Summary

Alkyldichloroamines react with Grignard reagents to form primary, secondary and tertiary amines.

Dialkylchloroamines form secondary and tertiary amines with Grignard reagents, and monoalkylmonochloroamines form primary and secondary amines.

IOWA CITY, IOWA

RECEIVED MARCH 6, 1933
PUBLISHED JULY 6, 1933

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

The Relative Stability of Penta-arylethanes. II.[1] Reactions of Penta-arylethanes

BY W. E. BACHMANN

The remarkable properties of Gomberg's hexaphenylethane have shown clearly that substitution of phenyl groups for the hydrogen atoms of ethane weakens the ethane carbon–carbon bond; with complete substitution, rupture of the bond occurs at room temperature and free radicals are formed. Of the polyarylethanes containing less than six aryl groups pentaphenylethane has been found to have a weak union between the ethane carbon atoms. Pentaphenylethane is stable at room temperature but undergoes decomposition at 180° as was first observed by Gomberg and Cone,[2] the discoverers of the compound, and this decomposition has been shown to consist of a rupture of the ethane carbon–carbon bond.[3] We have now investigated a number of penta-arylethanes in order to ascertain the effect of introducing into the penta-arylethane molecule those groups that have been found to exert a great influence in promoting dissociation of hexa-arylethanes. It was surmised that penta-arylethanes containing naphthyl, biphenyl and anisyl groups would be nearer in properties to the hexa-arylethanes than is pentaphenylethane itself.

Recently[1] we described a method of preparing penta-arylethanes of any desired structure. We found that in the region of the melting point all of the penta-arylethanes that were prepared suffered decomposition and were oxidized by the oxygen of the air. A number of methods have now been employed in order to obtain a comparison of the relative stabilities of the ethane carbon–carbon bonds.

Formation of Color.—Gomberg and Cone[2] observed the development of a yellow color when solid pentaphenylethane was heated. Schlenk and Herzenstein[3] noticed a similar color on heating a solution of pentaphenylethane in ethyl benzoate and they attributed the color to the forma-

---

[1] Bachmann, THIS JOURNAL, **55**, 2135 (1933).

[2] Gomberg and Cone, *Ber.*, **39**, 1466 (1906).

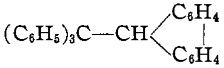
[3] Tschitschibabin, *ibid.*, **40**, 367 (1907); Schlenk and Herzenstein, *ibid.*, **43**, 3542 (1910).

tion of triphenylmethyl by dissociation of the pentaphenylethane. We have now found that all of the penta-arylethanes show a color when they are heated in solution and we have made the appearance of color serve as an indicator of the temperature at which rupture of the ethane carbon-carbon bond takes place. Solutions of similar molar concentrations of the ethanes were heated side by side in an atmosphere of nitrogen and the temperature at which color appeared was observed. The results of these determinations are presented in Table I.

TABLE I

TEMPERATURE AT WHICH COLOR DEVELOPS

Concentration, 0.02 molar. Solvent, ethyl benzoate

Name of ethane	Formula	Color	Temp., °C.
Tetraphenyl-*α*-naphthylethane	$(C_6H_5)_3C—CH(C_6H_5)C_{10}H_7$	Yellow	85
Triphenyldi-*p*-biphenylethane	$(C_6H_5)_3C—CH(C_6H_4C_6H_5)_2$	Yellow	93
Triphenyldianisylethane	$(C_6H_5)_3C—CH(C_6H_4OCH_3)_2$	Yellow	95
Tetraphenylanisylethane	$(C_6H_5)_3C—CH(C_6H_5)C_6H_4OCH_3$	Yellow	97
Tetraphenyl-*p*-biphenylethane	$(C_6H_5)_3C—CH(C_6H_5)C_6H_4C_6H_5$	Yellow	98
Triphenyldi-*p*-tolylethane	$(C_6H_5)_3C—CH(C_6H_4CH_3)_2$	Yellow	99
Tetraphenyl-*p*-tolylethane	$(C_6H_5)_3C—CH(C_6H_5)C_6H_4CH_3$	Yellow	102
Pentaphenylethane	$(C_6H_5)_3C—CH(C_6H_5)_2$	Yellow	105
Triphenylbiphenylene-ethane	 $(C_6H_5)_3C—CH\begin{cases}C_6H_4\\ \vert\\ C_6H_4\end{cases}$	Yellow	170

In confirmation of the idea of dissociation is the fact that all of the ethanes give the same color (yellow), which should be the case if the color is due to triphenylmethyl, common to all of the ethanes. If the solutions are heated rapidly and then quickly cooled, the colors can be discharged by oxygen or by iodine. It will be of interest to observe the colors produced from ethanes having a substituted triarylmethyl group; in such cases the color of the solution should correspond to the color of the particular triarylmethyl present as a group in the ethane molecule.

Thermal Decomposition.—Although decomposition of the penta-arylethanes begins at the temperatures indicated in Table I, the rate of the reaction is extremely slow at those temperatures. At 180–212° pentaphenylethane is rapidly and completely decomposed; the presence of tetraphenylethane among the decomposition products suggested the formulation given in Equation 1.[3] We find that all of the penta-arylethanes undergo a similar thermal decomposition.

$$\begin{array}{lcc} 2(C_6H_5)_3C—CHR_1R_2 \longrightarrow & 2(C_6H_5)_3C & +\ 2CHR_1R_2 \\ & \uparrow\downarrow & \downarrow \\ & (C_6H_5)_3CC(C_6H_5)_3 & R_1R_2HCCHR_1R_2 \end{array} \qquad (1)$$

Since the tetra-arylethanes that are formed do not dissociate under the conditions employed, the reaction is irreversible and the decomposition of the penta-arylethane is complete. For purposes of comparison 0.0025 gram mole of penta-arylethane in 10 cc. of ethyl benzoate was heated at the boiling point of the solution in an atmosphere of nitrogen for one hour;

the solutions became yellow, orange, orange-red and finally red in color. All of the penta-arylethanes except triphenylbiphenylene-ethane were completely decomposed in this time; the triphenylbiphenylene-ethane was only two-thirds decomposed under these conditions.

Cleavage by Hydrogen Iodide.—We have found that all of the penta-arylethanes except triphenylbiphenylene-ethane are rapidly and completely reduced when they are heated in acetic acid solution (118°) with hydrogen iodide, alone or with red phosphorus. In the process the ethane carbon–carbon bond is broken and the products are triphenylmethane and a diarylmethane.

$$(C_6H_5)_3C\text{—}CHR_1R_2 \xrightarrow{HI} (C_6H_5)_3CH + HCHR_1R_2 \qquad (2)$$

This reaction undoubtedly represents a direct cleavage of the single bond and there is evidence that dissociation into radicals is unnecessary for addition of hydrogen, and in fact it does not occur except to a slight extent. Support for this view is furnished by a comparison of the rate of dissociation at the same temperature; it was found that the reduction proceeds at least one hundred times as fast as dissociation. The fact that no tetra-arylethane (see thermal decomposition) is obtained in the reaction is also an indication that no appreciable dissociation into radicals takes place prior to addition of hydrogen.

The reactions were carried out in an atmosphere of nitrogen in the following manner: 0.2 g. of iodine and 0.6 g. of red phosphorus were allowed to interact in 20 cc. of acetic acid for twenty minutes; 0.3 cc. of water and 0.0025 gram mole of penta-arylethane were introduced and the mixture was refluxed for one hour. The mixture of triphenylmethane and diarylmethane which was obtained from the solution was separated into the two components by recrystallization from benzene; the cooled solution deposited the triphenylmethane. The mixture of triphenylmethane and di-*p*-biphenylmethane was separated by means of carbon tetrachloride in which the triphenylmethane is very soluble. In all cases except triphenylbiphenylene-ethane the yield of triphenylmethane and diarylmethane was quantitative. In order to determine the relative rates of cleavage and of dissociation, pentaphenylethane was heated with the reducing mixture for only ten minutes; complete reduction took place. A similar solution of pentaphenylethane in acetic acid without hydrogen iodide was then refluxed for ten minutes; 99% of the pentaphenylethane was recovered unchanged.

The stabilizing effect of the biphenylene group on the carbon–carbon bond is manifested again in this reaction. Practically no cleavage of triphenylbiphenylene-ethane by hydrogen iodide and phosphorus occurs in boiling acetic acid; in caproic acid (207°) complete rupture of the bond is effected. The hexa-arylethane, diphenyldibiphenylene-ethane, like the penta-arylethanes, is rapidly reduced by hydrogen iodide in acetic acid to phenylfluorene. The mixture of hydrogen iodide and phosphorus is a reagent that can be used to distinguish the penta-arylethanes from tetraphenylethane, for neither *s* nor *as*-tetraphenylethane is affected by the reducing mixture even at 207°.

Cleavage by Alkali Metals.—A comparison of the relative strengths of the ethane bonds in the penta-arylethanes was also obtained by reaction of the ethanes with liquid sodium–potassium alloy (2:5), with 40% sodium amalgam (liquid) and with 1% sodium amalgam (liquid).[4]

In these reactions a solution of 0.0015 gram mole of penta-arylethane in 12 cc. of ether and 12 cc. of benzene was shaken in an atmosphere of nitrogen with the metal or amalgam in a 30-cc. bottle; of the 1% sodium amalgam 30 g. was employed; of the 40% amalgam 6 g.; of the sodium–potassium alloy 2.8 g. The start of the reaction was apparent from the formation of a red color. With 1% sodium amalgam no color was developed in any case. With 40% sodium amalgam tetraphenyl-*α*-naphthylethane, triphenyldi-*p*-biphenylethane and tetraphenyl-*p*-biphenylethane showed a red color in one to five minutes. The reaction with the liquid sodium–potassium alloy was rapid in all cases; most of the penta-arylethanes developed a color within five minutes. The extent of reaction was determined by hydrolyzing the mixture and estimating the amounts of triarylmethane and diarylmethane that were formed. With triphenylbiphenylene-ethane no red color was obtained; instead the solution became light-brown and a brown precipitate was formed. The facts that hydrolysis gave no triphenylmethane and carbonation gave no triphenylacetic acid indicated that cleavage did not take place.

TABLE II

CLEAVAGE OF PENTA-ARYLETHANES BY ALKALI METALS

Ethane	Na-K alloy	Na-Hg, 40%	Na-Hg, 1%
Hexaphenylethane	++++	++++	++++
Tetraphenyl-*α*-naphthylethane	++++	++++	–
Triphenyldi-*p*-biphenylethane	++++	++++	–
Tetraphenyl-*p*-biphenylethane	++++	+++	–
Triphenyldianisylethane	++++	++	–
Tetraphenylanisylethane	++++	+	–
Triphenyldi-*p*-tolylethane	++++	+	–
Tetraphenyl-*p*-tolylethane	++++	+	–
Pentaphenylethane	++++	+	–
Triphenylbiphenylene-ethane		+	–
as-Tetraphenylethane	++++	+	–
s-Tetraphenylethane	++++	+	–

– indicates that no cleavage occurs in twenty-four hours.
\+ indicates that less than 5% cleavage occurs in twenty-four hours.
++ indicates that 5–25% cleavage occurs in twenty-four hours.
+++ indicates that 25–50% cleavage occurs in twenty-four hours.
++++ indicates that 50–100% cleavage occurs in twenty-four hours.

It is evident that by means of 1% sodium amalgam it is possible to distinguish between hexaphenylethane and the penta-arylethanes; 40% sodium amalgam distinguishes between individual members of the penta-arylethanes. Although the two tetraphenylethanes are cleaved by sodium–potassium alloy, the penta-arylethanes are cleaved at a greater rate; this is especially true of the ethanes containing the naphthyl and biphenyl groups. The reaction between the penta-arylethane and the metal may be written in the following manner.

---

(4) Compare Conant and Garvey, THIS JOURNAL, **49**, 2599 (1927), who employed the action of these reagents on dixanthyls.

$$(C_6H_5)_3C{-}CHR_1R_2 + 2Na(\text{or } K) \longrightarrow (C_6H_5)_3CNa + NaCHR_1R_2 \qquad (3)$$

Schlenk and Marcus,[5] who found that pentaphenylethane is cleaved by potassium into triphenylmethyl potassium and diphenylmethyl potassium, interpreted the reaction as proof of dissociation of pentaphenylethane into radicals at room temperature. Ziegler and Thielmann,[6] however, considered that the reaction is a reaction of the single bond. Our results leave no doubt that the view of Ziegler and Thielmann is correct. Thus, no cleavage of the ethane occurs with 1% sodium amalgam, a reagent that is known to react rapidly with triphenylmethyl. The reaction is a direct cleavage of the single bond by the metal not only in the case of pentaphenylethane but also with the substituted ethanes.

Cleavage by Bromine.—We have confirmed the observation of Gomberg and Cone that the reaction between pentaphenylethane and bromine in carbon disulfide is very slow at room temperature. At higher temperatures we have found that a rapid reaction takes place. Thus, when a mixture of 1.0 g. of pentaphenylethane and 0.6 g. of bromine in 10 cc. of ethylene dibromide was heated at 100°, the bromine color disappeared in a few minutes; from the solution there was isolated 0.45 g. (55%) of triphenylbromomethane. The reaction is a direct cleavage of the ethane bond by the bromine.

$$(C_6H_5)_3C{-}CH(C_6H_5)_2 + Br_2 \longrightarrow (C_6H_5)_3CBr + BrCH(C_6H_5)_2 \qquad (4)$$

Conclusion.—The penta-arylethanes undergo a series of reactions that are similar to those of the hexa-arylethanes. Unlike those of the hexa-arylethanes, the reactions of the penta-arylethanes represent reactions merely of a weakened ethane carbon–carbon bond and not of free radicals; as a result higher temperatures are required for the penta-arylethanes to react. The strength of the ethane bond in the penta-arylethanes is affected greatly by the nature of the groups attached to the two carbon atoms. The naphthyl group greatly weakens the bond while the biphenylene group has a remarkable strengthening effect. From the results that have been described the groups can be arranged in the following order of ability to weaken the ethane bond in the penta-arylethanes: α-naphthyl > *p*-biphenyl > anisyl > *p*-tolyl > phenyl > biphenylene. This series is similar to that representing the relative effect of the groups in promoting dissociation of the hexa-arylethanes. Further studies on these and other penta-arylethanes will be reported in future communications.

Summary

A study has been made of the reactions of a number of penta-arylethanes. The ethane carbon–carbon bond in the penta-arylethanes is a weak bond and breaks readily under the influence of heat. A comparison has been

---

[5] Schlenk and Marcus, *Ber.*, **47**, 1671 (1914).

[6] Ziegler and Thielmann, *ibid.*, **56B**, 1740 (1926).

obtained of the temperatures at which breaking of the bond in the various ethanes takes place.

The strength of the ethane bond is affected by the nature of the aryl groups.

The ethane bond is cleaved by hydrogen iodide, by bromine, by sodium–potassium alloy and in some penta-arylethanes by 40% sodium amalgam.

ANN ARBOR, MICHIGAN RECEIVED MARCH 9, 1933
PUBLISHED JULY 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Synthesis of Phthaloylnaphthol[1]

BY LOUIS F. AND MARY FIESER

To the yellow substance resulting from the condensation of β-naphthol and phthalic acid in the presence of aluminum chloride,[2] Rieche and Frühwald, in the first recorded investigation of the compound,[3] assigned the structure of 1,8-phthaloyl-2-naphthol (I, below). Since this structure appeared to be out of harmony with certain observations which had been made by one of us, objection was raised to Rieche's views and an alternate formula was suggested.[4] In a more recent study of the interesting yellow compound, Rieche and his collaborators[5] have discovered certain new facts which definitely exclude our formula and which furnish convincing if not altogether satisfying evidence that the substance actually has the structure originally favored by the German investigators. After elimination of the hydroxyl group, the resulting compound was reduced by distillation over zinc dust to a hydrocarbon, and this could be converted into the original diketone by oxidation. Though this is the sole evidence that the compound contains two carbonyl groups, it would furnish a sufficient basis for accepting the Rieche formula were it not for the isolation in this Laboratory[4] of an oxidation product which is difficult to reconcile with the formula under discussion. A secondary oxidation product isolated was assigned the structure III, and the formation of this degradation product is entirely consistent with Rieche's formula, I. A precursor of III, however, was a substance regarded as having the structure of II, and it is not easy to see how this can be formed from I in a permanganate oxidation.

This was our most serious objection to Rieche's formula and, although we must grant that this author has made adequate reply to our other objections, we cannot agree that he is justified in waiving the problem presented by this product of oxidation. He regards the structure as still

---

[1] Fifth paper in the series: Condensations and Ring Closures in the Naphthalene Series.

[2] Fr. Bayer and Co., German Patent, 298,345 (1916).

[3] Rieche and Frühwald, *Ber.*, **64**, 1603 (1931).

[4] Fieser, THIS JOURNAL, **53**, 3546 (1931).

[5] Rieche, Sauthoff and Müller, *Ber.*, **65**, 1371 (1932).