To deaminate diaminoquaterphenyl, solid sodium nitrite (30 g.) was added to a refluxing solution of diaminoquaterphenyl (34 g.) in 95% ethanol (400 cc.) and benzene (100 cc.), containing 96% sulfuric acid (55 g.). Refluxing was continued for 20 hours. The reaction mass was made alkaline with 28% ammonia and evaporated to a small volume on the steam-bath. The tarry product obtained was distilled and a pale yellow solid (11 g.) was obtained distilling from 280 to 300° (3 mm.). Upon crystallization from glacial acetic acid (9 g. in 50 cc.) crystals of presumably 2,2′-diphenylbiphenyl (4 g.) melting from 115 to 122° were obtained.

Anal. Calcd. for $C_{24}H_{18}$: C, 94.1; H, 5.9; mol. wt., 306. Found: C, 93.7; H, 6.1; mol. wt., 316.

Hydrogenation of Naphthalene (200 g.).—Naphthalene (200 g.) was hydrogenated slowly in the presence of hydrogen fluoride (127 g.) and platinum catalyst at 250° under a pressure of 200 atmospheres. Upon distillation tetrahydronaphthalene (172 g.) boiling range 198–209° was obtained. A small amount of a dimeric compound (8 g.) was obtained distilling from 180 to 186° (3 mm.) indicating some self condensation in the course of the hydrogenation.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

The Action of Aluminum Chloride on Ethyl-β-C^{14}-benzene[1a,b]

BY ROYSTON M. ROBERTS,[2a] GUS A. ROPP AND O. KENTON NEVILLE[2b]

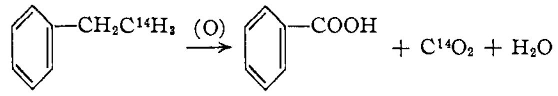
RECEIVED OCTOBER 21, 1954

Attempted aluminum chloride-catalyzed isomerizations of the ethyl group of ethyl-β-C^{14}-benzene revealed no rearrangement under a variety of conditions. Ethyl-β-C^{14}-benzene was converted to diethylbenzene without chain rearrangement. Ethyl-β-C^{14} chloride was condensed with benzene to give ethyl-β-C^{14}-benzene. Ethyl-β-C^{14} chloride was almost completely isomerized by standing over aluminum chloride at room temperature for one hour. Possible mechanisms of the reactions are discussed.

The action of Lewis acids as isomerization catalysts on alkylaromatic hydrocarbons has been a subject of much study[3] because of the preparative and commercial value of these reactions and because of the light they throw on the mechanisms of carbonium ion processes. When an alkylaromatic compound is treated with an isomerization catalyst such as aluminum chloride, several reactions involving the aliphatic groups can occur separately or in combination: (1) cleavage between the nucleus and a chain,[4] (2) re-orientation of the alkyl groups (intramolecular[5] migrations), (3) intermolecular[5] transfers of the alkyl groups, (4) fragmentation of the alkyl groups and (5) internal rearrangements of the alkyl chains.

Although no case has been reported of chain rearrangement in the absence of a group transfer, disagreement exists as to the extent of chain rearrangement occurring during re-orientation or intermolecular transfer of alkyl groups.[6]

In the present investigation, the extent of isomerization of the ethyl-β-C^{14} group under the influence of aluminum chloride was studied. Unlike the studies reported above which depended upon structure proof of the products, the degree of side chain isomerization in the present work was indicated by migration of radioactivity to the α-position in the alkyl group, complete isomerization being indicated by an equal distribution of C^{14} between the two positions. The extent of this migration was determined by oxidation of the recovered, purified ethylbenzene to benzoic acid and determination of its radioactivity.



The determination of the extent of isomerization depended therefore in only the most elementary way upon structure proof of the compounds.

Preliminary experiments involved the treatment of ethyl-β-C^{14}-benzene in nitrobenzene solution at 0° with aluminum chloride for increasing periods of time. Oxidation[7] of recovered ethylbenzene with nitric acid gave *non-radioactive* *p*-nitrobenzoic acid in every case. Increasing the temperature to 72° and the reaction time to 6 hours also gave non-isomerized ethyl-β-C^{14}-benzene. Neither the addition of a small amount of water[8] nor of α-chloroethylbenzene[9] caused isomerization to occur.

Since the ameliorating influence of nitrobenzene on aluminum chloride catalysis is recognized[10] and since every reported case of side chain rearrangement has been in combination with either an inter-

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(1) (a) This paper is based upon work performed under Contract Number W-7405-eng 26 for the Atomic Energy Commission at the Oak Ridge National Laboratory. (b) Presented in part before the Division of Organic Chemistry at the Los Angeles, California, Meeting of The American Chemical Society, March 15–19, 1953.

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(3) For discussions of these various isomerization reactions see: (a) G. Egloff, "Reactions of Pure Hydrocarbons," Reinhold Publ. Corp., New York, N. Y., 1937; (b) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, N. Y., 1941; (c) L. I. Smith in Adams, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 370; (d) D. Nightingale, *Chem. Revs.*, **25**, 347 (1939).

(4) Although this is usually considered to be the reversal of the Friedel–Crafts condensation reaction, there is little evidence that a true thermodynamic equilibrium exists in the alkylation reaction. See A. W. Francis, *Chem. Revs.*, **43**, 257 (1948).

(5) The terms "intramolecular" and "intermolecular" as used here imply no insight into the actual mechanisms of the reactions. "Apparent" intermolecular and intramolecular migrations should be inferred.

(6) Discussed in reference 3d; for more recent work see R. E. Kinney and L. A. Hamilton, THIS JOURNAL, **76**, 786 (1954), and references given there.

(7) In the early experiments of this series, degradations of ethylbenzene were carried out by nitric acid oxidation (*cf.* ref. 11) to give *p*-nitrobenzoic acid. In the later experiments a more elegant procedure was developed which involved the bromination of the alkylaromatic compound, treatment with sodium acetate and oxidation with potassium permanganate. This procedure gave benzoic acid in excellent yields.

(8) *Cf.* R. C. Wackher and H. Pines, THIS JOURNAL, **68**, 1642 (1946).

(9) *Cf.* H. Pines, B. M. Abraham and V. N. Ipatieff, *ibid.*, **70**, 1742 (1948).

(10) C. A. Thomas, ref. 3b, p. 873.

or intramolecular migration of the alkyl group,[3] these results do not indicate whether the ethyl group is not removed or whether the ethyl fragment formed does not rearrange.

When ethylbenzene is heated at its boiling point for 2.5 hours with solid aluminum chloride, a mixture of benzene, ethylbenzene, *m*- and *p*-diethylbenzene and higher alkylated benzene derivatives is formed.[11] When ethyl-β-C^{14}-benzene was subjected to these vigorous conditions, two fractions were collected for degradative study, the ethylbenzene and the diethylbenzene. Oxidation of the ethylbenzene to benzoic acid and assay of this product revealed that no migration of radioactive carbon had occurred, even under these extreme conditions. Degradation of the purified diethylbenzene fraction to isophthalic and terephthalic acids revealed again no isomerization, thus demonstrating that the ethyl-β-C^{14} fragment had moved *intermolecularly* with *no rearrangement.* These results definitely exclude the possibility of ethylene[12] or another symmetrical intermediate as the migrating entity.

A reasonable explanation may be given in terms of a bimolecular displacement process[13] in which the ethyl fragment is never completely free of the aromatic groups during transfer.

A second possibility which is not excluded by our results is that an ethylcarbonium ion is produced, but no hydrogen shift occurs before the ethyl group rejoins an aromatic nucleus. There is no experimental basis for predicting the tendency of one primary carbonium ion to isomerize to another (which in this case is identical except for the isotopic label), but such an isomerization might well be slow compared to reaction of the ion with an aromatic nucleus.

It is well known that in the condensation of primary alkyl halides with benzene in the presence of aluminum chloride rearrangement of the alkyl group usually results, and this has been interpreted in terms of carbonium ion formation and rearrangement.[14,12,3d] All such mechanisms, however, involve primary-to-secondary carbonium ion conversions. It seemed of interest to determine whether evidence of primary-to-primary conversion would be provided by the condensation of ethyl-β-C^{14} chloride with benzene. This was carried out according to the procedure of Schreiner,[15] which involved heating a mixture of ethyl-β-C^{14} chloride, benzene and aluminum chloride on a steam-bath for one hour. The carefully purified ethylbenzene was oxidized to benzoic acid, which was assayed for radioactivity. That the benzoic acid was non-radioactive indicated that no isomerization of the ethyl group had occurred during condensation.

Brown and Grayson[16] have recently presented kinetic evidence for a displacement mechanism of alkylation, in terms of which they account for the *n*-propylbenzene produced along with isopropylbenzene from the alkylation of benzene with *n*-propyl halides. Such a mechanism will also account for the alkylation of benzene by ethyl-β-C^{14} chloride without isomerization, and there is certainly no evidence of a carbonium ion intermediate provided by this experiment. On the other hand, it is not necessarily excluded, since the reasoning outlined above is as applicable to alkylation as to intermolecular alkyl transfer; *i.e.*, an ethylcarbonium ion may be produced, and its rate of reaction with an aromatic nucleus may be much faster than its rate of internal rearrangement.[17] According to this latter possibility, isomerization of ethyl-β-C^{14} chloride by aluminum chloride might be expected to occur in the absence of aromatic compounds.

In a subsequent experiment, therefore, ethyl-β-C^{14} chloride was placed in contact with aluminum chloride for one hour at room temperature and was then recovered by careful low-temperature distillation. Precautions were taken to remove any ethylene produced. The recovered ethyl chloride was then condensed with benzene by the previously described method. After the ethylbenzene was isolated and oxidized, the molar activity of the benzoic acid was found to be 42% of that of the ethyl-β-C^{14} chloride. In a second experiment, with a larger proportion of aluminum chloride, 46% of the radioactivity was found in the benzoic acid. Thus, nearly complete equilibration of the α- and β-carbon positions of the ethyl chloride occurred during contact with aluminum chloride. The results clearly indicate that isomerization of ethyl-β-C^{14} chloride by aluminum chloride is possible under rather mild conditions in the absence of an aromatic hydrocarbon. These results should be compared with those of Roberts, MacMahon and Hine[18] who demonstrated that with *t*-amyl and *t*-butyl chlorides facile isomerization with aluminum chloride occurred. Their experiments were interpreted as demonstrating the ease of secondary-to-secondary and tertiary-to-tertiary carbonium ion conversion. In considering a possible carbonium ion process for the reactions herein reported, our results may be interpreted as demonstrating the relative ease of primary-to-primary carbonium ion conversion in the absence and presence of aromatic compounds. Roberts, MacMahon and Hine observed[19] inhibition of isomerization in some experiments, which they attributed to the presence of aromatic hydrocarbon. Pines, Aristoff and Ipatieff[20] reported similar inhibition by benzene of the aluminum bromide–hydrogen bromide catalyzed isomerization of methylcyclopentane. A carbonium ion chain mechanism was proposed for the latter isomerization.[9]

Thus, there appear to be two plausible interpre-

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(11) R. Anschütz, *Ann.*, **235**, 177 (1886).

(12) Although olefins have been suggested as intermediates in Friedel–Crafts alkylation reactions, the fact that certain alkylations occur in which an olefin intermediate is not possible has weakened the postulate. For a discussion of this see C. C. Price in Adams, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 7.

(13) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **75**, 2411 (1953).

(14) C. C. Price, *Chem. Revs.*, **29**, 37 (1941).

(15) E. Schreiner, *J. prakt. Chem.*, [2] **81**, 557 (1910).

(16) H. C. Brown and M. Grayson, THIS JOURNAL, **75**, 6285 (1953).

(17) The "instantaneous" nature of the aluminum chloride-catalyzed condensation of ethylene with benzene has been pointed out by A. W. Francis and E. E. Reid, *Ind. Eng. Chem.*, **38**, 1194 (1946).

(18) J. D. Roberts, R. E. MacMahon and J. S. Hine, THIS JOURNAL, **72**, 4237 (1950).

(19) Footnote 20 of reference 18.

(20) H. Pines, E. Aristoff and V. N. Ipatieff, THIS JOURNAL, **71**, 749 (1949).

tations of the observed reactions of ethyl-β-C^{14}-benzene and ethyl-β-C^{14} chloride: (1) displacement mechanisms involving no free ethyl fragments and (2) carbonium ion mechanisms in which the ions react with aromatic nuclei so rapidly as to exclude internal hydrogen shifts. More information is necessary in order to decide whether one of these is exclusively correct and, if so, which one.

Although the present research casts no direct light on the degree of chain isomerization which can be expected with alkylaromatic compounds with chains of greater length or of different configuration, they do lend support to the possibility of group migration without rearrangement and suggest that the extent of such rearrangement may be a function of the reaction conditions. This work will be extended by further study of the ethyl-aromatic system as well as by investigation of chain-isomerization in aromatic compounds of longer chain lengths and of such configuration that the facility of secondary-to-secondary and tertiary-to-tertiary carbon rearrangement may be determined under similar conditions.

Experimental

Ethyl-β-C^{14}-benzene.—A 2.1-ml. portion of (aceto-2-C^{14})-phenone[21] was dissolved in 6 ml. of glacial acetic acid containing five drops of 70% perchloric acid. Two grams of 5% palladium-on-carbon catalyst was added and the material was subjected to 50 lb. of hydrogen pressure for 72 hours. The mixture was treated with 100 ml. of pure ethylbenzene, filtered and distilled. The ethyl-β-C^{14}-benzene fraction which distilled at 132° (743 mm.) was assayed for radioactivity and redistilled. The millimolar activity, which did not change after two successive distillations, was 1.71 microcuries. The radiochemical yield from acetophenone was 85.2%.

Attempted Isomerizations of Ethyl-β-C^{14}-benzene in Nitrobenzene Solutions.—In each experiment, a flask equipped with a stirrer, a reflux condenser and a helium inlet tube and containing 10 ml. of ethyl-β-C^{14}-benzene (1.71 μc./mmole), 10 ml. of nitrobenzene and one gram of dry aluminum chloride was immersed in a thermostated bath for the appropriate period of time. At the end of the isomerization time, water was added and the organic material was extracted into ether. The ether layer was washed, dried and distilled through a 100-cm. Vigreux column. The ethylbenzene fraction was collected and degraded. Reaction times and temperatures used for these studies were: 1 hr., 0°; 6 hr., 0°; 6 hr., 40°; 6 hr., 72°. Two additional experiments were performed for 6 hr. at 55° in one of which 0.1 ml. of water was added. In the other experiment 0.1 ml. of water and one ml. of α-chloroethylbenzene were present. In each case the carefully purified ethylbenzene was oxidized to *p*-nitrobenzoic acid and assayed for radioactivity. Every sample of the collected solid acid was non-radioactive.

Degradation of Ethylbenzene to *p*-Nitrobenzoic Acid.—A 3-ml. sample of ethylbenzene was mixed with 18 ml. of concd. nitric acid and heated at 100° in an oil-bath for 40 hours. The solution was treated with water and extracted with ether. The ether layer was washed and extracted with sodium bicarbonate solution. The *p*-nitrobenzoic acid which precipitated on acidification was crystallized from water several times to give light yellow crystals, m.p. 235–236°. Since the emphasis was on purity rather than yield, only 10–15% yields were realized.

Disproportionation of Ethylbenzene at the Boiling Point.—A 15-ml. portion of ethyl-β-C^{14}-benzene was heated at the boiling point with 4.5 g. of dry aluminum chloride for 2.5 hours. The mixture was treated with water and extracted with ether. The ether layer was washed, dried and distilled through a 100-cm. Vigreux column. The fractions boiling at 133–135° (ethylbenzene) and 175–185° (diethylbenzenes) were collected for degradation to benzoic and phthalic acids as described below. Radioassay of the acids revealed no radioactivity.

Degradation of Ethylbenzene to Benzoic Acid.—A 0.5-ml. portion of ethylbenzene in a small conical flask equipped with a dropping funnel and reflux condenser was heated to 60° and treated with 0.4 ml. of liquid bromine under strong ultraviolet irradiation. After the solution had cooled, 0.64 g. of potassium acetate in 5 ml. of ethanol was added. The mixture was heated to reflux 20 minutes, cooled to 5°, and the solution was filtered from the precipitated potassium bromide. The ethanol was removed by distillation. A 10-ml. portion of benzene was added and about 8 ml. were removed by distillation. To the reaction solution was added 0.5 g. of potassium hydroxide, 2 g. of potassium permanganate and 20 ml. of water. After the mixture was heated under reflux for 3 hr., it was acidified with sulfuric acid and heated another two hours. The mixture was then made basic with potassium hydroxide, heated to boiling, and the manganese dioxide was removed by filtration. The solution was acidified and the precipitated benzoic acid was collected. Recrystallization from water yielded in most cases about 0.25 g. of white crystals, m.p. 120.5–122°.

Degradation of Diethylbenzene to Phthalic Acids.—The procedure was parallel to that above. A 0.5-g. sample of diethylbenzene was treated with 0.6 ml. of bromine at 65°. The resultant solution was treated with one gram of potassium acetate in 7 ml. of absolute ethanol and heated under reflux for 20 minutes. After removal of the ethanol the solution was treated with 0.8 g. of potassium hydroxide. 3.2 g. of potassium permanganate and 30 ml. of water. The solution was heated at reflux for 3.5 hours, treated with 2.4 ml. of 18 *N* sulfuric acid, and heated for two additional hours. The solution was made alkaline with potassium hydroxide and filtered. The filtrate was extracted with ether and acidified. The mixed phthalic acids which precipitated were collected and assayed for radioactivity. The mixed acids were tentatively identified by paper chromatography with 75–20–5 ethanol, water, ammonia solution as isophthalic and terephthalic acids only.[11] A sample of pure methyl terephthalate was recovered by esterification of the mixed acids and recrystallization of the resulting esters from ethanol. The melting point, 139–140°, showed no depression after mixture of the recovered sample with authentic compound. Radioassay of this compound showed no radioactivity.

Ethyl-2-C^{14} Chloride.—A one-gram sample of acetic-2-C^{14} acid[22] containing 343 μc./mmole was dissolved in ether and added to a vigorously stirred solution of 634 mg. of lithium aluminum hydride in 30 ml. of dry ether. At the end of the reaction period 0.6 ml. of water was added to the mixture. After the reaction had subsided, 20 ml. of anhydrous ethanol was added and the liquid was distilled through a 100-cm. Vigreux column. The ether fraction was discarded and the ethanol fraction was retained. Two additional 10-ml. volumes of ethanol were added and distilled to recover radioactivity from the alkoxide mixture. A total of 33.6 ml. of ethanol-2-C^{14} was recovered which was shown by assay to have a millimolar activity of 5.28 microcuries. The radiochemical yield was 56.5%.

A 10-g. portion of the ethanol-2-C^{14} was transferred by distillation in a vacuum system onto 50 g. of phosphorus pentachloride maintained at liquid nitrogen temperature. The reaction mixture was allowed to warm very slowly with stirring at such a rate that the reaction did not become violent. The evolved gases were allowed to pass through a trap containing solid potassium hydroxide pellets to remove hydrogen chloride and through water to remove unreacted ethanol. Several 10-ml. portions of ethyl chloride were passed into the reaction mixture and allowed to expand through the system to scavenge radioactive ethyl-2-C^{14} chloride. The collected ethyl chloride was distilled at atmospheric pressure to give 61.2 g. of ethyl-2-C^{14} chloride, b.p. 12° (742 mm.) which by assay was shown to have a radioactivity of 0.825 μc./mmole. This was a radiochemical yield of 65.4%.

Condensation of Ethyl-2-C^{14} Chloride with Benzene.[15]—To a mixture of 1.5 g. of aluminum chloride and 21 g. of benzene in a flask equipped with stirrer, addition funnel,

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[21] The (aceto-2-C^{14})-phenone was prepared by Dr. H. W. Davis, by condensation of acetic-2-C^{14} acid with benzene according to the procedure described for (aceto-1-C^{14})-phenone by O. K. Neville, This Journal, **70**, 3499 (1948).

[22] The acetic-2-C^{14} acid was prepared by D. N. Hess, *ibid.*, **73**, 4038 (1951).

and condenser was added a cold solution of 10 g. of ethyl-2-C^{14} chloride (0.825 μc./mmole) in 27 g. of benzene. The mixture was heated at reflux for 1.25 hours and hydrolyzed with water. The washed and dried benzene layer was distilled through a 100-cm. Vigreux column. The collected ethylbenzene fraction, boiling at 133–135°, weighed 4.1 g. or 25% of theoretical. Degradation of the ethylbenzene by the procedure described above gave non-radioactive benzoic acid.

Isomerization of Ethyl-2-C^{14} Chloride.—A 20-g. portion of ethyl-2-C^{14} chloride (0.825 μc./mmole) was transferred in a vacuum line onto 2 g. of solid aluminum chloride. The mixture was quickly brought to room temperature and atmospheric pressure and allowed to stand at room temperature for one hour. At the end of this time the product was distilled *in vacuo* through a trap containing potassium hydroxide pellets to remove hydrogen chloride. The product was distilled several times at atmospheric pressure and collected in a trap maintained at −80°. Uncondensed gases such as ethylene were removed. Finally the gas was passed through bromine water, a "Drierite" trap, and condensed. Distilled at atmospheric pressure, the product weighed 9.3 g., b.p. 12° (743 mm.).

The isomerized ethyl chloride was condensed with benzene in the presence of aluminum chloride as described above. The resultant ethylbenzene was degraded to benzoic acid which was assayed for radioactivity. Samples weighing 19.51 and 17.70 mg. had radioactivities of 0.0551 and 0.0503 μc., respectively. Since the millimolar activity was thus 0.345 microcurie, the percentage isomerization was 83.6%.

A previous experiment which was not quite so carefully carried out and which involved the isomerization of 12 g. of ethyl-2-C^{14} chloride over 7.5 g. of aluminum chloride revealed 92% isomerization of the ethyl chloride.

Radioactivity Measurements.—Determinations of radioactivity were made on 5- to 20-mg. samples of purified organic compounds by wet combustion of the sample and ion chamber-vibrating reed electrometer measurement of the resulting carbon dioxide. The method which is previously described[23] is subject to an error of less than ±1%.

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(23) O. K. Neville, THIS JOURNAL, **70**, 3501 (1948).

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

The Course of the Reaction of 1,4- and 1,5-Dihalo- and Di-(arylsulfonoxy)-alkanes with Diallylamine

BY GEORGE B. BUTLER AND RUDOLPH J. ANGELO[1]

RECEIVED JULY 12, 1954

In attempting to prepare 1,4-bis-(diallylamino)-butane and 1,5-bis-(diallylamino)-pentane by reaction of the 1,4- and 1,5-dihalo- and di-(arylsulfonoxy)-alkanes with diallylamine, neither of the desired products was obtained. In the presence of an excess of diallylamine, the products of the reaction were allylpyrrolidine and triallylamine from the 1,4-derivatives, and allylpiperidine and triallylamine from the 1,5-derivatives. The products of the reaction can be explained on the basis of an intramolecular cyclization to the five- or six-membered cyclic quaternary ammonium salt, followed by allylation of the excess diallylamine by the quaternary ammonium salt to produce triallylamine and the appropriate allyl-substituted heterocyclic amine. In order to check this proposed mechanism, diallylpyrrolidinium bromide was prepared and heated with diallylamine, resulting in the formation of allylpyrrolidine and triallylamine. The reaction products were identified by both chemical means and by infrared spectral analysis. The desired compounds were obtained by reduction of the corresponding amides with lithium aluminum hydride.

In preparing a series of unsaturated quaternary ammonium salts of the structure

$$Br^-R_3{}^+N(CH_2)_nN^+R_3Br^-$$

in which $n = 2$–10, it became necessary to prepare the corresponding bis-(diallylamino)-alkanes as intermediates. For those compounds in which n = 2, 3 or 6–10, acceptable yields were obtained by one of the following methods: (1) reaction of the 1,X-dihaloalkane with diallylamine in presence of sodium carbonate or (2) the method of Laakso and Reynolds[2] which employs the reaction of the di-(arylsulfonates) of the corresponding glycols with diallylamine. Although these authors reported acceptable yields of 1,4- and 1,5-bis-(dialkylamino)-alkanes by this procedure, use of this method, as well as method 1, in attempts to prepare 1,4-bis-(diallylamino)-butane and 1,5-bis-(diallylamino)-pentane did not prove satisfactory.

This paper deals with the isolation and identification of the products of the above reactions when applied to the 1,4- and 1,5-derivatives. On the basis of previously reported data[3] and on data obtained in this study, an explanation is given for the course of the reaction.

Experimental

Reaction of 1,4-Dibromobutane with Diallylamine.—(1) A mixture of 44.5 g. (0.206 mole) of 1,4-dibromobutane, 60 g. (0.618 mole) of diallylamine, 34.6 g. of sodium bicarbonate and 20 ml. of water was refluxed for seven hours. After filtration and addition of sodium hydroxide to the filtrate, the organic layer was distilled; however, no material was obtained boiling in the expected range for 1,4-bis-(diallylamino)-butane.

(2) To 4 ml. of 1,4-dibromobutane was added 12 ml. of diallylamine at a temperature of 35°. While the liquid was being stirred, the temperature rose to 100°. After standing overnight, the crystalline product was collected and washed with acetone; m.p., decomposition at 205°, liquid at 315–322°.

Anal. Calcd. for $[(CH_2{=}CHCH_2)_2N^+H(CH_2)_4N^+H(CH_2CH{=}CH_2)_2]2Br^-$: Br, 38.98. Calcd. for diallylpyrrolidinium bromide: Br, 34.49. Found: Br, 34.77.

Since diallylpyrrolidinium bromide has not been reported previously in the literature, it was prepared as follows:

To a cold mixture of 21.0 g. (0.19 mole) of N-allylpyrrolidine (b.p. 129–130°, n^{25}D 1.4486) and 75 ml. of acetone was added carefully 25.0 g. (0.207 mole) of allyl bromide with cooling. The hygroscopic compound which precipitated was washed with acetone; yield 39.0 g., 90.5%; m.p., decomposition at 202°, melted at 315–320°; mixed m.p. with above compound, decomposition at 198°, melted at 314–322°.

Since adequate physical constants could not be found in the literature on allylpyrrolidine, it was prepared by treating pyrrolidine with allyl bromide in the presence of sodium carbonate; b.p. 129–130°, n^{25}D 1.4486.

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(1) Abstracted from a dissertation to be presented by Rudolph J. Angelo to the Graduate School of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) T. M. Laakso and D. D. Reynolds, THIS JOURNAL, **73**, 3518 (1951).

(3) E. L. Eliel and P. E. Peckham, *ibid.*, **72**, 1209 (1950).