[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Relative Stability of Penta-Arylethanes. I. The Preparation of Penta-Arylethanes

BY W. E. BACHMANN

Gomberg and Cone[1] obtained pentaphenylethane for the first time by allowing magnesium, activated by iodine, to react with a mixture of triphenylchloromethane and diphenylbromomethane in ether

$$(C_6H_5)_3CCl + Mg + BrCH(C_6H_5)_2 \longrightarrow (C_6H_5)_3CCH(C_6H_5)_2 + MgBrCl$$

Schmidlin[2] is probably correct in his belief that triphenylmethylmagnesium chloride is formed as an intermediate product and that it reacts subsequently with diphenylbromomethane. Indeed, we have now found that the most feasible method of preparing pentaphenylethane is to carry out the reaction in these two distinct steps: (a) preparation of triphenylmethylmagnesium halide, followed by (b) reaction of the Grignard reagent with diphenylbromomethane

$$(C_6H_5)_3CBr + Mg \longrightarrow (C_6H_5)_3CMgBr \qquad \text{(a)}$$
$$(C_6H_5)_3CMgBr + BrCH(C_6H_5)_2 \longrightarrow (C_6H_5)_3CCH(C_6H_5)_2 + MgBr_2 \qquad \text{(b)}$$

By carrying out the reaction in two steps instead of in one the formation of hexaphenylethane and tetraphenylethane is avoided. By using different diarylmethyl halides eight new penta-arylethanes have been prepared.

All of the penta-arylethanes that were prepared have melting points which are lower in air than in nitrogen. There is no doubt that the lower value is caused by the formation of oxidation products by the oxygen of the air. Whether the reaction is an oxidation of the ethane itself at the ethane carbon–carbon bond or an oxidation of free radicals formed by dissociation as has been supposed in the case of pentaphenylethane[3] is left undecided at this time. In both air and in nitrogen the compounds soften and assume a yellow color as the melting point is approached and the compounds melt over a range of temperature to orange-red liquids, evidences of decomposition. In Table I are given the yields of the penta-arylethanes and also the melting points, or rather decomposition points, as determined in air and in nitrogen. For comparison is given the melting point under similar conditions of diphenyldibiphenylene-ethane, the hexa-arylethane which the penta-arylethanes resemble to some extent.

We have undertaken an investigation of the relative stability of the ethane carbon–carbon bond in the polyarylethanes and have begun with the study of the penta-arylethanes. In future communications there will be reported the reactions of the penta-arylethanes with a number of reagents. Other ethanes in which the triarylmethyl group is also sub-

---

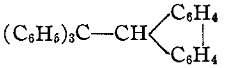
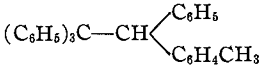
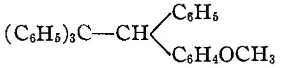
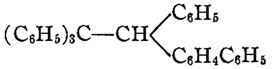
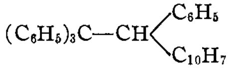
(1) Gomberg and Cone, *Ber.*, **39**, 1466 (1906).

(2) Schmidlin, "Das Triphenylmethyl," Ferdinand Enke, Stuttgart, 1913, p. 142.

(3) Tschitschibabin, *Ber.*, **40**, 367 (1907); Schlenk and Herzenstein, *ibid.*, **43**, 3542 (1910).

TABLE I

YIELDS AND MELTING POINTS OF PENTA-ARYLETHANES

Name, ethane	Formula	Yield, %	Melting point, °C. In air	Melting point, °C. In N_2
Pentaphenyl-	$(C_6H_5)_3C—CH(C_6H_5)_2$	90	166–178	182–185[4]
Triphenylbiphenylene-	 $(C_6H_5)_3C—CH\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}$	99	234–245	248–256
Tetraphenyl-*p*-tolyl-	 $(C_6H_5)_3C—CH\genfrac{}{}{0pt}{}{C_6H_5}{C_6H_4CH_3}$	80	176–181	183–185
Triphenyldi-*p*-tolyl-	$(C_6H_5)_3C—CH(C_6H_4CH_3)_2$	71	163–172	170–180
Tetraphenylanisyl-	 $(C_6H_5)_3C—CH\genfrac{}{}{0pt}{}{C_6H_5}{C_6H_4OCH_3}$	70	162–168	172–176
Triphenyldianisyl-	$(C_6H_5)_3C—CH(C_6H_4OCH_3)_2$	40	163–173	168–176
Tetraphenyl-*p*-biphenyl-	 $(C_6H_5)_3C—CH\genfrac{}{}{0pt}{}{C_6H_5}{C_6H_4C_6H_5}$	70	161–171	166–175
Triphenyldi-*p*-biphenyl-	$(C_6H_5)_3C—CH(C_6H_4C_6H_5)_2$	90	171–180	180–190
Tetraphenyl-α-naphthyl-	 $(C_6H_5)_3C—CH\genfrac{}{}{0pt}{}{C_6H_5}{C_{10}H_7}$	72	184–194	194–196
Diphenyldibiphenylene-	$C_6H_5(C_6H_4)_2CC(C_6H_4)_2C_6H_5$		205–230	254[5]

stituted are being prepared as well as penta-arylethanes of the type R_3-CCR_2A in which the hydrogen atom is replaced by an alkyl group A. An attempt was made to prepare the unsymmetrical hexa-arylethane, tetraphenylbiphenylene-ethane, $(C_6H_5)_3CC(C_6H_4)_2C_6H_5$, for comparison with the penta-arylethanes but the trial was unsuccessful (see experimental part).

Experimental

Preparation of Diarylmethyl Bromides.—We found that diarylmethyl bromides can be prepared readily by the action of a mixture of a 30% solution of hydrogen bromide in acetic acid and acetyl bromide on diarylcarbinols; the acetyl bromide serves to combine with the water liberated in the reaction. To 0.1 gram mole of carbinol is added 75 cc. of the hydrogen bromide solution and the mixture is heated on a steam-bath for one hour. The mixture is cooled slightly and treated with 15 cc. of acetyl bromide and heating is continued for another hour. Usually most of the solvent is removed by distillation under reduced pressure and the bromide is purified by recrystallization or by distillation under reduced pressure. In Table II are given the results obtained by following this procedure.

TABLE II

YIELDS OF DIARYLMETHYL BROMIDES

Diarylmethyl bromide	Yield, %	Diarylmethyl bromide	Yield, %
9-Bromofluorene	80	Phenyl-*p*-biphenylbromomethane[c]	78
Phenyl-*p*-tolylbromomethane[a]	70	Di-*p*-biphenylbromomethane[d]	90
Di-*p*-tolylbromomethane[b]	80	Phenyl-α-naphthylbromomethane[e]	90

[a] Phenyl-*p*-tolylcarbinol was prepared by the method described recently [Bachmann, THIS JOURNAL, **55**, 770 (1933)]; from 20 g. of ketone there was obtained 20 g. of

---

(4) Tschitschibabin reported 178–179° as the melting point in carbon dioxide.

(5) Schlenk, Herzenstein and Weickel, *Ber.*, **43**, 1754 (1910).

carbinol. The phenyl-*p*-tolylbromomethane was purified by distillation; b. p. 190–200° (15 mm.).

[b] Di-*p*-tolylcarbinol was prepared in quantitative yield by the method employed for phenyl-*p*-tolylcarbinol. Di-*p*-tolylbromomethane is extremely soluble in benzene and in acetic acid, readily soluble in hot ligroin but not in cold ligroin. It was obtained as colorless plates from ligroin; m. p. 48.5–49.0°. *Anal.* Calcd.: Br, 29.1. Found: Br, 29.2.

[c] Phenyl-*p*-biphenylbromomethane crystallizes in colorless needles from a mixture of benzene and ligroin; m. p. 104°. *Anal.* Calcd.: Br, 24.7. Found: Br, 24.5. This halide was also prepared by bromination of phenyl-*p*-biphenylmethane. Nine cc. of bromine was added drop by drop to 40 g. of phenyl-*p*-biphenylmethane which was heated to 185°; during the addition the mixture was well shaken. The product was cooled and recrystallized twice from a mixture of benzene and ligroin; yield, 22 g. The products obtained by the two methods are identical; however, it is easier to obtain a pure compound from the carbinol.

[d] Two hundred cc. of benzene was used as solvent in the preparation of the di-*p*-biphenylbromomethane; m. p. 145°.

[e] Acree, *Ber.*, **37**, 2757 (1904), obtained phenyl-α-naphthylcarbinol in 18% yield from benzaldehyde and α-naphthylmagnesium bromide. We were able to prepare the carbinol in 74% yield by the following procedure. The Grignard reagent was prepared from 130 g. of α-bromonaphthalene and 15 g. of magnesium in a mixture of 250 cc. of ether and 250 cc. of benzene. The solution was decanted from the excess of magnesium, cooled and treated with 53 g. of benzaldehyde drop by drop. After twelve hours the mixture was hydrolyzed; the carbinol was recrystallized from a mixture of benzene and petroleum ether; weight, 86 g.

Phenylanisylchloromethane, $C_6H_5(CH_3OC_6H_4)CHCl$.—Phenylanisylcarbinol was prepared by the Grignard reaction from anisaldehyde and phenylmagnesium bromide.[6] The Grignard reagent from 40 g. of bromobenzene in 120 cc. of ether was cooled in ice water; 28 g. of anisaldehyde was added drop by drop to the well-shaken Grignard reagent in the course of half an hour. When the addition was complete, the clear solution was kept at 0° for twenty-four hours; during this time practically all of the bromomagnesium salt of the carbinol crystallized. The crystals were filtered off, washed with ligroin and hydrolyzed with cold dilute acetic acid. The carbinol was taken up in benzene; from the benzene solution 40 g. (90%) of phenylanisylcarbinol was obtained.

Attempts to prepare the carbinol bromide from the carbinol were unsuccessful. The chloride was readily prepared by the action of hydrogen chloride gas on the carbinol in benzene at 0° in presence of calcium chloride. Phenylanisylchloromethane is very soluble in benzene but is little soluble in cold ligroin; it was obtained as colorless needles by recrystallization from ligroin; yield, 18.5 g. from 20 g. of carbinol; m. p. 64°.

Anal. Calcd. for $C_{14}H_{13}OCl$: Cl, 15.2. Found: Cl, 15.3.

Preparation of Triphenylbromomethane.—We have employed triphenylbromomethane instead of the chloride for the preparation of the Grignard reagent because it is easy to obtain quantitative yields of the Grignard reagent from the bromide.[7] To prepare triphenylbromomethane, a mixture of 180 g. of triphenylcarbinol and 110 cc. of acetyl bromide[8] is heated on a steam-bath for fifteen hours. The triphenylbromomethane is filtered off, washed with petroleum ether and recrystallized by dissolving it in hot benzene and adding an equal volume of petroleum ether. After being filtered and

---

(6) Kohler and Patch, *Ber.*, **38**, 1213 (1916), obtained unsatisfactory results by this method.

(7) Gomberg and Bachmann, *ibid.*, **52**, 2455 (1930).

(8) Gomberg and Davis, *ibid.*, **36**, 3925 (1903), prepared triphenylchloromethane by using acetyl chloride.

washed with petroleum ether the triphenylbromomethane is dried in a desiccator over soda-lime and paraffin; total yield, 190 g.; m. p. 151–152°.

Preparation of Pentaphenylethane.—A solution of triphenylmethylmagnesium bromide was prepared by refluxing a mixture of 32.3 g. (0.1 mole) of triphenylbromomethane, 2.5 g. of magnesium ribbon, 50 cc. of ether and 100 cc. of benzene in an atmosphere of nitrogen. After sixteen hours the solution was cooled slightly and decanted from the excess of magnesium into another flask; to the solution was added 27.8 g. (0.1 mole) of diphenylbromomethane in portions with cooling. The resulting mixture was warmed for two hours on a water-bath and then allowed to stand overnight. The mixture was treated with water containing a few cc. of acetic acid; the ether–benzene solution was separated from the aqueous solution, filtered and evaporated. The pentaphenylethane was obtained in the form of colorless plates by recrystallization from a mixture of chloroform and alcohol; weight, 37 g.

The other ethanes were prepared essentially according to the same procedure. A number of ethanes hold solvent of crystallization tenaciously; for analysis the compounds were dried at 80° under reduced pressure for fifteen hours. In Table III are given the properties of the penta-arylethanes; all of the ethanes were obtained as colorless crystals.

TABLE III

PROPERTIES OF PENTA-ARYLETHANES

Abbreviations: alc., alcohol; bz, benzene; ch., chloroform; lig., ligroin; ac., acetone; c., cold; h., hot; v., very; s., soluble; sls., slightly soluble; i., insoluble or very slightly soluble.

			Solubility				Analyses, %		
Ethane	Recryst. solvents	Cryst. form	Alc.	Bz	Lig.	Ac.		Calcd.	Found
1,1,1-Triphenyl-2-biphenylene-[a]	Ch. + alc.	Heavy needles	i	s(h)	i		C,	94.1	94.1
							H,	5.9	6.0
1,1,1,2-Tetraphenyl-2-(*p*-tolyl)-	Bz + alc.	Hexagon. plates	s	s	i		C,	93.4	94.0
							H,	6.6	6.9
1,1,1-Triphenyl-2,2-bis-(*p*-tolyl)-	Bz + alc.	Clusters needles	sls	vs(h)	i	s(h)	C,	93.1	93.0
							H,	6.9	7.0
1,1,1,2-Tetraphenyl-2-anisyl-[b]	Bz + alc.	Clusters needles	sls	vs	i		C,	90.0	89.8
							H,	6.4	6.4
1,1,1-Triphenyl-2,2-dianisyl-[c]	Bz + alc.	Diamond plates	sls	vs(h) s(c)	i		C,	86.8	86.4
							H,	6.4	6.4
1,1,1,2-Tetraphenyl-2-(*p*-biphenyl)-	Bz + alc.	Large needles	sls (h)	vs(h)	i		C,	93.8	94.0
							H,	6.2	6.2
1,1,1-Triphenyl-2,2-bis-(*p*-biphenyl)-[d]	Bz + alc.	Fine needles	i(h)	vs(h)	i	sls	C,	93.9	93.5
							H,	6.1	6.2
1,1,1,2-Tetraphenyl-2-(α-naphthyl)-	Bz + lig.	Prisms	i	s(h)	i	i	C,	93.9	93.7
							H,	6.1	6.2

[a] Triphenylbiphenylene-ethane crystallizes from benzene in large colorless prisms which contain benzene of crystallization.

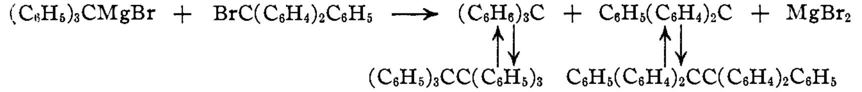
[b] Tetraphenylanisylethane was prepared by adding a benzene solution of phenylanisylchloromethane to an ice-cold solution of triphenylmethylmagnesium bromide; the resulting mixture was kept cold for several hours and then allowed to stand at room temperature for twenty hours.

[c] Triphenyldianisylethane was prepared from dianisylchloromethane and triphenylmethylmagnesium bromide in the manner of tetraphenylanisylethane.

[d] The ethane is soluble to the extent of 1 g. in 2 cc. of benzene: from benzene the ethane crystallizes in large colorless prisms.

Determination of Melting Points.—Since the compounds decompose in the neighborhood of the melting point the latter value will depend upon the rate of heating, presence of catalysts and other factors. In order to cut down the time of heating the melting point tubes were put into the bath at 150° and rather rapid heating was employed; the values reported in Table I were obtained in this manner under nearly identical conditions.

Reaction between Triphenylmethylmagnesium Bromide and Phenylbiphenylenebromomethane.—From the interaction of these two reagents there were obtained triphenylmethyl and phenylbiphenylenemethyl, both of which associated to the respective symmetrical hexa-arylethanes in preference to combining to give the unsymmetrical ethane, tetraphenylbiphenylene-ethane

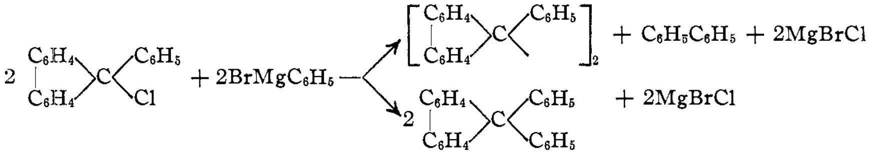


$$\begin{array}{ccccccc} (C_6H_5)_3CMgBr + BrC(C_6H_4)_2C_6H_5 & \longrightarrow & (C_6H_6)_3C & + & C_6H_5(C_6H_4)_2C & + & MgBr_2 \\ & & \uparrow\downarrow & & \uparrow\downarrow & & \\ & & (C_6H_5)_3CC(C_6H_5)_3 & & C_6H_5(C_6H_4)_2CC(C_6H_4)_2C_6H_5 & & \end{array}$$

A solution of 8.2 g. of phenylbiphenylenebromomethane in 30 cc. of benzene was added to a solution of triphenylmethylmagnesium bromide that had been prepared from 8.2 g. of triphenylbromomethane in 13 cc. of ether and 25 cc. of benzene. After a few minutes 5.9 g. (98%) of diphenyldibiphenylene-ethane precipitated while the hexaphenylethane remained in solution. A similar type of reaction occurs to some extent between phenylmagnesium bromide and phenylbiphenylenechloromethane.

Reaction between Phenylmagnesium Bromide and Phenylbiphenylenechloromethane.—Schmidt-Nickels[9] reported that diphenyldibiphenylene-ethane and not diphenylfluorene was formed in this reaction. When we[10] tried the reaction diphenylfluorene was obtained. We have now repeated the experiment and this time we obtained a mixture of diphenyldibiphenylene-ethane and diphenylfluorene in nearly equivalent quantities.

A solution of 21 g. of phenylbiphenylenechloromethane in 80 cc. of ether was added in portions to the Grignard reagent from 15 cc. of bromobenzene in 60 cc. of ether in an atmosphere of nitrogen; the mixture was refluxed for three hours and then hydrolyzed. From the products there was isolated 5.3 g. of diphenylfluorene (23% of the calculated value) and 4.8 g. of diphenyldibiphenylene-ethane (26%); the residue was a gum which did not crystallize. It is apparent that the reaction proceeds both as Schmidt-Nickels and as we formulated it.



Summary

Pentaphenylethane can be obtained in excellent yield by interaction of triphenylmethylmagnesium bromide and diphenylbromomethane. Eight new penta-arylethanes of the type $(C_6H_5)_3CCHRR'$ were prepared from triphenylmethylmagnesium bromide and diarylmethyl halides.

All of the penta-arylethanes show melting points, or rather decomposition points, which are lower in air than in nitrogen.

ANN ARBOR, MICHIGAN

RECEIVED DECEMBER 8, 1932
PUBLISHED MAY 6, 1933

---

[9] Schmidt-Nickels, *Ber.*, **62**, 917 (1929).

[10] Bachmann, THIS JOURNAL, **52**, 3289 (1930).