

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Reaction of Potassium Amide in Liquid Ammonia with Diarylbromoethenes

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The behavior of certain diarylchloroethenes and ethanes with potassium amide in liquid ammonia has been reported in a previous paper.¹ These compounds are not affected by boiling alcoholic potassium hydroxide but are very rapidly changed with the loss of hydrochloric acid by potassium amide in liquid ammonia to the corresponding tolanes. To illustrate, 1,1-di-*p*-tolyl-2-chloroethene forms *p,p'*-dimethyltolane. A series of such para substituted compounds was studied and as anticipated only symmetrical tolanes were obtained.

The present paper is a report of work with diarylbromoethenes having substituents in the ortho and in the meta positions of the aryl radicals. The bromoethenes were used since they could be prepared more easily than the corresponding chlorine compounds. In order to determine whether bromoethenes would undergo the rearrangement with potassium amide as readily as chloroethenes, the reaction was first tried with 1,1-diphenyl-2-bromoethene and 1,1-di-*p*-tolyl-2-bromoethene. Good yields of tolanes were formed.

The following ortho and meta substituted bromoethenes were used: 1,1-di-*o*-tolyl-2-bromoethene; 1,1-di-*o*-methoxyphenyl-2-bromoethene; 1,1-di-*m*-tolyl-2-bromoethene; and 1,1-di-*m*-methoxyphenyl-2-bromoethene. In each case the corresponding symmetrical tolane was obtained.

With respect to the mechanism of the reaction the question of whether a proton or the halide ion is first removed from the molecule was considered. The loss of a proton due to the presence of a base (in this case the amide ion, NH_2^-) has been proposed as the initial step in several related reactions.² However, the mechanism given by Whitmore and Fleming³ for the formation of trimethylethylene and *t*-amyl acetate in the reaction of neopentyl iodide with silver acetate in acetic acid seems more applicable to the present case. Ac-

cording to this mechanism the diarylbromoethene first loses the halide ion leaving a carbon atom with a sextet of electrons. This carbon attracts a pair of electrons from the next carbon atom, the aryl group held by the shifting electron pair moving with it. The system thus formed is still electronically deficient. This deficiency is satisfied by the shift of an electron pair to form a triple bond and liberate a proton, thus forming a tolane.

If the loss of a proton is assumed as the first step the formation of a tolane can also be explained by a somewhat similar mechanism. However Buttenberg⁴ obtained a mixture of diphenylvinyl ethyl ether and tolane when 1,1-diphenyl-2-chloroethene was heated with sodium ethylate at about 200°. The formation of diphenylvinyl ethyl ether is not readily explained if the removal of a proton is assumed as the first step. In the present work with potassium amide no amine was found in the reaction product but this would not necessarily exclude the mechanism proposed.

In the work with diarylchloroethenes¹ it had been observed that the yields of tolanes were 90% or above for all the compounds used except those containing the *p*-ethylphenyl, *p*-*n*-propylphenyl and *p*-*n*-butylphenyl groups. From these compounds liquid mixtures were formed containing not more than 60% of the pure tolanes. In seeking the cause for this difference the purity of the starting material was considered. Since these diarylchloroethenes were liquids the purity could not be as easily determined as with solids. Therefore several diaryldibromoethanes and diaryldichloroethanes, all of which were solids were prepared, carefully purified and treated with potassium amide in liquid ammonia. The compounds used were: 1,1-diphenyl-2,2-dibromoethane, 1,1-diphenyl-2,2-dichloroethane, 1,1-di-*p*-tolyl-2,2-dibromoethane, 1,1-di-*p*-tolyl-2,2-dichloroethane, 1,1-di-*p*-ethylphenyl-2,2-dibromoethane and 1,1-di-*p*-ethylphenyl-2,2-dichloroethane. From the phenyl and *p*-tolyl compounds the yields of tolanes were about 90–95% of the theoretical. With the *p*-ethylphenyl compounds the products were again oily mixtures from which yields of only 50–70% of pure tolanes could be separated.

(1) Coleman and Maxwell, *THIS JOURNAL*, **56**, 132 (1934).

(2) (a) Mills, *J. Soc. Chem. Ind.*, **51**, 750 (1932); (b) Hauser and Moore, *THIS JOURNAL*, **55**, 4526 (1933); (c) Drake and McElvain, *ibid.*, **56**, 699, 1810 (1934); (d) Olivier, *Rec. trav. chim.*, **53**, 1093 (1934); (e) Hauser, Le Maistre and Rainsford, *THIS JOURNAL*, **57**, 1056 (1935).

(3) Whitmore and Fleming, *J. Chem. Soc.*, 1269 (1934). See also *THIS JOURNAL*, **54**, 3274 (1932).

(4) Buttenberg, *Ann.*, **279**, 327 (1894).

TABLE I
DIARYLBROMOETHENES, *sym*-DIARYLDIBROMOETHANES AND TOLANES

Substances	°C.	B. p. and m. p.	Mm.	Br Analyses, %	
				Calcd.	Found
1,1-Di- <i>o</i> -tolyl-2-bromoethene	150–155		1.5	27.87	28.01
1,1-Di- <i>m</i> -tolyl-2-bromoethene	186–191		10	27.87	28.22
1,1-Di- <i>o</i> -methoxyphenyl-2-bromoethene	M. p. 101.6–102.6			25.08	25.25
1,1-Di- <i>m</i> -methoxyphenyl-2-bromoethene	225–230		6	25.08	25.86
1,2-Di- <i>o</i> -tolyl-1,2-dibromoethane	M. p. 171–172			43.48	43.41
1,2-Di- <i>m</i> -tolyl-1,2-dibromoethane	M. p. 166.5–167			43.48	43.64
<i>m,m'</i> -Dimethyltolane	M. p. 73.5–74				
<i>m,m'</i> -Dimethoxytolane	M. p. 63–63.5				
<i>o,o'</i> -Dimethoxytolane	M. p. 124.5–125				
<i>o,o'</i> -Dimethyltolane	138–142		0.75	<i>n</i> _D ²⁰ 1.6228	

The structures of the tolanes were proved by two methods. One was the synthesis of the corresponding stilbene from monochloroacetal and Grignard reagents and the conversion of the stilbene to the symmetrical dibromoethane from which the tolane was formed by treatment with alcoholic potassium hydroxide. The other method was the reduction of the tolanes to bibenzyls with boiling absolute alcohol and sodium.⁵ This method was also used to prove more conclusively the structures of some of the tolanes reported in the previous paper.¹

Experimental Part⁶

Diarylbromoethenes.—The bromoethenes were prepared by treating the corresponding unsymmetrical diarylethenes with bromine by a modification of the method used by Hepp.⁷ The dibromo compounds formed by the addition of bromine were unstable and lost hydrogen bromine either during the reaction or the subsequent heating.

The unsymmetrical diarylethenes were prepared by treating the methyl diarylcarbinols with phosphorus pentachloride or thionyl chloride to form the methyl diarylchloromethanes followed by subsequent splitting out of hydrochloric acid by treatment with alcoholic potassium hydroxide or pyridine. The methyl diarylcarbinols were prepared by the method of Allen and Converse.⁸

The general procedure used in preparing the diarylbromoethenes is illustrated by the following preparation of 1,1-di-*o*-tolyl-2-bromoethene. Fourteen and one-half grams of di-*o*-tolylmethylcarbinol was dissolved in 100 cc. of carbon tetrachloride. After cooling the mixture to 0°, 7.6 g. of thionyl chloride was slowly added with occasional shaking. After addition, the reaction was allowed to proceed at room temperature for four hours. Fifteen grams of pyridine was added and the mixture was allowed to stand overnight. A solid, pyridine hydrochloride, formed and was filtered off, after which the solution was washed with water to remove excess pyridine and then dried with calcium chloride. After separating from the calcium

chloride 11 g. of bromine was added and the mixture allowed to stand one hour with occasional shaking. A little cyclohexene was added to remove the excess bromine and the solvent evaporated under reduced pressure. Thirteen grams of crude liquid remained. Upon distillation under reduced pressure, two fractions were obtained: Fraction (1) 1.9 g. boiling below 120° (1.5 mm.). Fraction (2) 10.9 g. boiling at 140–155° (1.5 mm.) (90% at 150–155°).

Anal. of Fraction (2). Calcd. for C₁₆H₁₆Br: Br, 27.87. Found: Br, 28.01.

The physical properties and analyses of the bromoethenes not previously recorded are given in Table I.

Tolanes.—The general procedure used in carrying out the reaction of potassium amide with bromoethenes was essentially the same as that reported by Coleman and Maxwell¹ with chloroethenes. The following preparation of *m,m'*-dimethyltolane will illustrate. Two grams of metallic potassium was dissolved in 350 cc. of liquid ammonia contained in a Dewar flask. The potassium was converted to the amide and 5 g. of 1,1-di-*m*-tolyl-2-bromoethene dissolved in ether was slowly added. After evaporation of the ammonia, the product was extracted with ether and the ethereal solution washed and dried. The solvent was evaporated under reduced pressure and 3.4 g. (91%) of crude solid, melting at 68–70°, remained. Upon recrystallization from 95% alcohol, 3.2 g. (89%) of pure *m,m'*-dimethyltolane melting at 73.5–74° was obtained. The tolanes prepared are given in Table I.

Stilbenes.—The preparation of the symmetrically substituted stilbenes was carried out by the method described by Späth.⁹ *o,o'*-Dimethylstilbene and *m,m'*-dimethylstilbene were both obtained in this manner.

Bromination of Stilbenes.—The procedure followed is illustrated by the following preparation of 1,2-di-*o*-tolyl-1,2-dibromoethane. One gram of *o,o'*-dimethylstilbene was dissolved in 10 cc. of dry carbon tetrachloride. To this solution 0.8 g. of bromine in 10 cc. of carbon tetrachloride was added. A white crystalline solid melting at 171–172° was obtained; yield 1.6 g. The two *sym*-diaryldibromoethanes prepared are given in Table I.

Tolanes from *sym*-Diaryldibromoethanes.—One gram of 1,2-di-*m*-tolyl-1,2-dibromoethane was refluxed with alcoholic potassium hydroxide for three hours. The solution was decanted from the potassium bromide and 50 cc. of ether added. This solution was washed with water, sepa-

(5) Aronstein and Holleman, *Ber.*, **21**, 2833 (1888).

(6) All melting points and boiling points are corrected.

(7) Hepp, *Ber.*, **7**, 1410 (1874).

(8) Allen and Converse, *Organic Syntheses*, Coll. Vol. I, 1932, p. 221.

(9) Späth, *Monatsh.*, **35**, 469 (1914).

rated and dried. The solvent was evaporated under reduced pressure. One-half gram of the crude tolane melting at 66–68° was obtained. Upon recrystallization from 95% alcohol, 0.48 g. of pure *m,m'*-dimethyltolane melting at 73.5–74° was obtained. A mixed melting point with *m,m'*-dimethyltolane prepared from 1,1-di-*m*-tolyl-2-bromoethene showed no depression.

The same procedure was used with 1,2-di-*o*-tolyl-1,2-dibromoethane. *o,o'*-Dimethyltolane was obtained, n_D^{20} 1.6214. The index of refraction of the tolane prepared from 1,1-di-*o*-tolyl-2-bromoethene was n_D^{20} 1.6228.

Bibenzyls.—All tolanes were reduced by the following method which is a modification of the one described by Aronstein and Holleman.⁵ One gram of tolane was dissolved in 15 cc. of absolute alcohol. The solution was heated to boiling and immediately poured, with caution, into a flask containing 1.5 g. of metallic sodium, cut in small pieces and freed from oxide and ligroin. The flask was then attached to a reflux condenser and the mixture refluxed until all the sodium was dissolved.

The mixture was cooled and 60 cc. of distilled water was added to decompose the sodium ethylate after which the entire solution was extracted with 100 cc. of ether. The ethereal solution was dried, filtered and the solvent evaporated under reduced pressure. One and one-tenth grams of crude bibenzyl melting at 49–51° remained. One gram of pure bibenzyl melting at 51.5–52.5° was obtained upon recrystallization from 95% alcohol. A mixed melting point with pure bibenzyl showed no depression. The bibenzyls prepared by this procedure are given in Table II.

TABLE II
BIBENZYLs

Substance	M. p., °C.	Reported in literature, °C.
Bibenzyl	51.5–52.5	52.5
<i>p,p'</i> -Dimethylbibenzyl	81–81.5	82
<i>m,m'</i> -Dimethylbibenzyl	Oil	Oil
<i>o,o'</i> -Dimethylbibenzyl	65.5–66	66.5
<i>p,p'</i> -Dimethoxybibenzyl	126.4–126.8	126–127
<i>m,m'</i> -Dimethoxybibenzyl	39.5–39.8	39–40
<i>o,o'</i> -Dimethoxybibenzyl	84–84.4	86–87
3,3',5,5'-Tetramethylbibenzyl	86–86.6
<i>p,p'</i> -Diethylbibenzyl	69.8–70.2

unsym-Diaryldichloroethanes.—The following unsymmetrical diaryldichloroethanes were prepared from dichloroacetal and aromatic hydrocarbons by the methods described by Buttenberg⁴ and by Wiechell:¹⁰ 1,1-diphenyl-2,2-dichloroethane, 1,1-di-*p*-tolyl-2,2-dichloroethane and 1,1-di-*p*-ethylphenyl-2,2-dichloroethane.

(10) Wiechell, *Ann.*, **279**, 337 (1894).

unsym-Diaryldibromoethanes.—Three unsymmetrical diaryldibromoethanes corresponding to the chloroethanes were prepared from dibromoacetal and aromatic hydrocarbons. The following procedure for the preparation of 1,1-di-*p*-tolyl-2,2-dibromoethane is typical.

Twenty-five grams of dibromoacetal¹¹ was dissolved in 20 g. of toluene in a 500-cc. Erlenmeyer flask. This mixture was cooled to 5–8° and 75 cc. of concd. sulfuric acid added with stirring at such a rate that the temperature did not rise above 50°. The mixture was stirred for one hour after addition of the acid. It was then poured into 600 cc. of ice and water, whereupon a solid separated; 16.8 g. (50%) melting at 93–96° was obtained. After recrystallization from 95% alcohol the melting point was 95.5–96.5°.

Tolanes from Diaryldibromoethanes and Diaryldichloroethanes.—The reactions of these compounds with potassium amide were carried out in essentially the manner described for the ethenes except that the relative amount of potassium amide was doubled. The results for the six compounds used are listed in Table III. The products were identified by mixed melting points with authentic samples.

TABLE III
DIARYLDICHLOROETHANES AND DIARYLDIBROMOETHANES
WITH POTASSIUM AMIDE IN LIQUID AMMONIA

Substance	M. p., °C.	Yield of tolanes, %
1,1-Diphenyl-2,2-dibromoethane	79.5–80.5	95
1,1-Diphenyl-2,2-dichloroethane	74–75	91
1,1-Di- <i>p</i> -tolyl-2,2-dibromoethane	95.5–96	92
1,1-Di- <i>p</i> -tolyl-2,2-dichloroethane	80–80.5	86
1,1-Di- <i>p</i> -ethylphenyl-2,2-dibromoethane	79–79.5	73
1,1-Di- <i>p</i> -ethylphenyl-2,2-dichloroethane	56–56.5	52

Summary

1. The action of potassium amide in liquid ammonia on 1,1-diaryl-2-bromoethenes causes the loss of a molecule of hydrogen bromide and the rearrangement of the molecule to form substituted tolanes.

2. A mechanism for the reaction is suggested. A given substituent in the phenyl group of the ethene is found in the same position relative to the point of attachment of the phenyl radical in the corresponding tolane.

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(11) Dworzak, *Monatsh.*, **46**, 255 (1925).