**Benzoic Acid.**—If equimolecular amounts of the above listed compounds were dissolved in carbon tetrachloride, a quantitative separation could be performed by extraction of the acid with saturated sodium bicarbonate solution, the imide with 2 *N* sodium hydroxide solution, leaving the benzonitrile in the carbon tetrachloride.

**Experiments with Silver Decanoate and Cyanogen Bromide.**—From a mixture of 111.6 g. (0.4 mole) of silver salt and 700 ml. of carbon tetrachloride, 100 ml. of solvent was distilled. Afterwards 47 g. (0.45 mole) of cyanogen bromide dissolved in 450 ml. of carbon tetrachloride was added at room temperature over the period of 45 minutes. No carbon dioxide evolution could be observed. The mixture was refluxed on a steam-bath for 12 hr. The carbon dioxide evolution was slow. Using the usual working-up procedure the following yields and products were obtained: 49 g. (75%) of anhydride[27] and 10.7 g. (17%) of nitrile, b.p. 109–110° (10 mm.) (lit.[28] 243.7°). Only traces of acid were recovered in this experiment.

In a second experiment, where the cyanogen bromide was added to the heated mixture over a period of 1.5 hr., the carbon dioxide evolution was complete after a total heating time of 3 hr. The yield of nitrile was 4.5 g. (7%).

**Experiment with Silver γ-Phenylbutyrate and Cyanogen Iodide.**—Cyanogen iodide (39 g., 0.25 mole) dissolved in 400 ml. of carbon tetrachloride was added in the usual manner in portions to 62.4 g. (0.23 mole) of the silver salt in 600 ml. of carbon tetrachloride heated on a steam-bath over a period of 1 hr. The carbon dioxide evolution ceased about 0.5 hr. after the last addition of cyanogen iodide. The reaction mixture was refluxed with stirring overnight. After the usual working-up procedure 0.5 g. (1.5%) of nitrile, 24.2 g. (68%) of anhydride and 6.8 g. (18%) of acid were obtained.

**Silver γ-Phenylbutyrate and Cyanogen Chloride.**—Approximately 60 ml. (excess) of cyanogen chloride (b.p. 13°) was distilled over the period of 1.5 hr. directly into a slurry of 112 g. (0.41 mole) of the silver salt and 1100 ml. of carbon tetrachloride at room temperature. The reaction flask was equipped with a cold finger condenser filled with Dry Ice and *n*-butyl Carbitol. The content of the cold finger was then replaced with a Dry Ice and methanol mixture and the temperature in the cold finger kept at −20 to −10°. The reaction mixture was heated to about 60–70° and stirring was continued. There was a great initial carbon dioxide evolution, but the evolution came to an end after about 1 hr., albeit cyanogen chloride was still escaping. The mixture was stirred and refluxed for 7 more hours. Using the usual working-up procedure 4.0 g. (7%) of nitrile, 45.1 g. (73%) of anhydride, 5.4 g. (8%) of acid and 1.2 g. (2%) of 3-phenylpropyl chloride[29] were obtained.

---

[27] J. M. Wallace and J. E. Copenhaver, THIS JOURNAL, **63**, 699 (1941).

[28] Reference 24, p. 421.

[29] J. B. Conant and W. R. Kirner, THIS JOURNAL, **46**, 232 (1924).

BERKELEY 4, CALIFORNIA

---

[CONTRIBUTION FROM THE ROHM & HAAS CO.]

# Chemistry of the 1,4-Diamino-1,3-butadienes. I. Preparation[1]

BY MARIAN F. FEGLEY, NEWMAN M. BORTNICK AND CHARLES H. MCKEEVER

RECEIVED NOVEMBER 3, 1956

1,4-Bis-(dimethylamino)-2-butyne (I), on heating with sodium, was rearranged to 1,4-bis-(dimethylamino)-1,3-butadiene (II). The preparation and rearrangement of several homologs of I are described. On standing at room temperature, II is isomerized to a geometric isomer. Infrared evidence is adduced to assign the initial form the *cis,trans* and the new isomer, the *trans,trans* structure. In the presence of potassium bases, dimerization of I rather than intramolecular rearrangement occurred. This mixture of isomeric dimers was itself subject to rearrangement. The structures of the dimeric products were not definitely ascertained. The mechanism for these transformations of I is discussed.

We have found that 1,4-bis-(dimethylamino)-2-butyne (I) may be rearranged to 1,4-bis-(dimethylamino)-1,3-butadiene (II) by means of finely divided metallic sodium.

$$\underset{\text{I}}{(CH_3)_2NCH_2C{\equiv}CCH_2N(CH_3)_2} \xrightarrow{\text{Na}} \underset{\text{II}}{(CH_3)_2NCH{=}CHCH{=}CHN(CH_3)_2}$$

II had first been prepared in these laboratories by McKeever and Nemec[2] by passage of I over chromium oxide-containing catalysts at 300–450° in the vapor phase. Our present discovery has permitted the facile preparation of II on a large laboratory scale.

In order to control this exothermic rearrangement, dried, redistilled I was added dropwise to a stirred boiling mixture of hexane and metallic sodium dispersed in xylene.[3] From 50 g. to 300 g. of I, depending on its purity, could be converted to II per gram of sodium. The product was isolated in yields of 80 to 90% of the theoretical by distillation without prior removal or destruction of the catalyst. Alfin catalyst[4] (55% yield), metallic lithium (81% yield), metallic potassium (9% yield) and sodamide (12% yield) were catalysts of limited utility, while sodium acetylide and metallic calcium were inactive.

This rearrangement was extended to the 1,4-diamino-2-butyne derivatives shown in Table I. These were prepared by means of the cuprous chloride-catalyzed Mannich reaction[5,6] applied to acetylene and to the intermediate 3-dialkylamino-1-propynes. Properties of the corresponding 1,4-diamino-1,3-butadienes are shown in Table II. Dispersed sodium alone was not a satisfactory catalyst for the isomerization of many of the higher

---

[1] Given in part at the 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March 16, 1953.

[2] C. H. McKeever and J. W. Nemec (Rohm & Haas Co.), U. S. Patent 2,617,827 (Nov. 11, 1952); *C. A.*, **48**, 1429 (1954). Their product was probably the *trans,trans*-modification. The similar rearrangement of 3-amino-1-butynes to the corresponding 1,3-butadienes over activated alumina at 250–300° has been described recently by W. Reppe, *Ann.*, **596**, 12 (1955).

[3] V. L. Hansley, *Ind. Eng. Chem.*, **43**, 1759 (1951); U. S. Patent 2,394,608 (E. I. du Pont de Nemours & Co.) Feb. 12, 1946; *C. A.*, **40**, 2598 (1946). We wish to thank the U. S. Industrial Alcohol Division of National Distillers, Inc., for samples of these dispersions.

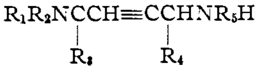
[4] A. A. Morton, *Ind. Eng. Chem.*, **42**, 1488 (1950); A. A. Morton, E. E. Magat and R. L. Letsinger, THIS JOURNAL, **69**, 950 (1947).

[5] (a) C. Mannich and F. T. Chang, *Ber.*, **66**, 418 (1933). (b) W. Reppe, E. Keyssner and O. Hecht, U. S. Patent 2,273,141 (General Aniline & Film Corp.) Feb. 17, 1942; *C. A.*, **36**, 3807 (1942). (c) W. Reppe, *Ann.*, **596**, 12 (1955).

[6] The processes which have permitted the satisfactory preparation of these materials at low pressures of acetylene were worked out in collaboration with Dr. J. O. Van Hook, Dr. L. R. Freimiller and Dr. J. S. Strong and are described in the Experimental section.

TABLE I

1,4-DIAMINO-2-BUTYNES



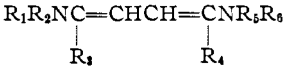
$R_1R_2N\underset{R_3}{C}CH\equiv C\underset{R_4}{C}HNR_5H_6$

| $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | $R_6$ | Method[a] | B.p. °C. | Mm. | $n^{20}D$ | Nitrogen, % Calcd. | Nitrogen, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3$ | $CH_3$ | H | H | $CH_3$ | $CH_3$ | A | 181–183[b] | | 1.4550 | 20.0 | 19.9 |
| $C_2H_5$ | $C_2H_5$ | H | H | $C_2H_5$ | $C_2H_5$ | A | 95 | 7 | 1.4587 | 14.3 | 14.6 |
| $n$-$C_4H_9$ | $n$-$C_4H_9$ | H | H | $n$-$C_4H_9$ | $n$-$C_4H_9$ | A | 136 | 0.7 | 1.4600 | 9.1 | 9.1 |
| $O(CH_2CH_2)_2$ | | H | H | $O(CH_2CH_2)_2$ | | A or B | M.p. 88–90 | | .... | 12.5 | 12.7 |
| $(CH_2)_4$ | | H | H | $(CH_2)_4$ | | B | 97 | 2.0 | 1.5008 | 14.6 | 14.4 |
| $O(CH_2CH_2)_2$ | | $CH_3$ | H | $CH_3$ | $CH_3$ | E D | 112–114 | 1.0 | 1.4828 | 14.3 | 14.0 |
| $CH_3$ | $CH_3$ | $C_8H_{17}$[c] | $C_8H_{17}$[c] | $CH_3$ | $CH_3$ | C D | 140–143 | 1.1 | 1.4617 | 7.7 | 7.4 |

[a] Refers to description in the Experimental. [b] Reference 5b lists b.p. 180°. [c] $C_8H_{17} = (CH_3)_3CCH_2CH(CH_3)CH_2–$.

TABLE II

1,4-DIAMINO-1,3-BUTADIENES



$R_1R_2N\underset{R_3}{C}{=}CHCH{=}\underset{R_4}{C}NR_5R_6$

| $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | $R_6$ | Method[a] | B.p. °C. | Mm. | $n^{20}D$ | Nitrogen, % Calcd. | Nitrogen, % Found | U.v. absorption spectrum (in 2,2,4-trimethylpentane) $\epsilon_{max}$ | Wave length, mμ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3$ | $CH_3$ | H | H | $CH_3$ | $CH_3$ | F | 108 | 15 | 1.5500 | .. | .. | 19,600 | 291 |
| $C_2H_5$ | $C_2H_5$ | H | H | $C_2H_5$ | $C_2H_5$ | F | 64 | 0.25 | 1.5155 | 14.3 | 14.4 | 19,400 | 292.5 |
| $n$-$C_4H_9$ | $n$-$C_4H_9$ | H | H | $n$-$C_4H_9$ | $n$-$C_4H_9$ | G | 142 | 0.35 | 1.5020 | 9.1 | 9.1 | 20,400 | 300 |
| $O(CH_2CH_2)_2$ | | H | H | $O(CH_2CH_2)_2$ | | F, G | M.p. 139–140 | | .... | 12.5 | 12.2 | 28,000 | 285 |
| $(CH_2)_4$ | | H | H | $(CH_2)_4$ | | F | 125–132 | 0.3[b] | 1.601 | 14.6 | 14.5 | 19,300 | 306 |
| $O(CH_2CH_2)_2$ | | $CH_3$ | H | $CH_3$ | $CH_3$ | F | 110–115 | 0.3 | 1.5625 | 14.2 | 13.9 | 20,800 | 287.5 |
| $CH_3$ | $CH_3$ | $C_8H_{17}$[c] | $C_8H_{17}$[c] | $CH_3$ | $CH_3$ | G | 187–192 | 3.8 | 1.4982 | 7.7 | 7.5 | 21,900 | 295 |

[a] Refers to description in the Experimental. [b] Isomerization occurred rapidly on standing. The solid *trans,trans* derivative isolated from one run had m.p. 94–97°, $\epsilon_{max}$ 22,600 at 300 mμ. [c] $C_8H_{17} = (CH_3)_3CCH_2CH(CH_3)CH_2–$.

homologs of I. However, a previously prepared mixture of dispersed sodium and a small amount of I served well.

Although the products were not obtained in analytical purity, the large index of refraction change which was observed when 1,4-bis-(dimethylamino)-1,4-diphenyl-2-butyne was heated with the "sodium-I" catalyst indicated that rearrangement had occurred. A corresponding change was noted when 1,4-bis-(dimethylamino)-1,4-diisopropyl-2-butyne was treated in the same fashion. No pure product was isolated from the attempted rearrangement of 1,4-bis-(methylphenylamino)-2-butyne.

Our attempts to rearrange 1-dimethylamino-2-butyne and 1-dimethylamino-2-heptyne to the corresponding 1,3-butadienes failed. Inconclusive results were obtained with 1,4-dihydroxy-2-butyne, its diacetate or its dimethyl ether.

The ultraviolet absorption spectra of the butyne–butadiene pairs provided a means of estimating semi-quantitatively whether rearrangement had occurred. Since the molar extinction coefficients of most of the butadienes were 20,000–25,000 at their maxima (which fell at 280–310 mμ), while the butynes were transparent, an estimate of conversion and purity could be made on the very first experiment. The refractive indices proved more convenient for purity estimation once the best values were established for the two pure materials.

As initially formed, II is a liquid which melts below −100°. It can be stored in full containers at 5° or in carefully dried, sealed vials at room temperature for many months without change. It may be stabilized by simply not distilling the rearrangement reaction mixture. On prolonged storage at room temperature II isomerized to a form which had m.p. −1 to −3°. This isomerization occurred more rapidly when II was heated or was exposed to moisture, carbon dioxide or acids. Figures 1, 2 and 3 show the infrared absorption spectra of the two forms of II and the initial form after standing. The second form shows the relatively weak single C=C stretching absorption (Fig. 1) and strong sharply peaked hydrogen wagging absorption (Fig. 2) characteristic of *trans*-olefins and accordingly has the *trans,trans* (*t–t*) structure.

The direct rearrangement product contains a *trans*-type olefin group (Fig. 2) by its hydrogen wagging absorption; *cis* geometry is indicated by strong, doubly peaked absorption in the C=C stretching region (Fig. 1) and by broad hydrogen-wagging absorption at long wave lengths (Fig. 3). These results are consistent with the assignment of the *cis,trans* (*c–t*) structure to the isomer formed directly by rearrangement of I. This conversion of *c–t* to *t–t* II probably occurs by way of an intermediate such as $(CH_3)_2N{=}CHCH_2CH{=}CH\overset{+}{N}(CH_3)_2$.

When compound I was heated with solid potassium hydroxide, an exothermic reaction occurred at 150–180°. No II was obtained. The product was almost exclusively dimeric. The exothermic reaction was controlled by gradual addition of I to a solution of potassium *n*-octoxide in boiling xylene. At 120–140°, conversions of 70–85% to similar dimeric products were conveniently realized. These products were mixtures which rearranged on further heating in the presence of sodium dispersion with

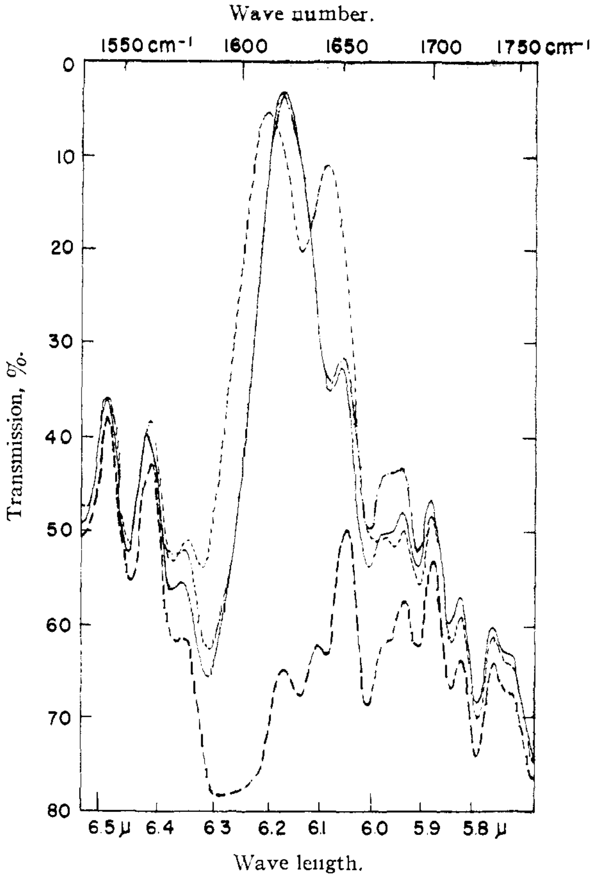


Fig. 1.—Infrared spectra of 1,4-bis-(dimethylamino)-1,3-butadienes, double bond stretching region: ———, *t,t*-II; - - - -, *c,t*-II; — · —, *c,t*-II on standing; ▬ ▬ ▬ ▬, $CHCl_3$.

changes in refractive index and ultraviolet absorption spectra but without noticed changes in boiling range and empirical formula, $C_{16}H_{32}N_4$.

Hydrogenation in ethanol solution in the presence of Raney nickel catalyst led to the absorption of 2.8 ± 0.5 moles of hydrogen. A liquid, $C_{14}H_{31}N_3$, and a small amount of a solid, $C_{16}H_{36}N_4$,[7] were isolated, together with dimethylamine.

The dimeric product mixture decomposed slowly with evolution of dimethylamine when heated at 200°. Presence of solid potassium hydroxide stabilized the system so that heating to 240° was required to observe this decomposition. The presence of a trace of hydrogen chloride lowered the decomposition temperature to 140°, two moles of dimethylamine were eliminated per mole of dimer and a brittle black resin remained.

Attempts to extend the dimerization reaction to higher homologs were largely unsuccessful. 1,4-Bis-(diethylamino)-2-butyne gave dimeric material in very poor yield while neither the 1,4-bis-(dibutylamino) nor the 1,4-dimorpholino derivative could be converted by means of potassium *n*-octoxide in boiling xylene.

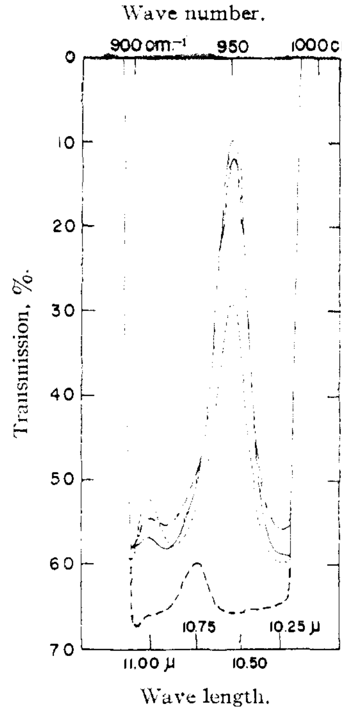


Fig. 2.—Infrared spectra of 1,4-bis-(dimethylamino)-1,3-butadienes, *trans*-olefin hydrogen wagging region: ———, *t,t*-II; - - - -, *c,t*-II; — · —, *c,t*-II on standing; ▬ ▬ ▬ ▬, $CHCl_3$.

Dimerization was effected concurrent with rearrangement to II when metallic potassium or sodamide was employed. Although other sodium derivatives (the hydroxide, methoxide and *n*-octoxide) were ineffective in short time, small scale experiments, prolonged heating of I with sodium ethyleneglycoxide gave some dimeric material.

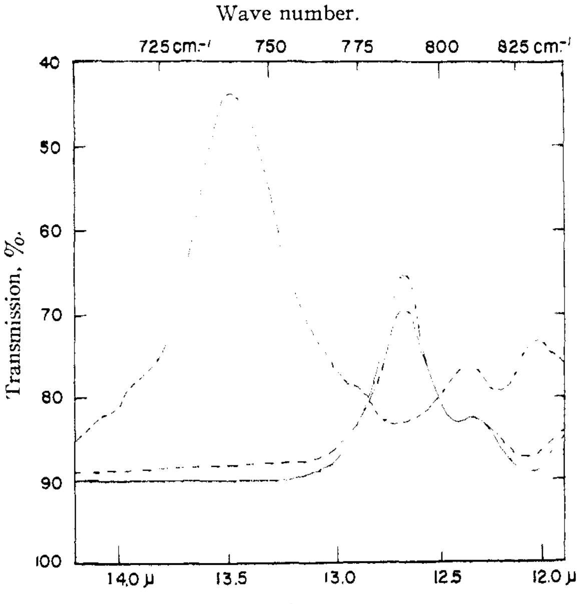


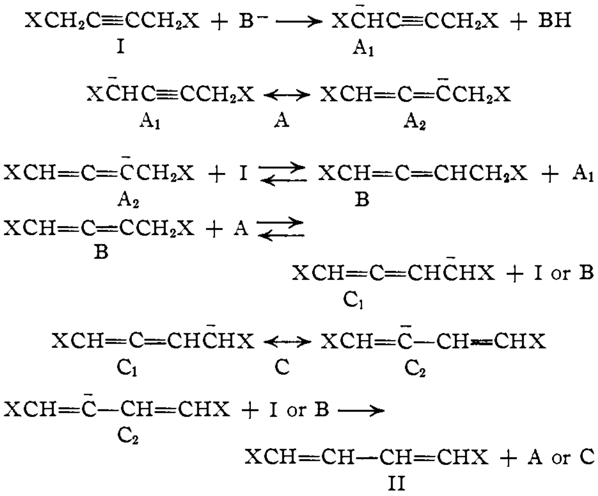
Fig. 3.—Infrared spectra of 1,4-bis-(dimethylamino)-1,3-butadienes, *cis*-olefin hydrogen wagging region: ———, *t,t*-II; - - - -, *c,t*-II; — · —, *c,t*-II on standing.

---

(7) The similarity between the ultraviolet absorption spectra of 1,4-bis-(dimethylamino)-2-butene and of the solid suggested the possibility that the grouping N—C—C=C—C—N may be present in the latter. If the remaining double bond is sufficiently hindered, hydrogenolysis of the allylic bond might be expected to occur in preference to double bond saturation to give $C_{14}H_{31}N_3$ + $(CH_3)_2NH$.

Complete recovery of II in experiments in which it was heated with potassium hydroxide, in the presence or absence of I, showed that II was not an intermediate in the dimerization process.

We propose a mechanism for these base-catalyzed transformations of I similar to that recently described by Jones, Whitham and Whiting[8] for the case of prototropic rearrangements of acetylenic acids.



$$\underset{\text{I}}{XCH_2C{\equiv}CCH_2X} + B^- \longrightarrow \underset{A_1}{X\bar{C}HC{\equiv}CCH_2X} + BH$$

$$\underset{A_1}{X\bar{C}HC{\equiv}CCH_2X} \underset{A}{\longleftrightarrow} \underset{A_2}{XCH{=}C{=}\bar{C}CH_2X}$$

$$\underset{A_2}{XCH{=}C{=}\bar{C}CH_2X} + \text{I} \rightleftharpoons \underset{B}{XCH{=}C{=}CHCH_2X} + A_1$$

$$\underset{B}{XCH{=}C{=}CCH_2X} + A \rightleftharpoons \underset{C_1}{XCH{=}C{=}CH\bar{C}HX} + \text{I or B}$$

$$\underset{C_1}{XCH{=}C{=}CH\bar{C}HX} \underset{C}{\longleftrightarrow} \underset{C_2}{XCH{=}\bar{C}{-}CH{=}CHX}$$

$$\underset{C_2}{XCH{=}\bar{C}{-}CH{=}CHX} + \text{I or B} \longrightarrow \underset{\text{II}}{XCH{=}CH{-}CH{=}CHX} + \text{A or C}$$

The geometrical configuration is not set until the very last step in this series. Ion C must assume the conformation which makes carbon atom 2 most amenable to approach by I or B. Inspection of molecular models suggests that the $\Delta^{1,2}$-double bond must have the *cis* and the $\Delta^{3,4}$-double bond should have the *trans* orientation for this situation to obtain.

In the presence of potassium bases or if higher temperatures are used with sodium bases, ions A and C may add to I or B to give intermediates which abstract protons from I to give dimeric products. These in turn could isomerize to more highly conjugated structures.[9]

**Acknowledgments.**—We wish to thank Dr. James D. Stroupe and Mrs. Florence Farnum of these laboratories for their determination and interpretation of the ultraviolet and infrared absorption spectra reported herein.

## Experimental[10]

**1.4-Bis-(dimethylamino)-2-butyne** (I). **Method A.**—Bis-(dimethylamino)-methane (5.0 moles, 543 g. of 94% purity) was treated with aqueous formaldehyde solution (5.75 moles, 539 g. of 36.2% concentration) with stirring and cooling to keep the temperature below 50°. Cuprous chloride (20 g., 0.2 mole) was added. The flask was then fitted with a gas inlet tube which extended below the surface of the liquid and a gas outlet tube which was connected to a manometer. All stoppers and connections were wired in place. A stream of acetylene, which had been washed with water and with concentrated sulfuric acid, then dried over soda lime, was admitted at about 1.33 atm. The absorption of acetylene was very rapid; in 50 minutes, 136 g. (5.23 moles) was absorbed. The temperature was maintained at about 50° by intermittent cooling. The mixture was maintained at 50° for an additional 3 hr., then cooled and filtered with the aid of Celite. The mixture was dried over flaked sodium hydroxide then distilled at atmospheric pressure. 3-Dimethylamino-1-propyne (78 g., 9%), b.p. 82°, and I (491 g., 73%), b.p. 181–183°, were obtained.

**Method B.**—Method A was modified by preparing the intermediate, $R_2NCH_2OH$, by adding $R_2NH$ (1.0 mole) to 36% aqueous formaldehyde solution (1.02–1.05 moles) with cooling. The lower concentration of $R_2NCH_2OH$ thus employed led to higher ratios of mono- to disubstituted acetylene derivatives than did method A.

**Method C.**—Method A was modified by preparing the intermediate, $R_2NHCH(R^1)OH$, by adding $R_2NH$ (1.0 mole) to the aldehyde (1.0 mole) in the absence of solvent, while maintaining the temperature below 35°. When $R^1$ was not H, the monosubstituted acetylene derivative was the major product of the reaction.

**2,2,4,11,13,13-Hexamethyl-6,9-bis-(dimethylamino)-7-tetradecyne. Method D.**—3,5,5-Trimethylhexanal (1066 g., 7.5 moles) was treated with dimethylamine (339 g., 7.5 moles) through a gas inlet while the mixture was stirred and maintained below 50° by external cooling. An aqueous phase separated and was discarded. The organic layer, after drying over anhydrous sodium sulfate (1141 g., 6.1 moles of crude alkylolamine), 3-dimethylamino-5,7,7-trimethyl-1-octyne (1171 g., 6.0 moles) and cuprous chloride (2 g.) were combined and heated at 170–190° for 6 hr. The reaction mixture was cooled and filtered. The filtrate was distilled under reduced pressure to give the product (1541 g., 4.24 moles, 71%), b.p. 128–133° (1 mm.), $n^{20}\text{D}$ 1.4617.

**1,4-Bis-(methylphenylamino)-2-butyne.**—This compound was prepared from 1,4-dichloro-2-butyne and N-methylaniline according to the procedure of W. Reppe (reference 5c, p. 79).

*Anal.* Calcd. for $C_{18}H_{20}N_2$: N, 9.1. Found: N, 9.1.

**3-Morpholino-1-butyne.**[11,5c] **Method E.**—A solution of cuprous chloride (13.5 g.) in concentrated hydrochloric acid (84 g.) was added to morpholine (200 g., 2.3 moles) with stirring and cooling. Acetylene (89 g., 3.4 moles) was introduced through a gas inlet tube and was absorbed at about 1.33 atm. during 20 hours while the temperature was maintained at 105–115°. The mixture was diluted with ethanol (1 volume) and filtered. The ethanol was removed by distillation under reduced pressure, and the residue was washed with 13% sodium hydroxide solution (230 ml.). The organic layer was separated, the aqueous layer was washed with diethyl ether (two 100-ml. portions), and the combined organic layers were dried over anhydrous potassium carbonate. Distillation gave 3-morpholino-1-butyne (108 g., 0.77 mole), b.p. 55–62° (0.1 mm.), $n^{20}\text{D}$ 1.4715, in 34% yield based on morpholine and 45% yield based on the acetylene absorbed.

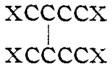
***cis,trans*-1,4-Bis-(dimethylamino)-1,3-butadiene** (II). **Method F.**—Sodium (16 g., of 50% dispersion[3] in xylene, 0.35 mole) was treated with xylene (90 ml.) and hexane (500 ml.), and the mixture was heated to reflux (72°). The heat source was removed and freshly distilled 1,4-bis-(dimethylamino)-2-butyne (I, 1500 g., 10.7 moles) was added in a fine stream during 3.5 hr. A log was kept of the refractive index *vs.* I added to ensure that unreacted I did not accumulate. The product was distilled under reduced pressure to remove first the hexane then the xylene. The product (1275 g., 85% yield) had b.p. 75–80° (7 mm.), $n^{20}\text{D}$ 1.549.

***trans,trans*-1,4-Bis-(dimethylamino)-1,3-butadiene.**—On standing in a stoppered bottle at room temperature for two

---

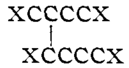
[8] E. R. H. Jones, G. H. Whitham and M. C. Whiting, *J. Chem. Soc.*, 3201 (1954).

[9] Partial structures D and E with three double bonds represent such materials. One possible structure for the tetrahydrodimer $C_{16}H_{36}N_4$ is F, and G would be the corresponding $C_{14}H_{31}N_3$ hydrogenolysis product.



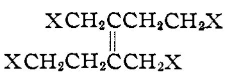
$$\begin{array}{c} XCCCCX \\ | \\ XCCCCX \end{array}$$

D



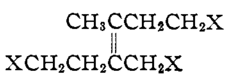
$$\begin{array}{c} XCCCCX \\ | \\ XCCCCX \end{array}$$

E



$$\begin{array}{c} XCH_2CCH_2CH_2X \\ \| \\ XCH_2CH_2CCH_2X \end{array}$$

F



$$\begin{array}{c} CH_3CCH_2CH_2X \\ \| \\ XCH_2CH_2CCH_2X \end{array}$$

G

[10] Elemental analyses were carried out by the analytical laboratories of the Rohm & Haas Co. All melting and boiling points are uncorrected.

[11] C. Gardner, V. Kerrigan, J. D. Rose and B. C. L. Weedon, *J. Chem. Soc.*, 780 (1949), described the preparation of this compound at acetylene partial pressures of 100–200 p.s.i.g.

months *cis,trans*-II had darkened somewhat and had rearranged to a form which had m.p. −4°. Redistillation gave the pure *trans,trans*-II, b.p. 80° (2 mm.), $n^{20}$D 1.555, m.p. −3 to −1°.

*Anal.* Calcd. for $C_8H_{16}N_2$: N, 19.97. Found: N, 19.91, 19.95.

This rearrangement could be carried out much more rapidly by adding traces of acids or water. In 24 hr. at room temperature or 3 hr. at 65–70° in the presence of 1 drop of water or acetic acid, the melting point of II (10 g.) rose from < −70° to −4°. Prolonged room temperature storage of *trans,trans*-II led to resinification.

***2,2,4,11,13,13*-Hexamethyl-6,9-bis-(dimethylamino)-6,8-tetradecadiene. Method G.**—Hexane (50 g.) and 50% sodium dispersion[3] in xylene (4 g.) were heated to reflux, the source of heat was removed and compound I (14 g., 0.10 mole) was added dropwise. Thereafter, 2,2,4,11,13,13-hexamethyl-6,9-bis-(dimethylamino)-7-tetradecyne (136 g., 0.37 mole) was added during 39 minutes. The reaction mixture was stirred and heated for an additional 2.5 hr. Distillation under reduced pressure gave (a), 10 g., b.p. 68–187° (4 mm.), $n^{20}$D 1.5420; and (b), 131 g., b.p. 187–192° (4 mm.), $n^{20}$D 1.4986. Cut a was chiefly II while cut b represented a 94.5% yield of the desired product in high purity as judged by its ultraviolet spectrum ($\epsilon_{max}$ 21,900 at 295 m$\mu$).

**Dimerization of 1,4-Bis-(dimethylamino)-1,3-butadiene.**—A mixture at I (150 g., 1.07 mole), xylene (150 ml.) and potassium metal (0.75 g., 0.02 mole) dissolved in 1-octanol (4.25 g.) was stirred and heated under reflux for 5 hr. Distillation under reduced pressure gave the product (126 g., 84%), b.p. 72–132° (0.2 mm.). Redistillation (powdered potassium hydroxide in the pot) of a combination of products from several such runs gave a series of fractions at 1.0 mm. whose physical properties indicated that a mixture of dimeric materials was present.

**Hydrogenation of 1,4-Bis-(dimethylamino)-2-butyne Dimer.**—The once-distilled dimer, b.p. 115–118° (0.15 mm.), $n^{19}$D 1.5220–1.5250, prepared as above (133 g., 0.475 mole), ethanol (30 ml.) and Raney nickel (10 g. of catalyst rinsed with ethanol) were hydrogenated at 170 atm. and 110–116° during 8.5 hr. Dimethylamine (0.227 mole) was recovered in the processing. Distillation and redistillation of selected cuts gave 8.5 g. of liquid, b.p. 81–90° at 0.20 mm., $n^{20}$D 1.4693. (*Anal.* Calcd. for $C_{14}H_{31}N_3$: N, 17.41; mol. wt., 241. Found: N, 17.46; mol. wt., 253) along with some solid material m.p. after recrystallization from heptane 104–105.5°.

*Anal.* Calcd. for $C_{16}H_{36}N_4$: C, 67.60; H, 12.68; N, 19.72; mol. wt., 284. Found: C, 67.76; H, 12.57; N, 19.04; mol. wt., 277.[12]

The same solid was obtained in low yields by hydrogenation in ethanol solution at 3 atmospheres in the presence of platinum oxide catalyst.

---

[12] By a modified Menzies–Wright ebulliometric procedure; W. E. Barr and V. J. Anhorn, "Scientific and Industrial Glass Blowing and Laboratory Techniques," Instrument Publishing Co., Pittsburgh, Pa., 1949, p. 284.

PHILADELPHIA, PENNA.

---

[CONTRIBUTION FROM THE ROHM & HAAS CO.]

# Chemistry of 1,4-Diamino-1,3-butadienes. II. A New Synthesis of N-Substituted Pyrroles[1]

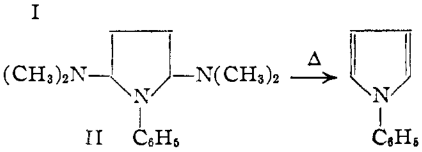
BY MARIAN F. FEGLEY, NEWMAN M. BORTNICK AND CHARLES H. MCKEEVER

RECEIVED NOVEMBER 3, 1956

N-Substituted pyrroles have been prepared by interaction of 1,4-bis-(dimethylamino)-1,3-butadiene and primary amines in the presence of an acidic catalyst.

Primary amines have been found to react with 1,4-bis-(dimethylamino)-1,3-butadiene (I)[2] in the presence of catalytic amounts of acids. The unstable cyclic addition product II was formed with evolution of heat when I and aniline were mixed in the presence of a trace of acetic acid,

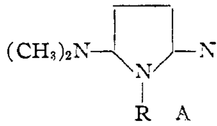
$$C_6H_5NH_2 + \underset{\displaystyle I}{(CH_3)_2NCH{=}CHCH{=}CHN(CH_3)_2} \longrightarrow$$



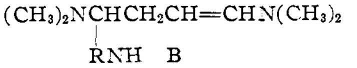
II

When II was distilled at atmospheric pressure, a low yield of N-phenylpyrrole was isolated together with dimethylamine, aniline, I and polymeric products.

The reaction of benzylamine with I required the addition of more acetic acid for its initiation than was the case with aniline and I. Ultraviolet spectroscopic assay[2] of an equimolar mixture showed that 85% of I had disappeared. Thus, a 1:1 addition product must have constituted a major portion of the mixture. It seems likely that products having the structures A–C were all in equilibrium with the starting materials.

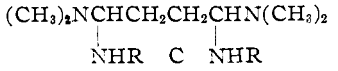


A



$$(CH_3)_2N\underset{\displaystyle RNH}{CH}CH_2CH{=}CHN(CH_3)_2$$

B



$$(CH_3)_2N\underset{\displaystyle NHR}{CH}CH_2CH_2\underset{\displaystyle NHR}{CH}N(CH_3)_2$$

C

Distillation of the reaction mixture gave a 40% yield of N-benzylpyrrole.

*n*-Butylamine failed to react with I in the presence of acetic acid. Addition of a few drops of concentrated hydrochloric acid led to evolution of dimethylamine and formation of N-*n*-butylpyrrole. This observation has formed the basis for a general procedure for the preparation of N-substituted pyrroles (Table I).

The mixtures of primary amine and I were treated with acid while a stream of inert gas was used to sweep out the dimethylamine as it was liberated. The reaction mixtures were treated with solid potassium carbonate and then distilled to isolate the pyrroles. In some experiments, removal

---

[1] Given in part at the 124th Meeting of the American Chemical Society, Chicago, Ill., September 9, 1953.

[2] M. F. Fegley, N. M. Bortnick and C. H. McKeever, THIS JOURNAL in press.