Methylbromanilate.—Three grams of 2-methoxy-3,5,6-tribromobenzoquinone, dissolved in 25 cc. of 2 *N* potassium hydroxide solution, warmed on the steam-bath, saturated with salt, cooled, and filtered, yielded 3 g. of fine long needles of potassium methylbromanilate, chocolate colored in the mass but colorless under the microscope. The same salt was prepared from 2-methoxy-3,5,6-tribromohydroquinone by dissolving 1 g. of that material in 10 cc. of 2 *N* potassium hydroxide solution and allowing to stand in the air for a day. The salt does not fuse at 350°. Its solutions in organic solvents are red, in water permanganate colored. Methylbromanilate was prepared from the potassium salt by dissolving 3 g. of the latter in 10 cc. of hot water, acidifying with 40 cc. of concd. hydrochloric acid, cooling, etc., and drying the red powder at 100° and finally in vacuum over potassium hydroxide. It does not melt at 350°.

Anal. Calcd. for $C_7H_4O_4Br_2$: Br, 51.25. Found: Br, 51.03, 51.00.

2-Methoxy-3,5,6-tribromohydroquinone.—Three and seventy-five hundredths grams of 2-methoxy-3,5,6-tribromobenzoquinone, reduced with sulfur dioxide in aqueous solution, yielded 3.5 g. (90%) of pure 2-methoxy-3,5,6-tribromohydroquinone, m. p. 175–176°, flat plates from benzene, diamond-shaped, probably monoclinic, having an extinction parallel to one of the edges, and having indices which "straddle" 1.72.

Anal. Calcd. for $C_7H_5O_3Br_3$: Br, 63.60. Found: Br, 63.55, 63.40.

Summary

Tribromoresorcinol evidently exists in the tautomeric pseudoquinoid form, for the effect of reagents upon it is the effect which the reagents would be expected to have upon the pseudoquinone or upon the 2,6-dibromo-3-hydroxybenzoquinyl-4, which corresponds to the loss of hydrogen bromide from that tautomer.

Tribromoresorcinol monomethyl ether on oxidation with chromic acid in glacial acetic acid solution yields methoxy-tribromobenzoquinone.

CAMBRIDGE, MASS. RECEIVED JULY 20, 1933

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

The Reaction of Potassium Amide in Liquid Ammonia with Chloroethenes[1]

BY GEORGE H. COLEMAN AND ROY D. MAXWELL

Tolane together with diphenylvinyl ethyl ether was obtained by Buttenberg[2] by heating 1,1-diphenyl-2-chloroethene with sodium ethylate in a sealed tube at 180–200° for eight hours. It has been observed in this Laboratory that tolane is formed in good yields and in a short time when the same chloroethene is treated with potassium amide in liquid ammonia. The present work was undertaken in order to study this reaction more fully and to determine the effect of substituents in the phenyl groups.

The chloroethenes used were: (a) 1,1-diphenyl-2-chloroethene, (b) 1,1-di-*p*-tolyl-2-chloroethene, (c) 1,1-di-*p*-ethylphenyl-2-chloroethene, (d) 1,1-di-*p*-*n*-propylphenyl-2-chloroethene, (e) 1,1-di-*p*-*n*-butylphenyl-2-chloroethene, (f) 1,1-di-3,4-dimethylphenyl-2-chloroethene, (g) 1,1-di-*p*-methoxyphenyl-2-chloroethene. With compounds (b), (f) and (g), the substituents in the phenyl groups evidently have little effect on the reaction since the yields of the substituted tolanes were about the same as the yield of tolane. In each reaction the yield of crude product was 90 to 95% of the theoretical. The melting points of the crude products were only a few degrees below the melting points of the pure compounds. With the ethylphenyl, propylphenyl and butylphenyl compounds the crude yields were above 90% of the theoretical and did not contain halogen. The products were, however, oily in character and not more than 55% of pure recrystallized material could be isolated.

Undried liquid ammonia obtained directly from a tank was found to be as satisfactory for the reaction as that purified by distillation after treatment with metallic sodium. In contrast to the reaction with sodium ethylate, which required eight to ten hours, the reaction with potassium amide is complete in ten minutes or less. In one reaction sodium amide was used in place of potassium amide and was found to be just as effective.

The preparation of tolanes by this method directly from dichloroethanes was also tried. For this purpose 1,1-diphenyl-2,2-dichloroethane and 1,1-dibiphenyl-2,2-dichloroethane were used.

(1) This communication is an abstract of a dissertation submitted by Roy D. Maxwell in partial fulfilment of the requirements for the degree of Doctor of Philosophy in chemistry at the State University of Iowa. A part of this work was presented at the Washington meeting of the American Chemical Society, March 1933.

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

The percentage yields of the corresponding tolanes were nearly as large as those from the chloroethenes.

The dichloroethanes from which the chloroethenes were formed were prepared by the condensation of aromatic hydrocarbons or ethers with dichloroacetal according to the method of Buttenberg.[2] The generalization has been made by Fritsch[3] that this condensation occurs in the position para to the side chain of the aromatic compound when that position is open. It has been shown by Buttenberg[2] and by Wiechell[4] that when 1,1-di-*p*-tolyl-2-chloroethene and 1,1-di-*p*-methoxyphenyl-2-chloroethene, as prepared through this condensation, are heated with sodium ethylate at 180–200° the disubstituted tolanes formed have the substituents in the para positions. In this work therefore the substituents in the phenyl groups in both the chloroethenes and the tolanes, which had not been previously prepared, were assumed to be in the para positions. In order to test this assumption in the case of diphenyltolane the compound was oxidized to *p*-phenylbenzoic acid.

Tiffeneau[5] has suggested that phenylcyclopropene may be an intermediate compound in the formation of phenylallylene from 1-methyl-1-phenyl-2-bromoethene when the latter is treated with fused potassium hydroxide. The rearrangements of the diarylchloroethenes to tolanes evidently cannot be explained in a similar manner. In these rearrangements a given substituent in the para position in the phenyl group of the chloroethene is found in the para position in the corresponding tolane. It will be of interest to determine whether or not this is true also for the ortho and meta positions.

The absorption spectra[6] of the chloroethenes and the corresponding tolanes in the ultraviolet region between 3200 and 2000 Å. units were determined by means of a quartz spectrograph and a sectorphotometer. The tolanes showed two characteristic bands, while the chloroethenes showed non-selective absorption in the region between 2800 and 2000 Å. units. For the series of compounds: tolane, dimethyl, diethyl, di-*n*-propyl and di-*n*-butyl tolane a slight but regular shift in the position of the absorption bands was observed.

Experimental

Diarylchloroethenes and Ethanes.—The methods used for the preparation of the chloroethanes and chloroethenes were essentially those described by Buttenberg[2] and by Wiechell.[4] The physical properties and analyses of the chloroethenes not previously recorded are given in Table I.

TABLE I

DIARYLCHLOROETHENES

Substance	B. p., °C. (corr.) (1 mm.)[a]	n^{20}_{D}	Yield,[b] %	Formula	Cl analyses, % Calcd.	Found
1,1-Di-*p*-ethylphenyl-2-chloroethene	165–166	1.5898	63	$C_{18}H_{19}Cl$	13.12	13.27
1,1-Di-*p*-*n*-propylphenyl-2-chloroethene	178–181	1.5782	60	$C_{20}H_{23}Cl$	11.81	11.61
1,1-Di-*p*-*n*-butylphenyl-2-chloroethene	190–192	1.5652	62	$C_{22}H_{27}Cl$	11.15	11.06
1,1-Di-3,4-dimethylphenyl-2-chloroethene	166–170	1 6035	57	$C_{18}H_{19}Cl$	13.12	13.22

[a] Distillation pressure was usually less than 1 mm. [b] Yields were calculated from the dichloroacetal used.

1,1-Dibiphenyl-2,2-dichloroethane.—Five grams of diphenyl was mixed with 5 g. of dichloroacetal and 40 cc. of sulfuric acid. The mixture was heated to 50° for ten minutes and then poured into ice water. The oily condensation product was filtered off and triturated with 50% alcohol. After filtering, the powder-like material was recrystallized from 95% alcohol. The melting point was 139–140°.

Anal. (Parr bomb) Calcd. for $C_{26}H_{20}Cl_2$: Cl, 17.98. Found: Cl, 18.02.

Tolanes.—The general procedure used in carrying out the reaction of potassium amide with chloroethenes is illustrated by the following preparation of *p,p'*-dimethyltolane. Three and five-tenths grams of metallic potassium was dissolved in 350 cc. of liquid ammonia contained in a Dewar flask or a flask immersed in a mixture of solid carbon dioxide and acetone. The potassium was converted to the amide by suspending a rusty iron nail in the solution. This required forty-five minutes to one hour. Nine and one-tenth grams of 1,1-di-*p*-methylphenyl-2-chloroethene was dissolved in ether and added to the solution, fifteen minutes being required for the addition. After evaporation of the ammonia, water was added to the residue and the mixture filtered. Seven and three-tenths grams (92% of the theoretical amount) of crude dimethyltolane was obtained, melting at 127–132°. This was recrystallized from acetic acid, and melted at 136–136.5°. Buttenberg[2] recorded 136° as the melting point of dimethyltolane.

Usually water was not added to the reaction mixture until after the evaporation of the ammonia. The yields of tolanes were not affected, however, when water was added ten minutes after the addition of the chloroethene.

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[3] Fritsch, *Ann.*, **279**, 323 (1894).

[4] Wiechell, *ibid.*, **279**, 337 (1894).

[5] Tiffeneau, *Compt. rend.*, **135**, 1347 (1902).

[6] The authors are indebted to Mr. D. C. McCann and Dr. L. J. Waldbauer of this Laboratory for the determination of the absorption spectra.

TABLE II

TOLANES

Substance	M. p., °C. (corr.)	Solvent	Formula	Molecular weight Calcd.	Molecular weight Found	Method
p,p'-Diethyltolane	71.5–72.5	Methanol	$C_{18}H_{18}$	234	226	Rast
p,p'-Di-*n*-propyltolane	69.5–70.5	Methanol	$C_{20}H_{22}$			
p,p'-Di-*n*-butyltolane	41–42	Methanol	$C_{22}H_{26}$	290	270	Freezing benzene
3,3',4,4'-Tetramethyltolane	143–144	Acetic acid	$C_{18}H_{18}$			
p,p'-Diphenyltolane	243–244	Benzene	$C_{26}H_{18}$	330	347	Boiling benzene

With the low melting tolanes the crude products were oils and were extracted with ether. The ethereal solutions were dried with calcium chloride and the ether evaporated. The residues crystallized upon standing several hours in a vacuum desiccator.

Tolane and *p,p'*-diphenyltolane were prepared by the action of potassium amide on the corresponding dichloroethanes. The yields of crude product were 85 and 91%, respectively. A sample of the *p,p'*-diphenyltolane was oxidized with ozone by the method used by Harries[7] for other acetylene derivatives. The acid obtained was shown to be *p*-phenylbenzoic acid by its melting point and by a mixed melting point with known *p*-phenylbenzoic acid.

In Table II are given the physical properties of the tolanes not previously recorded.

Absorption Spectra.—In studying the absorption spectra a Hilger quartz spectrograph and a Hilger sector photometer were used. A tungsten steel spark was the source of light. The reference line from which the wave lengths were determined was that of iron at 4957 Å. units.

In Table III are given the positions of the absorption bands of tolane and substituted tolanes. Chloroethenes show non-selective absorption in the region between 200–280 millimicrons.

TABLE III

POSITIONS OF ABSORPTION BANDS OF TOLANE AND SUBSTITUTED TOLANES (WAVE LENGTHS IN mμ)

	Wave length	Wave length
Tolane	298	279
Dimethyltolane	304	284
Diethyltolane	305	287
Di-*n*-propyltolane	305	288
Di-*n*-butyltolane	306	287
Tetramethyltolane	306	286
Dimethoxytolane	314	294

Summary

The action of potassium amide in liquid ammonia on 1,1-diaryl-2-chloroethenes causes the removal of hydrogen chloride and the rearrangement of the molecules to form tolane or substituted tolanes. With dichloroethanes two molecules of hydrogen chloride are removed and a similar rearrangement occurs.

The ultraviolet absorption spectra of the chloroethenes and the tolanes were determined. The chloroethenes show non-selective absorption in the region between 200–280 millimicrons. Tolane and substituted tolanes show characteristic absorption bands.

IOWA CITY, IOWA RECEIVED JULY 24, 1933

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[7] Harries, *Ber.*, **40**, 4905 (1907).

[CONTRIBUTION FROM FIXED NITROGEN DIVISION OF THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Action of Alkali and Ammonia on 2,4-Dialkoxypyrimidines

BY GUIDO E. HILBERT AND EUGENE F. JANSEN

There is a fundamental analogy[1] between acid chlorides, imido chlorides and 2,4-dichloropyrimidines;[2] esters, imido ethers and 2,4-dialkoxypyrimidines; and acid amides, amidines and 2,4-diaminopyrimidines as is evident by the similarity, not only of their structures, but also of their properties and chemical reactions. The essential difference between the structure of an imido derivative and a pyrimidine is in the mode of combination of the common grouping —C(R)=N—; in the former it is acyclic and in the latter it is an integral portion of the ring. In the case of 2,4-dialkoxypyrimidines apparently only two types of reactions, both of which have their analogs in the ester series, have been recorded; one involves hydrolysis with acids[3] and the other

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[1] Wheeler and Bristol, *Am. Chem. J.*, **33**, 448 (1905), call attention to the relationship between imido chlorides and chloropyrimidines. Bergstrom and McAllister, THIS JOURNAL, **52**, 2845 (1930) [see also Bergstrom, *ibid.*, **53**, 3027 and 4065 (1931)], suggest that nitrogen ring compounds containing the grouping —CH=N— are cyclic ammono aldehyde acetals and that the corresponding α-chloro and α-methyl derivatives are similar to acid chlorides and ketones, respectively; the logical extension of this suggests that the α-alkoxy derivatives are analogous to esters.

[2] The numbering of the pyrimidine cycle is the same as that used by *Chemical Abstracts*.

[3] Gabriel and Colman, *Ber.*, **36**, 3379 (1903).