Stoermer[6] concerning the dealkylating action of acetyl chloride or phosphorus pentachloride on the acid.



From the ethylenes containing higher aromatic systems (I,19, I,21 and I,22) approximately equal

---

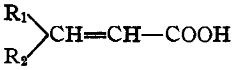
(4) v. Braun, Manz and Reinsch, *Ann.*, **468**, 277 (1929).

(5) Natelson and Gottfried, THIS JOURNAL, **61**, 970 (1939).

(6) Stoermer and Friderici, *Ber.*, **41**, 324 (1908); Heilbron, Hill and Walls, *J. Chem. Soc.*, 1701 (1931).

TABLE II

UNSYMMETRICAL β,β-DIARYLACRYLIC ACIDS (II)

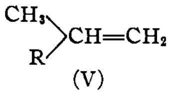


$$R_1R_2C{=}CH{-}COOH$$

No.	R_1	R_2	Ratio ethylene to oxalyl chloride	Reaction period, hrs.	Method of separation[a]	Yield, %		Melting point, °C.	Mixed m. p. of isomers
8	Phenyl	*p*-Fluorophenyl	1:2	4	C	85		151–152	...
9	Phenyl	*p*-Chlorophenyl[b]	1:3	30	C	Total	90–95		140
						α	40–45	172	
						β	50–55	165–166	
10	Phenyl	*p*-Bromophenyl	1:3	30	C, D	Total	90		147
						α	45	175	
						β	45	169–170	
11	*p*-Tolyl	*p*-Fluorophenyl	1:3	6	C	74		145	...
12	Phenyl	*p*-Tolyl[c]	1:3	20	C	Total	80		140
						α	..	172	
						β	..	159	
13	Phenyl	*p*-Ethylphenyl	1:3	25	D				118
						α	..	173–174	
						β	..	135	
14	Phenyl	*p*-Isopropylphenyl	1:3	20	D	Total	90		123
						α	..	156–157	
						β	..	152	
15	Phenyl	*p*-Butylphenyl	1:3	20	C				...
						α	..	178	
						β	..	(?)	
16	Phenyl	*p*-Cyclohexylphenyl	1:2	10	..	...		190	
17	Phenyl	*p*-Anisyl	1:3	1	A	Total	95		115–120
						α	43	181	
						β	(?)	132–133	
18	Phenyl	*o*-Anisyl	1:3	5[d]	C	...		151[e]	
19	Phenyl	*p*-Xenyl	1:3	45	C	Total	95		...
						α	56	245	
						β	31	194	
20	Phenyl	α-Naphthyl	1:3	8	C	Total	70–75		...
						α	3	222–223[f]	
						β	63	165	
21	Phenyl	β-Naphthyl	1:3	4	B, C	Total	90		...
						α	39	225–226[g]	
						β	33	175	
22	Phenyl	9-Phenanthryl	1:3	20	B	Total	80		200
						α	∼20	221–222	
						β	∼20	206	

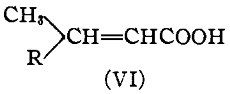
proportions of the isomeric acids were obtained. 1-Phenyl-1-(α-naphthyl)-ethylene (I,20) gave only a very small amount of the high-melting isomer, m. p. 222°. This was in sharp contrast to the result obtained when the acid was made by the Reformatsky reaction, which has been found by various investigators to yield only the high-melting isomer.[7]

The oxalyl chloride reaction was applied to a series of 1-methyl-1-arylethylenes (V) but in no case were two isomeric β-arylcrotonic acids (VI) isolated. Yields were low and the method was inferior to the Reformatsky preparation of these acids (Table IV).



$$(CH_3)RC{=}CH_2$$

(V)



$$(CH_3)RC{=}CHCOOH$$

(VI)

When it was hydrogenated, β-phenyl-β-(*p*-chlorophenyl)-acrylic acid (II,9) absorbed about 150% of the calculated amount of hydrogen and produced a mixture of neutral and acidic products. The neutral substance was identified as 1,1-diphenylethane; the acidic portion yielded about 23% of β,β-diphenylpropionic acid and about 16% of the expected β-phenyl-β-(*p*-chlorophenyl)-propionic acid (III,9).

Similar results were obtained with β,β-di-(*p*-chlorophenyl)-acrylic acid (II,5). In this case

---

[7] Pirrone, *Chem. Centr.*, **105**, II, 2078 (1934), claims to have evidence for the formation of both isomers of II, 20—although not isolated—in the dehydration of ethyl β-phenyl-β(1-naphthyl)-β-hydroxypropionate. This claim is based on the conversion of the hydroxy ester into a mixture of two indones. However, both of the indones are derived from the same (α-) form of acid II,20. De Fazi, *Gazz. chim. ital.*, **49**, I, 242 (1919); Lipkin and Stewart, THIS JOURNAL, **61**, 3295 (1929).

TABLE II (*Continued*)

Recrystallized from	Crystal form	Formula	Composition, %			
			Calcd.		Found	
			C	H	C	H
Benzene	Polyhedric prisms	$C_{16}H_{11}FO_2$	74.4	4.5	74.6	4.8
Acetic acid	Prismatic plates	$C_{15}H_{11}ClO_2$	69.8	4.3	70.0	4.4
Benzene–petr. ether	Needles				69.6	4.3
Acetic acid	Prisms	$C_{15}H_{11}BrO_2$	59.4	3.6	59.4	3.9
Acetic acid	Rods				59.8	3.6
Benzene–petr. ether	Needles	$C_{16}H_{13}FO_2$	75.0	5.1	74.7	4.9
Benzene–petr. ether	Flat prisms	$C_{16}H_{14}O_2$	80.7	5.9	80.4	6.0
Benzene–petr. ether	Prismatic columns				80.5	6.0
Benzene–petr. ether	Twinned prismatic rods	$C_{17}H_{16}O_2$	80.95	6.35	80.85	6.3
Benzene–petr. ether	Needles				80.8	6.4
Acetic acid	Prismatic plates	$C_{18}H_{18}O_2$	1.2	6.8	81.5	7.1
Dilute acetic acid	Needles				81.6	7.0
Benzene–petr. ether	Prismatic needles	$C_{19}H_{20}O_2$	81.4	7.1	81.3	7.4
Acetic acid	Rods				..	..
Butyl acetate–petr. ether	Clusters of rods	$C_{21}H_{22}O_2$	82.4	7.2	82.2	7.4
Benzene–petr. ether	Pointed prisms	$C_{16}H_{14}O_3$	75.6	5.5	75.7	5.6
Benzene–petr. ether	Needles				..	...
Benzene–petr. ether	Twinned prisms	....	...	..	..	...
Butyl acetate	Scales	$C_{21}H_{16}O_2$	84.0	5.3	84.3	5.6
Butyl acetate	Prisms	$C_{21}H_{16}O_2$	84.0	5.3	84.1	5.5
Isopropanol	Prismatic rods	$C_{19}H_{14}O_2$	83.2	5.1	83.0	4.8
Dilute ethanol	Needles	$C_{19}H_{14}O_2$	83.2	5.1	83.4	5.3
Butyl acetate	Elongated plates	$C_{19}H_{14}O_2$	83.2	5.1	83.2	5.1
Benzene–petr. ether	Pointed rods	$C_{19}H_{14}O_2$	83.2	5.1	..	...
Xylene	Yellow-brown prisms	$C_{23}H_{16}O_2$	85.2	4.9	85.6	5.1
Xylene	Pale-yellow rods	$C_{23}H_{16}O_2$	85.2	4.9	85.2	5.2

[a] Various methods of separation are described in the Experimental Part. [b] Alexander, Jacoby and Fuson, THIS JOURNAL, 57, 2208 (1935), describe one form of this acid, prepared by Reformatsky's method, with a melting point of 168°. Prof. Fuson kindly compared both isomers with his preparation and found our α-form to be identical with his. [c] Compare ref. 4. [d] After ten hours of reflux a neutral substance was isolated which crystallized from benzene–petroleum ether in prismatic plates, m. p. 104–105°. It was identical with 4-phenylcoumarin. *Anal.* Calcd. for $C_{15}H_{10}O_2$: C, 81.1; H, 4.5. Found: C, 80.9; H, 4.4. [e] Stoermer (ref. 5) reported a melting point of 153°. [f] Compare ref. 6. Proof of structure of this isomer was given by Koelsch, *J. Org. Chem.*, **6**, 558 (1941), who cyclized it to perinaphthindone. [g] v. Braun (ref. 4) gave the melting point as 217°

the neutral portion was 1,1-di-(p-chlorophenyl)-ethane with probably a small amount of diphenylethane. The only acid obtained was β,β-di-(p-chlorophenyl)-propionic acid.

These observations indicated that partial decarboxylation occurred, probably under the influence of hydrochloric acid which was formed by catalytic dehalogenation of the aromatic ring. This was surprising since the p-chlorophenyl-substituted acids have been found to be stable even under the influence of boiling hydrochloric acid. It is also remarkable that the chlorine atoms in the dichloro acid and in the dichloroethane appeared to be much more stable than the corresponding monochloro derivatives.

Experimental[8]

Synthesis of 1,1-Diarylethylenes (I) and 1-Methyl-1-aryl-methylenes (V).—Most of the ethylenes were prepared as described in earlier papers of this series[9] or else-

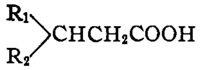
---

[8] All melting points are uncorrected.

[9] Bergmann, Szmuszkowicz and Fawaz, THIS JOURNAL, **69**, 1773 (1947); Szmuszkowicz and Bergmann, *ibid.*, **69**, 1779 (1947); Bergmann and Szmuszkowicz, *ibid.*, in press.

TABLE III

β,β-DIARYLPROPIONIC ACIDS (III)



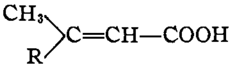
$$\begin{matrix} R_1 \diagdown \\ R_2 \diagup \end{matrix} CHCH_2COOH$$

No.	R_1	R_2	Melting point, °C.	Recrystallized from	Crystal form	Formula	Composition, % Calcd. C	Calcd. H	Found C	Found H
1	Phenyl[a]	Phenyl	157	Benzene–petr. ether	Prismatic rods	$C_{15}H_{14}O_2$	..	..	..	...
2	*p*-Tolyl[b]	*p*-Tolyl	188	Alcohol	Prismatic rods	$C_{17}H_{18}O_2$	..	..	..	...
3	*p*-Anisyl[c]	*p*-Anisyl	138–139	Benzene–petr. ether	Needles	$C_{17}H_{18}O_4$	71.3	6.3	71.0	6.5
4	*p*-Fluorophenyl[d]	*p*-Fluorophenyl	108–109	Petroleum ether	Long lancets	$C_{15}H_{12}F_2O_2$	68.7	4.6	68.4	4.6
5	Phenyl	*p*-Fluorophenyl	118	Benzene–petr. ether	Twinned, pointed plates	$C_{15}H_{13}FO_2$	73.8	5.3	74.0	5.4
6	Phenyl	*p*-Chlorophenyl	108	Petroleum ether	Pointed prisms	$C_{15}H_{13}ClO_2$	69.2	5.0	69.4	5.2
7	*p*-Tolyl	*p*-Fluorophenyl	138–139	Petroleum ether	Long rods	$C_{16}H_{15}FO_2$	74.4	5.8	74.7	6.0
8	Phenyl	*p*-Tolyl	144	Acetic acid	Prismatic rods	$C_{16}H_{16}O_2$	80.0	6.7	79.8	6.7
9	Phenyl[e]	*p*-Anisyl	122	Dilute acetic acid	Prismatic rods	$C_{16}H_{16}O_3$	75.0	6.25	74.8	6.3

[a] Ejkman, *Chem. Zentr.*, **79**, II, 1100 (1908); see also Simons and Archer, THIS JOURNAL, **61**, 1521 (1939). [b] This acid was originally reported by Bergmann (Table I, footnote *d*) to melt at 163–164°. Our findings, however, are in agreement with the melting point reported by Cope, THIS JOURNAL, **56**, 721 (1934). [c] Two "isomeric" β,β-di-(*p*-anisyl)-acrylic acids were described by Vyas and Bokil, *Rasayanam*, **1**, 195 (1939); *C. A.*, **34**, 5067 (1940). One of m. p. 141–142°, made by saponification and decarboxylation of the methyl chloride–ethyl sodiomalonate condensation product, was identical with our acid. The other, m. p. 160–161°, was obtained from anisole and acetonedicarboxylic acid. The constitution of the latter acid is now under investigation. [d] Hydrogenated in methanol. [e] Fosse, *Ann. chim.* **13** 105 (1920); Baillon, *ibid.*, **15**, 61 (1921).

TABLE IV

β-ARYLCROTONIC ACIDS (VI)



$$\begin{matrix} CH_3 \diagdown \\ R \diagup \end{matrix} C{=}CH{-}COOH$$

No.	R	Ratio ethylene to oxalyl chloride	Reaction period, hrs.	Yield, %	Melting point, °C.	Recrystallized from	Crystal form	Formula	Composition, % Calcd. C	Calcd. H	Found C	Found H
1	Phenyl[a]	1:6	..	40	97	....	.....	.....	..	...	..	...
2	*p*-Xenyl	1:2	4.5	5.5	199	Dilute ethanol	Plates	$C_{16}H_{14}O_2$	80.7	5.9	80.6	5.9
3	α-Naphthyl[b]	1:4	14	..	...	....	.....	.....	..	...	..	...
4	β-Naphthyl[c]	1:4	13	3.2	172	Butyl acetate	Needles	$C_{14}H_{12}O_2$	79.2	5.7	79.4	5.8
5	9-Phenanthryl	1:4	15	15	214	Butanol	Lancets	$C_{18}H_{14}O_2$	82.4	5.3	82.7	5.5

[a] Kharasch, THIS JOURNAL, **64**, 333 (1942), prepared the acid but did not give experimental details. [b] Because of difficulties encountered in attempts to purify the product, the crude acid was converted to the anilide which crystallized readily from benzene in long needles, m. p. 187°. *Anal.* Calcd. for $C_{20}H_{17}NO$: C, 83.6; H, 5.9; N, 4.9. Found: C, 83.9; H, 6.1; N, 5.2. [c] Banchetti, *Gazz. chim. ital.*, **69**, 398 (1939); *C. A.*, **33**, 8602 (1939), reported a melting point of 170°.

where in the literature. 1,1-Di-(*p*-tolyl)-ethylene (I, 2), which we prepared previously from *p*-methylacetophenone and *p*-tolylmagnesium bromide, was more conveniently synthesized by the method of Bistrzycki[10] in about 60% yield. 1-Phenyl-1-(*p*-cyclohexylphenyl)-ethylene (I,16) and 1-methyl-1-(*p*-xenyl)-ethylene (V,2) are new compounds and were made as follows:

1-Phenyl-1-(*p*-cyclohexylphenyl)-ethylene (I,16): *p*-Cyclohexylbenzophenone[11] (45 g.) in 100 cc. of benzene was added to methylmagnesium iodide (from 38 g. of methyl iodide) in 200 cc. of a 1:1 ether–benzene mixture, and the solution was refluxed for four hours. The crude carbinol was dehydrated by heating to 150–160° for one hour, and the ethylene was purified by distillation, b. p. 181° (0.05 mm.); yield, 100%.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.6; H, 8.4. Found: C, 91.7; H, 8.6.

1-Methyl-1-(*p*-xenyl)-ethylene (V, 2): This ethylene was prepared in an analogous way from 4-acetylbiphenyl and methylmagnesium iodide. The intermediate carbinol was dehydrated at 210–220°. The ethylene crystallized spontaneously and was recrystallized from ethanol. It melted at 108–109°; yield, 60%.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.8; H, 7.2. Found: C, 92.5; H, 7.4.

Synthesis of β,β-Diarylacrylic Acids (II).—As a standard procedure, one mole of ethylene and 3 to 5 moles of oxalyl chloride were refluxed until the evolution of hydrogen chloride ceased. In the case of 1,1-di-(*p*-anisyl)-ethylene (I,3) the reaction was virtually over after one-half hour at room temperature and was completed by refluxing for fifteen minutes.

Excess oxalyl chloride was removed *in vacuo* and the sirupy residue was stirred into an ice-cold sodium carbonate solution. The acid chlorides required from one to two hours for hydrolysis.

The mixture then was boiled with a large amount of water (about one liter per 50 g. of substituted ethylene) to dissolve the sodium salt and to separate it from tars formed as by-products. Charcoal was added and the solution filtered. Part of the sodium salt crystallized from the cooled filtrate; this portion, upon acidification, immediately yielded a pure sample of the desired acid. The remainder of the acid was recovered from the filtrate by acidification and was purified by recrystallization. It was essential in some cases, *e. g.*, with β,β-di-(*p*-anisyl)-acrylic acid (II,3), to avoid high-boiling solvents, because of the possibility of decarboxylation.

The ethylenes containing halogenated phenyl groups

---

(10) Bistrzycki and Reintke, *Ber.*, **38**, 839 (1905).

(11) Kleene, THIS JOURNAL, **62**, 3523 (1940).

were partially converted into tarry material by the long reflux time necessary to cause them to react. Because of this a lower yield was obtained in these cases.

Details of the conversion of 1,1-diarylethylenes into β,β-diarylacrylic acids are given in Tables I and II.

Reaction of 1,1-Di-(*p*-anisyl)-ethylene and Phosgene.—A slow stream of phosgene was bubbled during ten hours through a boiling solution of 10 g. of 1,1-di-(*p*-anisyl)-ethylene in 50 cc. of benzene. The solvent was distilled *in vacuo* and the residue decomposed with cold sodium carbonate solution. The sodium salt of the acid (II,3) was dissolved by heating and filtered from the insoluble, neutral material. Acidification of the filtrate precipitated 3.5 g. (30%) of β,β-dianisylacrylic acid, m. p. 139–140°.

The dianisylethylene was recovered unchanged when refluxed in a solution of ethyl or amyl chlorocarbonate.

Separation of Isomeric, Unsymmetrical β,β-Diarylacrylic Acids.—Method A—Separation of the acid chlorides: It was found that in the case of β-phenyl-β-(*p*-anisyl)-acrylic acid (II,17), the isomeric acid chlorides differed considerably in their hydrolysis rates. A benzene solution of the mixed chlorides was shaken with water; the solid which separated was the α-isomer, m. p. 181°. After separation of the layers, the benzene solution was shaken with aqueous sodium carbonate. This converted the β-acid chloride into the sodium salt of the β-acid, contaminated with some of the α-acid.

Method B—Separation of the free acids: The mixture of isomers was separated in a few cases by fractional crystallization. This method was especially applicable when the two aryl groups differed appreciably in their molecular weight or in the polar character of the substituent.

Method C—Separation of the sodium salts: In most cases it was observed that on cooling slowly the hot solution of the mixed sodium salts, the salt of the higher-melting acid separated in a fairly pure state. The filtrate upon acidification then gave a mixture enriched in the low-melting isomer, which usually could be separated by fractional crystallization in a Dewar. The separation temperature proved to be critical in some cases. Thus, the α-form of β-phenyl-β-(*p*-chlorophenyl)-acrylic acid (II,9) crystallized in a fairly pure condition at 30–35°. However, at about 15° the β-form also precipitated as its sodium salt. It was important for securing satisfactory separations that very dilute solutions of the sodium salts were used.

Method D—Mechanical separation of the free acids: In some cases Methods A, B and C failed. The mixture of acids was then dissolved in an organic solvent, and the solution was cooled very slowly in a Dewar. The crystals which formed were separated by passing them through a sieve or picking them out with the help of forceps.

Other methods tried, such as chromatographic adsorption on calcium sulfate, fractional acidification or separation of the methyl esters, either were unsuccessful or did not possess any advantage over the four methods outlined.

β-Arylcrotonic Acids (VI).—The reaction of oxalyl chloride with 1-methyl-1-arylethylenes (V) was much more sluggish than with 1,1-diarylethylenes (I), and the products were much more difficult to purify. β-(α-Naphthyl)-crotonic acid (VI,3) was obtained only as an amorphous mass, and was therefore characterized as its anilide. The preparation of five β-arylcrotonic acids is summarized in Table IV.

β,β-Diarylpropionic Acids (III).—The diarylacrylic acids were hydrogenated in ethanol over palladium-barium sulfate at room temperature and normal pressure. Yields were almost quantitative. In a few cases two isomeric acids (IIα and IIβ) were hydrogenated separately in order to prove the existence of geometrical isomerism. When the crude, yellow acrylic acids were used for catalytic reduction, the color faded in the initial phase of the hydrogenation, and the diarylpropionic acids were obtained in an excellent state of purity. Results are given in Table III.

Hydrogenation of β-Phenyl-β-(*p*-chlorophenyl)-acrylic Acid (II,9).—When 4.3 g. of 1-phenyl-1-(*p*-chlorophenyl)-acrylic acid (II,9) was reduced, 50% more hydrogen was absorbed than was calculated for the reduction of the double bond. The reaction mixture smelled strongly of hydrogen chloride and formed a heavy precipitate with silver nitrate. The ethanol was evaporated, the oily residue dissolved in benzene and extracted with warm sodium carbonate solution. The neutral portion was distilled, b. p. 135–140° (0.8 mm.).

Anal. Calcd. for $C_{14}H_{14}$: C, 92.3; H, 7.7. Found: C, 92.1; H, 7.7.

The alkaline extract was boiled with charcoal and filtered. Upon slow cooling a precipitate formed and was filtered; on acidification it yielded 0.7 g. of β-phenyl-β-(*p*-chlorophenyl)-propionic acid (III,6), m. p. 108° (see Table III).

When the sodium carbonate filtrate was acidified, 1 g. of β,β-diphenylpropionic acid precipitated. It crystallized from benzene–petroleum ether in long rods, m. p. 153°; mixed m. p. with authentic sample (m. p. 155°), 154–155°.

Hydrogenation of β,β-Di-(*p*-chlorophenyl)-acrylic Acid (II,5).—The reduction of 6 g. of β,β-di-(*p*-chlorophenyl)-acrylic acid (II,5) was stopped after one molar equivalent of hydrogen had been absorbed. The reaction mixture fumed strongly and was shown to contain hydrogen chloride. It was separated into a neutral and an acidic portion.

The neutral product, after a small forerun at 145° (3 mm.), boiled at 195° (3 mm.). It gave a positive Beilstein test.

Anal. Calcd. for $C_{14}H_{12}Cl_2$: C, 67.0; H, 4.8. Found: C, 66.6; H, 5.0.

The hot sodium carbonate extract was boiled with charcoal, filtered and left overnight. The precipitate was separated and acidified; it proved to be unchanged starting material.

The alkaline filtrate, when acidified, yielded about 1 g. of oily β,β-di-(*p*-chlorophenyl)-propionic acid which solidified when triturated with petroleum ether. It recrystallized from benzene–petroleum ether in flat, rhombic prisms, m. p. 187°. Fuson reported 188–189°.[12]

Anal. Calcd. for $C_{15}H_{12}Cl_2O_2$: C, 61.0; H, 4.1. Found: C, 61.3; H, 4.2.

Summary

The reaction between 1,1-diarylethylenes and oxalyl chloride represents a general method for the preparation of β,β-diarylacrylic acids. The influence of substituents on the speed of the reaction indicates that oxalyl chloride attacks the terminal carbon atom like an electrophilic reagent.

With unsymmetrical 1,1-diarylethylenes a mixture of isomeric β,β-diarylacrylic acids is produced in most cases. Substituents which increase strongly the electron density at the β-carbon atom of the diarylethylenes either yield one isomer only or tend to make the second isomer unstable.

Catalytic hydrogenation of halogenated β,β-diphenylacrylic acids causes partial dehalogenation and decarboxylation.

RECHOVOT, PALESTINE RECEIVED NOVEMBER 3, 1947

---

[12] Fuson, Kozacik and Eaton, THIS JOURNAL, **55**, 3799 (1933).