bined solution was distilled under reduced pressure. The major part of the charge distilled at 130–150° at 3 mm. and crystallized on cooling. Recrystallization from alcohol gave colorless product, m. p. 76–77°, which was identified as tetraethyl ethanetetracarboxylate. Further distillation of the residue after the removal of the above fraction yielded 25 g. of a yellow oil which distilled only with very considerable decomposition at 180–200° at 3 mm. Redistillation failed to improve the product and led to further decomposition.

Anal. Found 12.6, 12.65% P; calcd. for dibutyl diethyl phosphonomalonate 8.8%. Hydrolysis by hydrochloric acid led to de-phosphonation as observed in the above examples.

Summary

It was shown that the synthesis of triethyl phosphonoacetate is favored by the use of a neutral solvent like hexane. The corresponding tributyl ester was synthesized.

The reaction of trialkyl phosphites, or to a lesser extent that of sodium dibutyl phosphite, leads to formation, with diethyl bromomalonate, of phospho-organic esters of rather poor stability, which appear to be phosphonomalonic esters.

RECEIVED MARCH 15, 1946

[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES, MONSANTO CHEMICAL COMPANY]

Vinyl Aromatic Compounds. I. The Vapor Phase Dehydration of Arylmethylcarbinols

BY DAVID T. MOWRY, MARY RENOLL[1] AND W. FREDERICK HUBER

The more common methods of preparing vinyl aromatic compounds include decarboxylation of cinnamic acids, simultaneous decarboxylation and dehydrohalogenation of β-aryl-β-halopropionic acids, dehydrogenation of ethyl aromatic compounds and dehydrohalogenation of α- or β-haloethyl aromatic compounds. A number of styrene derivatives have been prepared by the liquid phase dehydration of β-arylethyl alcohols over a basic catalyst such as potassium hydroxide[2,3] and of α-arylethyl alcohols over an acid catalyst[4–6] such as potassium bisulfate, phosphoric or oxalic acids. Of the two methods the latter is more useful because of the availability of the secondary alcohols from the reduction of the corresponding acetophenones or from the reaction of an aryl or methyl Grignard reagent with the appropriate aldehyde.

Both methods give good yields in the preparation of the more volatile vinyl aromatic compounds which do not contain substituents that are susceptible to attack by acidic or basic reagents. Unless the quantities of carbinol employed are small enough for the product to be rapidly distilled from the reaction flask, considerable loss of product through polymerization is inevitable. Furthermore, both high conversions and high yields have not often been obtained in a liquid phase reaction. To obviate these difficulties, the vapor phase dehydration[7,8] of α-phenylethyl alcohol and a few of its lower homologs has been carried out over such catalysts as alumina, thoria, or tungsten oxide at temperatures ranging from 250–500°.

After considerable experimentation with many of the above techniques, we have found that the method which most consistently gives good results for the preparation of a wide variety of vinyl aromatic compounds is the vapor phase process. Most of the twenty-three compounds listed in Table I were obtained in good yields by this method. The compounds for which ultimate analyses are given have not been previously reported.

The products were analyzed for unsaturation by the bromide–bromate method[9] and gave values ranging from 95–100% with the exception of the halogen or nitrogen substituted derivatives which gave anomalous low results by this method.

The carbinols used were prepared by reduction of the corresponding ketones. Whenever possible, hydrogenation at 120–150° using a copper chromite catalyst was employed. The by-product of this reaction was always a small amount of the analogous ethyl compound which was easily separated by distillation or crystallization. 3,4-Dichloroacetophenone and 1-chloro-4-acetylnaphthalene were reduced only with difficulty by this method, because of the tendency of the halogen compound to poison the catalyst, but were reduced smoothly with aluminum isopropoxide. Kuhn and Dann[10] obtained a 47% yield of methyl-α-thienylcarbinol together with appreciable amounts of the isopropyl ether of the product when acetothienone was reduced with aluminum isopropoxide. By using only half as much reducing agent as was employed by these authors, the yield was raised to 84% with negligible amounts of by-product ether formation. *p*-Cyanoacetophenone was also reduced with aluminum iso-

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[2] Sabatay, *Bull. soc. chim.*, **45**, 69 (1929).

[3] Sontag, *Ann. chim.*, [11] **1**, 359 (1934).

[4] Klages and Allendorff, *Ber.*, **31**, 1003, 1298 (1898).

[5] Gauthier and Gauthier, *Bull. soc. chim.*, **53**, 323 (1933).

[6] Brooks, THIS JOURNAL, **66**, 1295 (1944).

[7] French Patent 682,569 (1929), *C. A.*, **24**, 4523 (1930); German Patent 533,827 (1935).

[8] Yamamoto and Kawata, *J. Soc. Chem. Ind. Japan*, **43**, suppl. binding 279 (1940).

[9] Mulliken and Wakeman, *Ind. Eng. Chem.*, *Anal. Ed.*, **7**, 59 (1935).

[10] Kuhn and Dann, *Ann.*, **547**, 293 (1941).

TABLE I

VINYL AROMATIC COMPOUNDS

Compound	Yield,[l] %	B. p.		M. p., °C.	n^{25}_D	Analyses, % Carbon		Analyses, % Hydrogen	
		°C.	Mm.			Calcd.	Found	Calcd.	Found
p-Methylstyrene[a]	83	65–66	18	.....	1.5402	...	...	...	...
p-Ethylstyrene[b]	83	68	16	.....	1.5350	...	...	...	...
m-Ethylstyrene	93	74	14	.....	1.5315	90.85	90.45	9.15	9.21
3,5-Diethylstyrene	83	106–108	15	.....	1.5280	89.94	90.05	10.06	10.03
p-*t*-Butylstyrene	76	99–100	14	.....	1.5245	89.94	90.02	10.06	10.07
p-Cyclohexylstyrene	87	105–107	2	.....	1.5515	90.25	90.16	9.72	9.97
6-Vinyl-1,2,3,4-tetrahydronaphthalene	86	89–90	2.0	.....	1.5699	91.08	90.96	8.92	9.16
p-Methoxystyrene[c]	65	45–46	0.5	.....	1.5553	...	...	...	...
p-Ethoxystyrene[d]	69	56–59	1.0	.....	1.5454	...	...	...	...
p-Phenoxystyrene	72	110–112	1.0	.....	1.6006	85.69	86.14	6.16	6.36
3,4-Dichlorostyrene[k]	87	63–64	1.5	.....	1.5839	55.52	55.59	3.50	3.49
p-Cyanostyrene[m]	71	88–90	1.5	−15	1.5750	83.69	83.10	5.47	5.44
p-Aminostyrene[e]	20	76–81	2.5	.....	1.6070	...	...	...	...
α-Vinylthiophene[f]	74	62–63	50	.....	1.5698	...	...	...	...
α-Vinylfurane	20	96–98	748	.....	1.4950	...	...	...	...
p-Divinylbenzene[g]	83	46	1	31	....	...	...	...	...
α-Vinylnaphthalene[h]	57	86–87	2.0	.....	1.6436	...	...	...	...
β-Vinylnaphthalene[i]	75	76–81	2.5	65–66	....	...	...	...	...
1-Chloro-4-vinylnaphthalene	38	118–120	2.0	.....	1.6408	...[j]	...	...	...
2-Vinylfluorene	28	.....	...	133–134	....	93.71	93.70	6.29	6.48
1-Vinylacenaphthene	32	132–137	2	.....	1.6512	92.26	93.10	7.74	7.03
2-Vinyldiphenylene oxide	63	127–128	1.5	38–39	1.6597	86.58	86.52	5.19	5.19
4-Chloro-4′-vinylbiphenyl	46	.....	...	125–126	....	78.31[n]	78.00	5.17	5.10

[a] von Auwers, *Ber.*, **45**, 2777 (1912), reported b. p. 65–66° (19 mm.), $n^{16.3}_D$ 1.5447. [b] Klages, *Ber.*, **35**, 2250 (1902), reports b. p. 86° (20 mm.). [c] Shorygin and Shorygina, *J. Gen. Chem.* (U. S. S. R.), **9**, 845 (1939), report b. p. 104° (20 mm.), n^{17}_D 1.560. [d] Klages and Eppelsheim, *Ber.*, **36**, 3592 (1903), report b. p. 108–110° (12 mm.). [e] Shorygin and Shorygina, *loc. cit.*, give b. p. 125–127° (10 mm.), n^{14}_D 1.619. Checked by conversion in 90% yield to its acetate, m. p. 135–136°. [f] Kuhn and Dann, *loc. cit.*, report b. p. 62–63° (50 mm.), n^{20}_D 1.5618. [g] Deluchat, *Ann. chim.*, [11], 1, 181 (1934), gives b. p. 52° (3 mm.), m. p. 31°, n^{40}_D 1.5820. [h] Sontag, *loc. cit.*, reports b. p. 124–125° (15 mm.), n^{20}_D 1.6430. [i] Sontag, *loc. cit.*, gives b. p. 135–137° (18 mm.), m. p. 66°. [j] Chlorine calcd.: 18.80. Found: 18.60. [k] Michalek and Clark, *Chem. Eng. News*, **22**, 1559 (1944), give b. p. 76° (3 mm.), n^{25}_D 1.5840. Brooks, ref. 6, reports b. p. 69–70° (4 mm.) n^{20}_D 1.5857. [l] Conversion, or minimum yield. The quantities of unreacted carbinol were usually small, and were not recovered. [m] Marvel and Overberger, ref. 11, report b. p. 102–104° (9 mm.), n^{20}_D 1.5781. [n] Chlorine calcd.: 16.51. Found: 16.07.

TABLE II

ARYLMETHYLCARBINOLS

Compound	Method	Yield, %	B. p.		M. p., °C.	n^{25}_D	Analyses, % Carbon		Analyses, % Hydrogen	
			°C.	Mm.			Calcd.	Found	Calcd.	Found
m-Ethylphenylmethylcarbinol	H_2	97	120	15	.....	1.5171	80.05	79.87	9.39	9.30
3,5-Diethylphenylmethylcarbinol	H_2	83	139–142	15	.....	1.5120	80.85	81.15	10.18	10.11
p-*t*-Butylphenylmethylcarbinol	H_2	87	138–139	16	67–68	....	80.85	80.89	10.18	10.18
p-Cyclohexylphenylmethylcarbinol	H_2	87	122–129	1	82–83	....	82.30	82.55	9.87	9.84
1,2,3,4-Tetrahydro-6-naphthylmethylcarbinol	H_2	87	77–80	2	.....	1.5499	81.79	81.84	9.15	9.46
p-Phenoxyphenylmethylcarbinol	H_2	92	151–153	1	.....	1.5791	78.48	78.88	6.59	6.68
p-Cyanophenylmethylcarbinol	$Al(OPr)_3$	86	148–150	2	.....	1.5455	73.45[a]	73.40	6.03	6.32
1-Chloro-4-naphthylmethylcarbinol	$Al(OPr)_3$	85	....[c]	..	.....	1.6200	69.74[b]	69.23	5.37	5.87
2-Fluorenylmethylcarbinol	H_2	65	.....	..	139–140	....	86.09	85.93	6.26	6.75
1-Acenaphthylmethylcarbinol	H_2	83	.....	..	82–83					
2-(α-Hydroxyethyl)diphenylene oxide	H_2	91	173–179	2.5	63–64	....	79.24	79.28	5.70	5.82
4′-Chloroxenylmethylcarbinol	$Al(OPr)_3$	76	.....	..	129–130	....	72.25[d]	72.25	5.63	5.65

[a] Nitrogen calcd.: 9.51, found: 9.07. Marvel and Overberger, ref. 11, report b. p. 155–158° (6 mm.), n^{20}_D 1.5474. [b] Chlorine calcd.: 17.16, found: 17.22. [c] Decomposes below its boiling point. [d] Chlorine calcd.: 15.24, found: 15.19.

propoxide to the carbinol in 86% yield.[11] The previously unreported carbinols are listed in Table II.

Certain observations on the preparation of the intermediate aryl methyl ketones by the Friedel–Crafts reaction are worthy of comment. For the acetylation of alkylbenzenes, a modification of the Perrier[12] method, in which the hydrocarbon is added to a preformed complex of aluminum chlo-

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[11] A recent paper by Marvel and Overberger, THIS JOURNAL, **67**, 2250 (1945), which reports this reaction has just come to our attention. This is the first instance of the use of this method in the selective reduction of a ketonitrile to a hydroxynitrile. They also dehydrated the carbinol to *p*-cyanostyrene in 29% yield by the liquid phase potassium bisulfate technique.

[12] Perrier, *Ber.*, **33**, 815 (1900); Milton Kosmin, unpublished data.

ride and acetyl chloride in carbon tetrachloride solution, has proved far superior to the usual order of addition. The manipulation is easier, the reaction may be carried out more rapidly, little or none of the usual tar formation occurs, and the yields are markedly higher (85–98%).

In the preparation of α-acetothienone from equimolar quantities of thiophene, acetyl chloride and stannic chloride, it was found that no loss in yield occurred if the quantity of stannic chloride was reduced to almost half of that commonly prescribed.[13] This would indicate that in this case at least, one molecule of stannic chloride is capable of fixing two molecules of acetothienone in the reaction product complex. It was also observed that anhydrous aluminum chloride is a satisfactory catalyst for this reaction if the Perrier order of addition is used. This is contrary to previous experience with the usual procedures in which the thiophene is almost completely resinified. Apparently the acetothienone complex is not readily polymerized by an acetyl chloride–aluminum chloride complex and the acetylation reaction is much more rapid than the polymerization reaction.

Experimental

Synthesis of Aryl Methyl Ketones.—*p*-Methoxyacetophenone, *p*-ethoxyacetophenone, *p*-aminoacetophenone, methyl-α-naphthyl ketone, methyl β-naphthyl ketone and *p*-methylacetophenone were obtained from the Eastman Kodak Company.

Friedel–Crafts Acetylations.—For the preparation of acetophenone derivatives from alkylbenzenes, the Perrier modification of the Friedel–Crafts reaction was used. This technique involves the addition of the hydrocarbon at 0–5° to a preformed complex of acetyl chloride and aluminum chloride in carbon tetrachloride solution. A typical example follows:

To a suspension of 467 g. (3.5 moles) of anhydrous aluminum chloride in 2000 cc. of carbon tetrachloride was added 275 g. (249 cc. 3.5 moles) of acetyl chloride during fifteen minutes with vigorous stirring and cooling in an ice-bath. Cyclohexylbenzene, 481 g. (3.0 moles) was added dropwise over a period of three hours, keeping the temperature below 5°. After addition was complete, the product was stirred for another hour before hydrolyzing by pouring into ice and hydrochloric acid with stirring. The pale yellow carbon tetrachloride solution was washed with successive portions of dilute hydrochloric acid, sodium carbonate solution and water, and distilled through a 50 cm. Vigreux column to give 535 g. (91%)[14] of *p*-cyclohexylacetophenone, b. p. 128–129° (1.5 mm.), m. p. 67–69°.

In an analogous fashion the following were prepared: *p*-ethylacetophenone,[15] b. p. 116–117° (13 mm.), n^{25}D 1.5275 from ethylbenzene in 98% yield, *p*-*t*-butylacetophenone,[16] b. p. 137–138° (16 mm.), n^{25}D 1.5195, from *t*-butylbenzene[17] in 83% yield, and 6-acetyl-1,2-3,4-tetrahydronaphthalene,[18] b. p. 119–121° (2.0 mm.), n^{25}D 1.5591 from tetralin in 93% yield. These yields in the acetylation of alkylbenzenes are substantially higher than those previously reported by other techniques of the Friedel–Crafts reaction. The Perrier method offered little advantage in the acetylation of alkoxy or chloro substituted aromatic compounds.

p-Phenoxyacetophenone[19] was prepared from diphenyl ether by a method analogous to that of Adams and Noller.[20] A 68% yield of product, b. p. 153–154° (2 mm.), m. p. 49°, was obtained.

3,4-Dichloroacetophenone[21] was obtained by acetylation of *o*-dichlorobenzene with aluminum chloride and acetyl chloride at 50° in the absence of a solvent. After the addition was complete, the reaction was heated at 100° for three hours before hydrolysis. A 59% yield of the ketone, b. p. 130–133° (11 mm.), m. p. 73–74° was obtained.

2-Acetylfluorene was prepared by the method of Rieveschl and Ray,[22] a 62% yield of ketone, b. p. 189–192° (4 mm.), m. p. 128–130° being obtained.

1-Chloro-4-acetylnaphthalene was prepared by the addition of α-chloronaphthalene to a mixture of acetyl chloride and aluminum chloride in nitrobenzene solution at 10–15°. Four hours after the addition was complete the product was decomposed in the usual manner and distillation gave a 64% yield of the ketone, b. p. 140–150° (2-3 mm.), n^{25}D 1.6390.

Anal. Calcd. for $C_{12}H_9OCl$: Cl, 17.33. Found: Cl, 17.51.

4-Chloro-4′-acetylbiphenyl was prepared in a similar fashion by the acetylation of xenyl chloride. A 64% yield of ketone was obtained which, after recrystallization from a mixture of benzene and hexane, melted at 102–103°.

Anal. Calcd. for $C_{14}H_{11}OCl$: C, 72.89; H, 4.80; Cl, 15.37. Found: C, 72.91; H, 4.76; Cl, 15.05.

α-Acetothienone[23] was prepared by the method of Johnson and May[13] in which a dilute benzene solution of thiophene and acetyl chloride was treated with an equimolar portion of stannic chloride at 2–5°, an 84% yield of product being obtained on a 3.5-mole run. Since it was noted that the reaction was exothermic during only the first half of the addition, the amount of stannic chloride was reduced to 0.6 of an equivalent with no reduction in yield. A larger run using 5.3 lb. of thiophene, 5.0 lb. of acetyl chloride and 9.0 lb. of stannic chloride in 6 gallons of benzene gave a 75% yield of pure product. According to the above authors, aluminum chloride has not been a satisfactory catalyst for this reaction because of the tendency for thiophene to polymerize in contact with this reagent. This was verified in an attempt to prepare acetothienone by the addition of acetyl chloride to a benzene solution of thiophene and aluminum chloride, the total product being a tarry resin. However, when the Perrier technique (outlined above for *p*-cyclohexylacetophenone), in which the thiophene was added to the preformed acetyl chloride–aluminum complex was used, a 75% yield of acetothienone was obtained. Attempts to obtain this ketone from thiophene and acetic acid in anhydrous hydrogen fluoride solution under a variety of conditions were all unsuccessful, only tarry polymers being obtained.

Oxidation of Arylethanes.—The liquid phase air oxidation of commercial diethylbenzene and triethylbenzene to *m*-ethylacetophenone and 3,5-diethylacetophenone was effected by previously described[24] methods.

In a similar fashion *p*-ethylacetophenone was oxidized to *p*-diacetylbenzene[25] in 40% conversion and 76% yields ac-

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[13] Johnson and May, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 8.

[14] Mayes and Turner, *J. Chem. Soc.*, 500 (1929), report a 60% yield of this compound by adding aluminum chloride to a mixture of the hydrocarbon and acetyl chloride in carbon bisulfide solution. In this Laboratory a similar preparation, in which acetic anhydride was substituted for acetyl chloride, gave only a 33% yield of crude product.

[15] Klages, *Ber.*, **35**, 2250 (1902).

[16] Verley, *Bull. soc. chim.*, [3] **19**, 73 (1898).

[17] This material was prepared from the sulfuric acid catalyzed condensation of isobutylene and benzene at 10–15° according to the method of Ipatieff, *et al.*, THIS JOURNAL, **58**, 921 (1936).

[18] Scharwin, *Ber.*, **35**, 2511 (1902).

[19] Kipper, *ibid.*, **38**, 2491 (1905).

[20] Adams and Noller, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 109.

[21] Glynn and Linnell, *Quart. J. Pharm. Pharmacol.*, **5**, 480 (1932).

[22] Rieveschl and Ray, THIS JOURNAL, **65**, 837 (1943).

[23] The authors are indebted to Dr. R. W. Shortridge for many of the observations recorded on the preparation of this compound.

[24] Mowry, THIS JOURNAL, **67**, 1050 (1945).

[25] Berend and Herms, *J. prakt. Chem.*, [2] **74**, 134 (1906).

cording to the method of Kosmin.[26] The product, b. p. 128–130° (3 mm.) melted at 114° after recrystallization from alcohol.

Other Ketone Syntheses.—1-Acetylacenaphthene was obtained by the addition of acetic acid to a 20% solution of acenaphthene in anhydrous hydrogen fluoride at room temperature.[27] After standing two days, the solution was quenched in ice-water and distilled to give an 84% crude yield of 1-acetylacenaphthene, b. p. 140–147° (1.0 mm.). Recrystallization from hexane gave the pure material, m. p. 104–105°.

p-Cyanoacetophenone was prepared from *p*-bromoacetophenone by the action of cuprous cyanide in pyridine solution. This method was used by Helberger and von Rebay[28] for the analogous preparation of *o*-cyanoacetophenone. Refluxing of the pyridine solution for four hours gave only a 20% conversion to the nitrile, but a 70% yield of product, b. p. 115–123° (3 mm.) was obtained by employing a reaction time of twenty hours. The crude product was recrystallized from a mixture of benzene and hexane to a melting point of 54–56° before use. *p*-Cyanoacetophenone was also prepared by the method of Ahrens,[29] who converted *p*-aminoacetophenone to *p*-cyanoacetophenone by diazotization and reaction with cuprous cyanide. A 48% yield of material melting at 54–55° was obtained.

Synthesis of Arylmethylcarbinols

Catalytic Hydrogenation of Ketones.—Catalytic hydrogenation methods were used whenever possible because of the high yields obtained and the simplicity of the procedure. Copper chromite catalyst prepared by the method of Adkins[30] was used in amounts of 2–4 weight per cent. of the ketone charged.

American Instrument Company rocking autoclaves of one or three liter capacity equipped with automatic temperature controls were used, usually with the aid of glass liners. Liquid and low melting ketones were hydrogenated without solvents, while the higher melting ketones were mixed with at least enough absolute ethanol to form a homogeneous solution at 100°. Most of the reductions proceeded at 120 to 160° and at 1000–2000 psi. depending on the reactivity of the catalyst and purity of the ketones. Higher temperatures were avoided since at 180–200° complete reduction to the arylethane occurred. The following reduction of *p*-tolyl methyl ketone is typical.

p-Tolyl methyl ketone (198 g.) and 8 g. of copper chromite catalyst were placed in the glass liner, the autoclave assembled and charged with hydrogen to 1400 psi. The bomb was heated slowly with rocking until absorption began at 120° and the temperature was maintained at 130° for two hours after absorption had ceased. After cooling and discharging the excess hydrogen, the catalyst was removed by filtration, and the product fractionated to give a 92% yield of *p*-tolylmethylcarbinol, b. p. 105–106° (13 mm.), n^{25}D 1.5203, together with a small amount of lower boiling material, presumably *p*-ethyltoluene. Klages and Keil[31] obtained a 60% yield of this carbinol, b. p. 120° (19 mm.) by the sodium and alcohol reduction of the ketone.

In a similar fashion were obtained *p*-ethylphenylmethylcarbinol, b. p. 89–90° (2.5 mm.), n^{25}D 1.5670 in 82% yield, *p*-methoxyphenylmethylcarbinol, b. p. 101.0–101.5° (1 mm.), n^{25}D 1.5310, in 89% yield, *p*-ethoxyphenylmethylcarbinol, b. p. 105–7° (1 mm.), m. p. 45–46° in 92% yield, α-naphthylmethylcarbinol, b. p. 119–125° (1 mm.), n^{25}D 1.6188 in 85% yield, β-naphthylmethylcarbinol,[32] m. p. 73° in 75% yield, 2-fluorenylmethyl carbinol, m. p. 139–140° in 65% yield, and 1-acenaphthenylmethylcarbinol, m. p. 82–83°, in 83% yield.

p-Diacetylbenzene was similarly reduced in 95% yield to *p*-di-(α-hydroxyethyl)-benzene, m. p. 80–81° after recrystallization from ethanol. This compound was reported by Deluchat[33] to melt at 81°. Repeated crystallization from dilute methanol did not raise the melting point further, but by fractional crystallization from benzene and hexane this mixture of meso and racemic forms of the glycol were at least partially separated into fractions melting at 90–91° and 114–115°.

The results of several other similar reductions are reported in Table II.

Aluminum Isopropoxide Reductions.—Since some of the ketones such as 3,4-dichloroacetophenone were only difficultly reduced by catalytic hydrogenation, the aluminum isopropoxide reduction was employed. For other sensitive compounds such as acetothienone and *p*-cyanoacetophenone, the selectivity of this reagent was desirable. The following reduction of α-acetothienone is typical:

A mixture of 219 g. of α-acetothienone (1.74 moles) and 306 g. of aluminum isopropoxide (1.5 moles) in 3 liters of dry isopropanol was slowly distilled under a Vigreux column taking off acetone as it was formed. When no more acetone was evolved (3–4 hours), most of the excess solvent was stripped off and the residue hydrolyzed with dilute hydrochloric acid. The product was extracted with benzene, and distilled giving 82–87% yields of α-thienylmethylcarbinol, b. p. 91–3° (11 mm.), n^{25}D 1.5422. When 3.5 moles of aluminum isopropoxide was used according to the procedure of Kuhn and Dann,[10] the yield of desired carbinol dropped to 48%, an equal amount of the isopropyl ether of methyl α-thienylcarbinol, b. p. 73–74° (11 mm.), n^{25}D 1.5018, being formed. Careful refractionation of a higher boiling material from this reduction failed to give evidence of a definite isolable compound.

In a similar fashion was obtained 3,4-dichlorophenylmethylcarbinol, b. p. 113–115° (2 mm.), n^{25}D 1.5572. The results for *p*-cyanophenylmethylcarbinol, 1-chloro-4-naphthylmethylcarbinol and 4′-chloroxenylmethylcarbinol are given in Table II.

Syntheses of Vinyl Aromatic Compounds.—The vapor phase dehydration of the carbinols was carried out in an electrically heated 25 mm. i. d. Vitreosil tube, 50 cm. in length, fitted at the top with a 2-mm. i. d. Vitreosil thermocouple well extending to a point 15 cm. from the bottom and two graduated dropping funnels which were equipped with pressure-equalizing side-arms. The bottom of the reactor was fitted with a water-cooled condenser leading to a receiver cooled in a Dry Ice-bath. In cases where the product was a fairly high melting solid, an electrically heated air-condenser was used. The tube was packed with 40 cm. of 4–8 mesh activated alumina above a 5-cm. layer of carborundum chips. The dehydrations were all effected at 290–310° (with the exception of *p*-aminophenylmethylcarbinol at 250°) and at 30 to 100 mm. pressure depending on the volatility of the product. Liquid carbinols were dehydrated by dropwise addition from one of the funnels at a rate of 40 to 60 cc. per hour. Solid carbinols were dissolved in benzene or xylene or in dioxane if the material was not sufficiently soluble in aromatic solvents. In this case, a somewhat higher rate (60 to 100 cc. per hour) was employed. In some cases the tube became plugged by excessive polymer formation, but this was remedied by momentarily halting the addition and adding pure solvent from the second funnel. On completion of the dehydration the reactor was flushed with a little solvent, the products separated from the water layer and distilled *in vacuo* after the addition of a few grams of a polymerization inhibitor such as sulfur, hydroquinone or pyrogallol. The catalyst was conveniently regenerated between runs by drawing a slow stream of air through the system at 500° overnight. The results of the dehydrations are listed in Table I.

Summary

The vapor phase dehydration of arylmethylcarbinols over activated alumina has been shown to be a versatile and satisfactory method for the

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[26] Milton Kosmin, private communication.

[27] Fieser and Hershberg, THIS JOURNAL, **61**, 1272 (1939).

[28] Helberger and von Rebay, *Ann.*, **531**, 229 (1937).

[29] Ahrens, *Ber.*, **20**, 2955 (1887).

[30] Lazier and Arnold, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 144.

[31] Klages and Keil, *Ber.*, **36**, 1635 (1903).

[32] This product melted slightly higher than the m. p. of 67–68° recorded by Sontag, *Compt. rend.*, **197**, 1130 (1933).

[33] Deluchat, *ibid.*, **190**, 438–440 (1930).

preparation of twenty-three varied vinyl aromatic compounds, of which the following have not been previously reported: *m*-ethylstyrene, 3,5-diethylstyrene, *p*-*t*-butylstyrene, *p*-cyclohexylstyrene, 6-vinyl-1,2,3,4-tetrahydronaphthalene, *p*-phenoxystyrene, 1-chloro-4-vinylnaphthalene, 2-vinylfluorene, 1-vinylacenaphthene, 2-vinyldiphenylene oxide and 4-chloro-4′-vinylbiphenyl.

The intermediate carbinols from which these eleven compounds were prepared are characterized and their preparation from the analogous arylmethyl ketones is described. The Perrier modification of the Friedel–Crafts synthesis is shown to be especially advantageous for the acetylation of alkylbenzenes and thiophene.

DAYTON, OHIO RECEIVED MARCH 4, 1946

[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES, MONSANTO CHEMICAL CO.]

Vinyl Aromatic Compounds. II. *o*-, *m*- and *p*-Vinylbiphenyls

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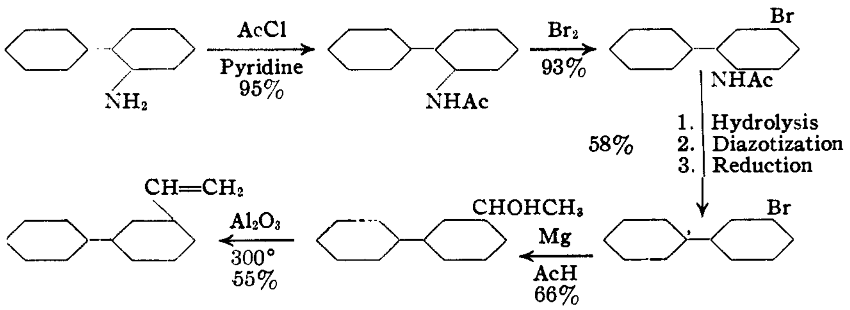
The vapor-phase dehydration of arylmethylcarbinols[2] to the analogous vinyl aromatic compounds has been extended to the preparation of all three isomers of vinylbiphenyl. *o*-Vinylbiphenyl has been synthesized by Bradsher and Wert,[3] who obtained a 24% yield by conducting the dehydration of *o*-biphenylylmethylcarbinol in the liquid phase over potassium bisulfate at 160°. By the vapor phase dehydration we have obtained a 70% yield of *o*-vinylbiphenyl.

p-Acetylbiphenyl has been prepared by the action of acetic acid on biphenyl in liquid hydrogen fluoride solution in 45% conversion and 70% yield.

p-Biphenylylmethylcarbinol, m. p. 97°, was prepared by catalytic hydrogenation of *p*-phenylacetophenone. This carbinol has been previously made by Adam[4] who reduced the ketone with sodium and alcohol and reported a melting point of 85–86°. It was our experience that when ethanol was used as a solvent for recrystallization the melting point could not be raised above 86°, but when a mixture of benzene and ligroin was used the purer material of m. p. 97° was easily obtained. Vapor phase dehydration of the carbinol gave 75–85% yields of *p*-vinylbiphenyl.

m-Vinylbiphenyl was prepared according to the synthesis outlined. The synthesis for *m*-bromobiphenyl in 51% over-all yield from readily available *o*-aminobiphenyl represents an improvement over the known[5] somewhat hazardous method of coupling *m*-bromobenzenediazonium hydroxide with benzene in 28%[6] yield.



In order to obtain comparative descriptive data the previously unreported *o*- and *m*-acetylbiphenyls and the *o*- and *m*-ethylbiphenyls were prepared.

p-Ethylbiphenyl also was synthesized by catalytic hydrogenation of *p*-biphenylylmethylcarbinol and melted, after repeated recrystallization from methanol, at 34.0–34.5°. Auwers and Julicher[7] have reported this compound to melt at 46–47°. Their compound originated from the formic acid dehydration and vacuum distillation of the compound

and it was stated to be identical with a sample prepared by the Clemmensen reduction of *p*-acetylbiphenyl. In order to clarify this discrepancy, *p*-ethylbiphenyl was synthesized by two more independent methods, *i.e.*, the Clemmensen reduction of *p*-acetylbiphenyl and by the repeated low-temperature recrystallization of the mixture of *m*- and *p*-ethylbiphenyls obtained by ethylation of biphenyl. Both samples melted at 34.0–34.5°, and were identical with the original sample. We have concluded, therefore, that the earlier work is in error. Since the ultimate analysis reported by Auwers and Julicher for their degradation product conforms to that required by *p*-methylbiphenyl almost as closely as to that required by *p*-ethylbiphenyl and, since the former compound is known[8] to melt at 47–48°, it is possible that the com-

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[2] Mowry, Renoll and Huber, THIS JOURNAL, **68**, 1105 (1946).

[3] Bradsher and Wert, *ibid.*, **62**, 2806 (1940).

[4] Adam, *Bull. soc. chim.*, [2] **49**, 97–102 (1888).

[5] Gomberg and Bachmann, THIS JOURNAL, **46**, 2339 (1924).

[6] Marvel, Ginsberg and Mueller, *ibid.*, **61**, 77 (1939), report 16% yields.

[7] Auwers and Julicher, *Ber.*, **55B**, 2167 (1922).

[8] Gattermann, *Ann.*, **347**, 381 (1906).