zalbisthymol[22] and other derivatives[15,20] of thymol indicate that position 6 is more reactive than the 2 position.

Direct Substitution of Methylene-, Ethylidene- and Benzalbisphenols. Method H.—Methylation was accomplished in acetone solution by the use of dimethyl sulfate and potassium carbonate.

I. Chloroacetic acid was refluxed with a sodium hydroxide solution of the methylenebisphenol for two hours.

J. Iodination[23] was effected by utilizing the method of Burger, *et al.*[24] on the appropriate methylene-, ethylidene- and benzalbisphenols. The amount of methanol was varied.

K. (a) The methylenebisphenol (40 g.) was heated at 100° for four hours with 31 g. of concentrated sulfuric acid. It was then diluted with 500 ml. of water, filtered and neutralized to *p*H 5.6 with sodium hydroxide. The water-washed precipitate which contained sodium was soluble in ethyl acetate. The calcium salt was formed by adding calcium chloride solution to a solution of the sodium salt. (b) By concentration of the main filtrate from K (a), an ethyl acetate-insoluble sodium salt was obtained. Barium chloride produced the barium salt from a solution of the sodium salt.

L. (a) 2,2′-Methylenebis-(4-chlorophenol) (0.25 mole) was treated in 550 ml. of glacial acetic acid with 34 g. of fuming nitric acid (d. 1.5) for one and one-half hours at 25°. (b) The dinitro derivative from L (a) was reduced in alcoholic hydrogen chloride with stannous chloride at 80° for one hour. (c) The diamino compound from L (b) was selectively acetylated by a method similar to one described.[25]

Condensation of 4-Chlorobenzenethiol with Formaldehyde. Bis-(4-chlorophenylmercapto)-methane.—Method A was used in effecting this condensation. The product was insoluble in aqueous and alcoholic sodium hydroxide. Its alkali insolubility, its inertness to iodine in acetic acid, and its analysis indicated that the compound was a mercaptal.[26] It gave a positive sulfur test. When crystallized from methanol, it melted at 44–45°; yield, 75%.

Anal. Calcd. for $C_{13}H_{10}Cl_2S_2$: C, 51.83; H, 3.35. Found: C, 51.60; H, 3.89.

Acknowledgment.—The author takes pleasure in expressing appreciation to Mr. John W. Lee for his suggestions and interest concerning this investigation.

Summary

The Baeyer and Lederer–Manasse reactions have been applied successfully by different methods to a variety of phenols and aldehydes to produce a number of symmetrical and mixed methylenebisphenols, and phenol alcohols. Direct substitutions were made in several methylenebisphenol derivatives.

p-Chlorobenzenethiol and formaldehyde were found to react in an acid medium to form a mercaptal.

---

(22) Bell and Henry, *J. Chem. Soc.*, 2215 (1928); Orndorf and Lacey, THIS JOURNAL, **49**, 818 (1927).

(23) The positions of the introduced substituents have not been proved conclusively. The chlorination of 2,2′-methylenebis-(4-chlorophenol) in this Laboratory to yield the known 2,2′-methylenebis-(4,6-dichlorophenol) indicates the reactivity of the positions ortho to the hydroxyl groups.

(24) Burger, Wilson, Brindley and Bernheim, THIS JOURNAL, **67**, 1416 (1945).

(25) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., Boston, Mass., 1935, p. 165.

(26) The formation of a mercaptal with benzenethiol and acetaldehyde has been reported: Escales and Bauman, *Ber.*, **19**, 2815 (1886).

INDIANAPOLIS, INDIANA RECEIVED MARCH 24, 1949

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Preparation of Aryl Acrylates and Methacrylates by Pyrolysis of the Corresponding Acetoxy Esters

BY E. M. FILACHIONE, J. H. LENGEL AND WILLIAM P. RATCHFORD

In an earlier paper[2] we have shown that phenyl acrylate was obtained in good yield by pyrolysis of phenyl α-acetoxypropionate at 500–550°. The present paper reports the results of further study of this pyrolysis method for the preparation of various new aryl acrylates, namely, *p*-chlorophenyl, *m*-tolyl, *o*-allylphenyl, *p*-*t*-butylphenyl, *p*-*t*-amylphenyl and *p*-cyclohexylphenyl acrylate, and phenyl methacrylate. Phenyl methacrylate, both monomer and polymer have been briefly reported in the literature.[3]

The following series of reactions was used to obtain the acrylic ester: (1) acetylation of lactic acid with acetic acid to give acetoxypropionic acid[2,4]; (2) conversion of acetoxypropionic acid into its acid chloride by treatment with thionyl chloride; (3) interaction of the acid chloride with the phenol to produce the aryl acetoxypropionate, yields (see Table I) being 85–95% and (4) pyrolysis of the acetoxypropionate at 500 to 550° to form the aryl acrylate, generally in 70–80% yields (see Table II). Phenyl methacrylate was produced in 90% yield (Table II) by pyrolysis of phenyl acetoxyisobutyrate.

With a contact time of approximately ten seconds, pyrolysis at 550° consistently gave somewhat lower yields of the acrylate than did pyrolysis at 525 or 500°. The pyrolysis runs giving low yields of acrylate, *i. e.*, *m*-tolyl, *p*-*t*-amylphenyl, and *o*-allylphenyl acrylate, were characterized by formation of relatively large amounts of gaseous by-products, mainly carbon dioxide and carbon monoxide, as well as formation of polymer. This was overcome, in part at least, in the pyrolysis of *o*-allylphenyl acetoxypropionate, by thermal decomposition at lower temperature, *i. e.*, 500°. Polymer formation particularly during distilla-

---

(1) One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) Filachione, Lengel and Fisher, THIS JOURNAL, **66**, 494 (1944).

(3) Anonymous, *Ind. Eng. Chem.*, **28**, 1161 (1936).

(4) Filachione and Fisher, *ibid.*, **36**, 472 (1944).

TABLE I

PREPARATION AND PROPERTIES OF ARYL α-ACETOXYPROPIONATES

α-Acetoxy-propionate	Yield, %	B. p. °C.	B. p. Mm.	n^{25}_D	n^{20}_D	d^{25}_4	MR Calcd.[a]	MR Found	Sapon. equiv. Calcd.	Sapon. equiv. Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
p-Chlorophenyl[b]	95	104–105	0.1	1.4985	1.5008	1.2244	57.57	58.13	121.3	118.2				
		126	2.0											
m-Tolyl	88	115–118	2.0	1.4855	1.4874	1.1042	57.32	57.73	111.1	107.2	64.85	64.20	6.35	6.21
o-Allylphenyl[c]	85	105–110	0.2	1.4950	1.4975	1.0882[c]	66.09	66.51	124.1	21.3	67.72	67.60	6.50	6.54
p-*t*-Butylphenyl[d]	89	115–117	0.2	1.4842	1.4860	1.0516[d]	71.18	71.61	132.2	131.0	68.16	68.19	7.63	7.66
		142–144	2.0											
p-*t*-Amylphenyl	88	133–135	0.3	1.4865	1.4895	1.0516	75.80	76.06	139.2	134.3	69.06	68.56	7.97	8.06
				(28°)		(28°)								
p-Cyclohexylphenyl	90	160	0.25	1.5035	1.5060	1.0848	78.21	79.09	145.2	150.5	70.32	70.07	7.64	7.53

[a] The atomic factors for calculating molecular refraction were taken from Gilman, "Organic Chemistry—An Advanced Treatise," ed. 2, John Wiley and Sons, New York, N. Y., 1943. [b] M. p. 38–44°. *Anal.* Calcd. for $C_{11}H_{11}O_4Cl$: Cl, 14.61. Found: Cl, 14.55. [c] d^{20}_4 1.0998. [d] d^{20}_4 1.0585.

TABLE II

PYROLYSIS OF THE ACETOXY ESTERS

Expt.	α-Acetoxypropionate pyrolyzed	G.	Temp., °C.	Feed rate, g./min.	Contact time, sec.	Ester dec., %	Yields, moles per mole of ester decomposed: Aryl acrylate	Acetic acid Titr.	Acetic acid Dist.	CO_2	CO	Unsat.	Sat.
1	*p*-Chlorophenyl	164	522	2.0	8.5	55	0.77	0.86	0.72	[a]	[a]	[a]	[a]
2	*m*-Tolyl	174	550	1.0	14.9	92	.59	.94	.78	.05	0.11	0.01	0.00
3	*o*-Allylphenyl	208	499	1.7	10.6	33	.76	.92	.72	[a]	[a]	[a]	[a]
4	*o*-Allylphenyl	206	550	1.8	9.8	100	.52	.81	.74	.12	.14	.07	.02
5	*p*-*t*-Butylphenyl	115	498	1.9	10.2	37	.72	.84	.68	[a]	[a]	[a]	[a]
6	*p*-*t*-Butylphenyl	142	549	1.8	10.0	85	.80	.92	.90	[a]	[a]	[a]	[a]
7	*p*-*t*-Amylphenyl	64	492	1.6	37.3	48	.40	.73	.67	.12	.06	.02	.03
8	*p*-*t*-Amylphenyl	67	547	3.7	14.6	63	.39	.80		.25	.12	.06	.03
9	*p*-*t*-Amylphenyl	104	584	4.3	12.0	46	.31	.72	.46	.31	.20	.18	.14
10	*p*-Cyclohexylphenyl	137	550	3.5	8.9	90	.71	.97	.83	.06	.05	.05	.01
11	Phenyl α-acetoxyisobutyrate	111[b]	450[b]	1.8[b]	8.9[b]	80[b]	.90[b]	.95[b]	.89[b]	[a]	[a]	[a]	[a]

[a] Negligible gas formation. [b] Phenyl α-acetoxyisobutyrate was pyrolyzed to produce phenyl methacrylate.

tion was most troublesome in the preparation of *p*-*t*-amylphenyl acrylate.

It was of interest that diacetyl was one of the minor pyrolysis products in the pyrolysis of *p*-chlorophenyl and *m*-tolyl acetoxypropionates. Probably phenols in small amount were also formed in the pyrolyses, inasmuch as phenyl acrylate undergoes pyrolysis to phenol, carbon monoxide and acetylene.[5] In the only attempted identification of the phenol, a small amount of *m*-cresol was observed in the pyrolysis of the *m*-tolyl ester.

The earlier paper[2] reported that styrene was a minor pyrolysis product in the thermal decomposition of phenyl acetoxypropionate to phenyl acrylate. Generally, the amount of styrene formed was most appreciable when the acetoxypropionate underwent almost complete decomposition. A hydrocarbon, apparently *p*-*t*-butylstyrene, was obtained in low yield (6%) from the pyrolysis of *p*-*t*-butylphenyl acetoxypropionate.

Experimental

***o*-Allylphenol.**—Allylphenyl ether was prepared and rearranged to *o*-allylphenol as described by Claisen[6] and others.[7,8] The constants obtained were: b. p., 80–84° at 13 mm., and n^{20}_D 1.5218 for allylphenyl ether; b. p., 105–109° at 18 mm., and n^{20}_D 1.5450 for *o*-allylphenol. The other phenols were available commercially.

α-Acetoxypropionyl Chloride.—Acetoxypropionic acid was prepared by the acetylation of lactic acid with acetic acid,[2,4] and this was then converted into the acid chloride by reaction with thionyl chloride.[2] In preparing the acid chloride, it was found convenient to use the crude undistilled acetoxypropionic acid which resulted from topping the acetylation mixture free of acetic acid.

α-Acetoxyisobutyryl Chloride.—This acid chloride was prepared by acetylating hydroxyisobutyric acid with acetic anhydride and treating the acetylated acid with thionyl chloride as described in an earlier publication.[9]

Aryl α-Acetoxypropionates.—These esters (Table I) were prepared essentially as described previously.[2] A mixture of the phenol and 10% excess of acetoxypropionyl chloride was heated on a steam-bath until evolution of hydrogen chloride ceased (four to fourteen hours), and the desired acetoxypropionate was isolated in 88 to 95% yields by distillation in vacuum. Table I lists the properties of *p*-chlorophenyl, *m*-tolyl, *o*-allylphenyl, *p*-*t*-butylphenyl, *p*-*t*-amylphenyl and *p*-cyclohexylphenyl acetoxypropionates. *o*-Allylphenyl acetoxypropionate, however, was prepared by acylation of the phenol (3 moles), in solution with pyridine (4 moles) and benzene (200 cc.), with acetoxypropionyl chloride (3.3 moles). After reaction and washing, the ester was isolated by vacuum distillation.

Phenyl α-Acetoxyisobutyrate.—A mixture of 445 g. (2.7 moles) of α-acetoxyisobutyryl chloride and 254 g. (2.7 moles) of phenol was heated on a steam-bath for four to five hours. At the end of this time evolution of gases had virtually ceased. Distillation of the reaction mixture in vacuum gave 482 g. (80% yield) of phenyl α-acetoxyisobutyrate collected at 88–89° at 0.8 mm. The physical constants determined on the redistilled material were:

---

(5) Hurd, "The Pyrolysis of Carbon Compounds," A. C. S. Monograph 50, Chemical Catalog Co., New York, N. Y., 1929.

(6) Claisen, Eisleb and Kremers, *Ann.*, **418**, 69–120 (1919).

(7) Adams and Rindfusz, THIS JOURNAL, **41**, 648 (1919).

(8) Jacobs and Heidelberger, *ibid.*, **39**, 2188 (1917).

(9) Filachione, Lengel and Fisher, *ibid.*, **68**, 330 (1946).

TABLE III

PROPERTIES OF MONOMERIC ARYL ACRYLATES AND PHENYL METHACRYLATE

Monomer	B. p. °C.	B. p. Mm.	n^{20}_D	d^{20}_4	*MR* Calcd.[a]	*MR* Found	Sapon. equiv. Calcd.	Sapon. equiv. Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
p-Chlorophenyl acrylate[b]	70	1.0	1.5352	1.2131	46.21	46.88	182.6	175.5	See footnote (b)			
m-Tolyl acrylate	70.5	1.5	1.5180	1.0490	45.97	46.85	162.2	...				
o-Allylphenyl acrylate	60–70	0.55	1.5226	1.0359	54.74	55.46	188.2	188.7	76.57	75.85	6.42	6.57
p-*t*-Butylphenyl acrylate[c]	68-72[c] 79–80	.12[c] .38	1.5102	1.0042	59.82	60.87	204.3	207.9	76.46	76.50	7.90	8.11
p-*t*-Amylphenyl acrylate	76–83	.1	1.5175									
p-Cyclohexylphenyl acrylate[d]	108–115	.2	Solid, m. p. 62–63°C.[d]				230.3	236.0	78.23	78.14	7.88	8.06
Phenyl methacrylate	47–50	.2	1.5147	1.0542	45.97	46.38	162.2	157.6	74.05	74.38[e]		..

[a] The atomic factors for calculating molecular refraction were taken from Gilman, "Organic Chemistry—An Advanced Treatise," John Wiley and Sons, New York, N. Y., 1943. [b] Calcd. for $C_9H_7O_2Cl$: Cl, 19.42. Found: Cl, 19.72. [c] M. p., 18–20°. [d] Solid was recrystallized from petroleum ether (boiling range 30–80°). This monomer has been stored (without added inhibitor) for a long period at room temperature without polymerizing. [e] By wet oxidation (Van Slyke and Folch, *J. Biol. Chem.*, **136**, 509 (1940)).

b. p. 82–86° at 0.5 mm., n^{20}_D 1.4850, d^{20}_4 1.1110, *MR*, calcd., 57.22, found, 57.33. *Anal.* Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.98; H, 6.43.

Pyrolysis.—The procedure was essentially that described in previous publications[2,10] from this Laboratory. To minimize polymerization, the pyrolyzate was collected in the presence of hydroquinone or phenyl-β-naphthylamine. The pyrolysis tube was vented through a trap immersed in solid carbon dioxide to a large gas-collecting bottle. The gas was analyzed for carbon dioxide, carbon monoxide, unsaturates and saturates by standard procedures.

Pyrolysis at 500 to 550° and approximately ten seconds of contact time was generally used, which gave decompositions of 50% or more of the acetoxypropionate (Table II).

Titration of a small aliquot of the pyrolyzate indicated the amount of acid formed, and this was calculated as acetic acid.

The pyrolyzates, inhibited by hydroquinone or phenyl-β-naphthylamine, were distilled in vacuum, through a 56-cm. Vigreux column, in an atmosphere of carbon dioxide. The acetic acid fraction was collected at a pressure of 10 to 30 mm.; a trap immersed in solid carbon dioxide was used to avoid loss of volatile substances. When the still pot temperature rose to 90–100°, the pressure was lowered to approximately 1 mm. and the remainder of the pyrolyzate fractionated to isolate the aryl acrylate and undecomposed ester. The various pyrolysis fractions were then redistilled (carbon dioxide atmosphere and inhibitor) in vacuum to obtain essentially pure acetic acid and the aryl acrylate or methacrylate.

Diacetyl was obtained from the acetic acid forerun, boiling range 80 to 100°, of Experiments 1 and 2, Table II. It was identified by conversion to dimethylglyoxime, m. p. and mixed m. p., 232°, and by the formation of the characteristic red nickel salt of dimethylglyoxime.

Table II summarizes the pyrolyses of the various aryl acetoxypropionates and phenyl acetoxyisobutyrate.

The physical properties of the monomeric aryl acrylates, and phenyl methacrylate are listed in Table III. The constants were determined on a middle cut of the monomer fraction.

***p*-*t*-Butylstyrene.**—In addition to *p*-*t*-butylphenyl acrylate, the pyrolysis of *p*-*t*-butylphenyl acetoxypropionate (Table II, Expt. 6) resulted in a small yield, 6%, of a substance which appeared to be *p*-*t*-butylstyrene. This substance was collected in the fraction intermediate between acetic acid and the butylphenyl acrylate and boiled at 83 to 86 at 7.5 mm., and 50 to 54° at 0.7 mm. A sample redistilled in carbon dioxide atmosphere from phenyl-β-naphthylamine and diethylamine (latter to absorb acid impurity) showed the following: n^{20}_D 1.5193; d^{20}_4 0.8972. *Anal.* Calcd. for $C_{12}H_{16}$: C, 89.93; H, 10.07; *MR*, 53.55. Found: C, 88.85; H, 10.79; *MR*, 54.24.

Polymeric Aryl Acrylates and Methacrylates.—The monomers, excepting phenyl methacrylate and recrystallized *p*-cyclohexylphenyl acrylate as isolated by distillation from the pyrolyzates, showed little tendency to polymerize when heated at 65° with 0.1 to 0.5% of benzoyl peroxide. However, after being washed with cold dilute (2%) sodium hydroxide saturated with salt, and subsequently distilled, they readily polymerized.

The cast polymers of *p*-*t*-butylphenyl, *p*-*t*-amylphenyl and *p*-cyclohexylphenyl acrylates were colorless, hard and brittle at room temperature but soft at 65°. The cast polymer of phenyl methacrylate was a crystal clear, colorless, hard polymer which did not soften at 65°. The mass polymer of allylphenyl acrylate was a crystal clear, pale-yellow, hard polymer, which was insoluble and infusible. Apparently the double bond in the allyl side chain of allylphenyl acrylate also underwent polymerization, producing a cross linked, *i. e.*, thermoset, polymer. *p*-Chlorophenyl acrylate polymerized vigorously in mass, the temperature rising to 170° during polymerization. This polymer was a soft plastic, which was partly converted to a hard plastic by baking overnight in an oven at 95°.

Acknowledgment.—The authors are indebted to Frances J. Cooper, Mary J. Welsh, C. L. Ogg and C. O. Willits for the gas analyses, saponification equivalents and the ultimate analyses for carbon, hydrogen and chlorine reported in this paper.

Summary

p-Chlorophenyl, *m*-tolyl, *o*-allylphenyl, *p*-*t*-butylphenyl, *p*-*t*-amylphenyl, and *p*-cyclohexylphenyl α-acetoxypropionates and phenyl α-acetoxyisobutyrate were prepared. The acetoxypropionates were pyrolyzed at 500 to 550° to give satisfactory yields of the corresponding acrylate.

Phenyl acetoxyisobutyrate was pyrolyzed at 450° to give a 90% yield of phenyl methacrylate.

Hard-cast resins were obtained by polymerizing the above aryl acrylates. Phenyl methacrylate polymer resembles methyl methacrylate polymer in appearance. *o*-Allylphenyl acrylate polymerizes to an insoluble, infusible, cross-linked resin.

PHILADELPHIA 18, PA. RECEIVED JUNE 20, 1949

---

[10] Filachione, Fein, Lengel and Fisher, THIS JOURNAL, **70**, 526 (1948).