explains the experimental result that hydrogen peroxide is "salted-in" more by potassium ion than by sodium ion, while other non-electrolytes are "salted-out" more by sodium ion than by potassium ion.

In conclusion I wish to express my gratitude to Professor W. C. Bray for suggesting the problem, and for his very helpful suggestions and criticism during the progress of the work.

BERKELEY, CALIFORNIA RECEIVED JULY 29, 1935

[CONTRIBUTION NO. 159 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. XXII. α-Dialkylaminomethyl-β-vinylacetylenes

BY DONALD D. COFFMAN

The reaction of primary acetylenic compounds with formaldehyde and secondary aliphatic amines in dioxane has recently been shown to give good yields of aminomethyl derivatives having the formula $RC{\equiv}CCH_2NR_2$.[1] This reaction has been applied to vinylacetylene, and it proceeds smoothly with low molecular weight secondary aliphatic amines according to the equation

$$CH_2{=}CHC{\equiv}CH + CH_2O + HNR_2 \longrightarrow$$
$$\text{(I) } CH_2{=}CHC{\equiv}CCH_2NR_2 + H_2O$$

Members of this new class of amines (I) have been prepared by allowing a dioxane solution of vinylacetylene and paraformaldehyde to react with dimethylamine, diethylamine, piperidine and dicyclohexylamine in an autoclave at 100°. The reaction furnishes the lower members of the series in good yields. The properties of the amines obtained in this way are indicated in Table I. The compounds are stable, colorless liquids with characteristic odors.

TABLE I

PHYSICAL PROPERTIES OF α-DIALKYLAMINOMETHYL-β-VINYLACETYLENES

Nature of amine		B. p., °C.	d^{20}_4	n^{20}_D	MR Calcd.	MR Found	Exaltation
(II)	$(CH_3)_2N$-	133–135 at 752 mm.	0.8208	1.4700	35.99	37.05	1.06
(III)	$(C_2H_5)_2N$-	166–167 at 766 mm.	.8272	1.4710	45.23	46.34	1.11
(IV)	$(CH_2)_5N$-	207–209 at 766 mm.	.9069	1.5064	47.65	48.89	1.24
(V)	$(C_6H_{11})_2N$-	138–140 at 0.5 mm.	.9492	1.5191	77.78	78.35	0.57

TABLE II

PROPERTIES OF α-DIALKYLAMINOMETHYL CHLOROPRENES

Nature of amine		B. p., °C.	d^{20}_4	n^{20}_D	MR Calcd.	MR Found	Exaltation
(VI)	$(CH_3)_2N$-	56–58 at 11 mm.	0.9615	1.4895	42.40	43.73	1.33
(VII)	$(C_2H_5)_2N$-	71–73 at 5 mm.	.9500	1.4895	51.63	52.78	1.15
(VIII)	$(CH_2)_5N$-	90–92 at 3.5 mm.	1.0137	1.5193	54.05	55.59	1.54

The reactions of several typical members of this new class of amines have been studied. Compounds (III) and (IV) are readily hydrogenated to the corresponding saturated tertiary amines whose properties and derivatives agree with those already recorded in the literature.

Compounds (II), (III) and (IV) add hydrogen chloride in the presence of cuprous chloride, but they react more slowly with aqueous hydrochloric acid than does the parent hydrocarbon[2] so that elevated temperatures are required. The products (VI), (VII) and (VIII) of the reaction correspond in composition to structure (IX). By analogy with the formation of chloroprene from vinylacetylene, structure (IX) seems most likely.

(IX) $CH_2{=}CHCCl{=}CHCH_2N(R)_2$

(X) $p\text{-}CH_3C_6H_4SCH_2CH_2C{\equiv}CCH_2N(CH_3)_2$

The physical properties of these substituted chloroprenes are indicated in Table II. They are colorless liquids which darken on standing. Like chloroprene, they react with α-naphthoquinone and with maleic anhydride but the products are black tars. Unlike chloroprene, they polymerize very slowly even at 100° or when exposed to light, and no rubber-like polymer has yet been obtained from them. It has already been shown that α-substitution in 1,3-dienes decreases con-

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[1] Mannick and Chang, *Ber.*, **66**, 418 (1933).

[2] Carothers, Williams, Collins and Kirby, THIS JOURNAL, **53**, 4203 (1931).

siderably the rate of polymerization.[3,4] Furthermore, these compounds have polymerization inhibiting groups cast directly in the molecule.

Thio-*p*-cresol readily adds to (II) in the presence of ultraviolet light. The product is a yellow oil corresponding in composition to formula (X). Since the mode of addition of thiophenols has been established thoroughly and since in the case of divinylacetylene only the ethylenic bonds are involved in the addition, the assigned structure seems likely.[5,6] Other addition reactions also take place. One molecule of methanol adds to (II) in the presence of sodium methoxide. The oily product is completely destroyed by permanganate. The theoretical amounts of bromine and iodine are absorbed by (II), but the products were black undistillable sirups. Exhaustive methylation of (II) with methyl iodide and silver oxide gives for the most part a tar, but an unsaturated hydrocarbon C_5H_4 is obtained in poor yield. The compound absorbs oxygen rapidly and when heated gelled and finally exploded violently.

Experimental Part

Preparation of α-Dialkylaminomethyl-β-vinylacetylenes.—The general method of preparation consisted in heating in an autoclave at 100–105° for fourteen to seventeen hours a dioxane solution of secondary aliphatic amine, vinylacetylene and paraformaldehyde. The only especial precaution observed in the preparation consisted in thoroughly cooling in an ice-bath the solution obtained by mixing the amine and paraformaldehyde. After the reaction had ceased for the most part, the vinylacetylene was added. During the heating period, care was taken that the thermal decomposition temperature of vinylacetylene (*ca.* 110°) was not reached. The products of the reaction were isolated in one of two ways. The reaction mixture from small runs was poured into dilute acid, and the aqueous solution was thoroughly ether extracted. The free amine was liberated from its salt by the addition of alkali, and after extraction was dried over potassium hydroxide and distilled under diminished pressure. In the case of large runs, the reaction mixture was separated into its components by fractional distillation under diminished pressure. Table III indicates the condition used and the yields of products obtained. Table IV contains the analytical data for the products.

TABLE III

Product	Moles of			Dioxane solvent, cc.	Time and temp., °C.	Yield of product, %
	Amine	Vinylacetylene	$(CH_2O)_x$			
$(CH_3)_2N$-	14.6	15	4.85	1825	16 hrs. at 50; 12 hrs. at 100	74
	9	9	3	1200	17 hrs. at 45; 7 hrs. at 100	58
	0.5	0.5	0.17	50[a]	12 hrs. at 100	55
$(C_2H_5)_2N$-	.44	.44	.16	60	15 hrs. at 100	91
$(C_2H_5)_2N$-	2.6	2.46	.96	36	8 hrs. at 60; 7 hrs. at 80	72
$(CH_2)_5N$-	0.44	0.44	.16	60	15 hrs. at 100	68
$(C_6H_{11})_2N$-	1.6	1.6	.52	120	14 hrs. at 100	9.6

[a] Dimethylcellosolve was employed as solvent rather than dioxane.

TABLE IV

ANALYSES OF α-DIALKYLAMINOMETHYL-β-VINYLACETYLENES

Nature of amine		Calcd., % N	Found, % N
(II)	$(CH_3)_2N$-	12.84	12.39
(III)	$(C_2H_5)_2N$-	10.22	10.38
(IV)	$(CH_2)_5N$-	9.39	9.26
(V)	$(C_6H_{11})_2N$-	5.71	5.75

Hydrogenation of (III) and (IV) to Corresponding Saturated Tertiary Amines.—α-Diethylaminomethyl-β-vinylacetylene (0.25 mole) and 0.2 g. of platinum catalyst in 100 cc. of absolute ethanol absorbed 0.757 mole of hydrogen (107% of the amount required by theory) during thirty minutes. The catalyst was filtered from the solution and the filtrate was fractionally distilled through a good column. There was received 24 g. (yield 67% of the theoretical amount) of colorless oil identified as *n*-amyldiethylamine. Its constants are: b. p. 155–157° at 760 mm.; d^{20}_4 0.7663; n^{20}_D 1.4250; MR (calcd.), 47.70; MR (obsd.), 47.77.

Anal. Calcd. for $C_9H_{21}N$: N, 9.80. Found: N, 9.96.

The amine readily formed a picrate which melted at 52–53° after recrystallization from ethanol. The constants of the amine and the melting of its picrate are in good agreement with those recorded in the literature.[7] The amine is recorded as boiling at 155–158° at 735 mm. and the picrate as melting at 55°.

α-Pentamethyleneaminomethyl-β-vinylacetylene (0.2 mole) and 0.2 g. of platinum catalyst in 50 cc. absolute ethanol absorbed 0.51 mole of hydrogen (85% of the amount required by theory) during forty minutes. The catalyst was filtered from the ethanol solution and the filtrate was fractionally distilled. There was received 25 g. (yield 80% of the theoretical amount) of N-*n*-amylpiperidine. Its constants are: b. p. 192–195° at 760 mm.; d^{20}_4 0.8412; n^{20}_D 1.4602; MR (calcd.), 50.12; MR (obsd.), 50.55.

Anal. Calcd. for $C_{10}H_{21}N$: N, 9.03. Found: N, 9.15.

The amine readily formed a picrate which melted at 100–101° after recrystallization from ethanol. N-*n*-Amylpiperidine boils at 196° at 769 mm. and its picrate melts at 107°.[8]

Conversion of α-Dialkylaminomethyl-β-vinylacetylenes to α-Substituted Chloroprenes

Addition of Hydrogen Chloride to (II).—The amine (55 g.) was dissolved with cooling in 200 g. of 38% hydrochloric acid containing cuprous chloride (5 g.). The solution was heated at 60° during sixteen hours. It was then added dropwise with cooling to a solution of potas-

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(3) Carothers and Coffman, THIS JOURNAL, **54**, 4071 (1932).

(4) Jacobson and Carothers, *ibid.*, **55**, 1624 (1933).

(5) Ashworth and Burkhardt, *J. Chem. Soc.*, 1791 (1928).

(6) Carothers, THIS JOURNAL, **55**, 2008 (1933).

(7) Meisenheimer and Link, *Ann.*, **479**, 267 (1930).

(8) Robinson and Robinson, *J. Chem. Soc.*, **123**, 541 (1923).

sium hydroxide (112 g.) in 200 cc. of water. The insoluble amine was separated, dried and distilled. There was received 42 g. of colorless product (VI). The yield was 58% of the theoretical amount. After standing a short time, the amine was badly discolored. The substituted chloroprene (VI) reacted very rapidly with maleic anhydride and with naphthoquinone, but the products were black tars. Unlike chloroprene, it polymerized very slowly when exposed to light. After two and one-half months under a 100-watt lamp, a sample contained 10% of insoluble gelatinous polymer.

In the absence of cuprous chloride (II) adds hydrogen chloride very slowly; the product of the reaction is chiefly a tar but a 10% yield of (VI) was received.

Anal. Calcd. for $C_7H_{12}NCl$: Cl, 24.40. Found: Cl, 24.24.

Addition of Hydrogen Chloride to (III).—The amine (68 g.) was dissolved with cooling in 200 g. of 38% hydrochloric acid containing cuprous chloride (5 g.). After the solution had been heated sixteen hours at 60°, the amine was freed by the addition of excess alkali, separated, dried and distilled. There was received 40 g. of the monohydrochloride (VII) or 46% of the theoretical amount. The product gave tars when allowed to react with maleic anhydride or naphthoquinone, and it polymerized very slowly. Only a trace of polymer was formed by heating the monomer during forty-three hours at 100°. When exposed to the light of a 100-watt lamp during three months, the monomer formed a semi-granular polymer (less than 10%).

Anal. Calcd. for $C_9H_{16}NCl$: Cl, 20.46. Found: Cl, 20.84.

Addition of Hydrogen Chloride to (IV).—The amine (75 g.) was dissolved with cooling in 200 g. of 38% hydrogen chloride containing cuprous chloride (5 g.). The solution was allowed to stand for sixty-six hours at 35° and was finally heated at 60° for five hours. The product was isolated in the usual manner and there was received a 56% yield of (VIII). This substituted chloroprene contained only a trace of polymer after exposure to the light of a 100-watt lamp during three months.

Anal. Calcd. for $C_{10}H_{16}NCl$: Cl, 19.13. Found: Cl, 18.85.

The Addition of Thio-*p*-cresol to (II).—Thio-*p*-cresol (62 g.) was dissolved in 55 g. of amine (II), and the solution was exposed to the light of a Cooper–Hewitt lamp for twenty-four hours. The pale yellow liquid was washed with dilute alkali and water, and was then dried and distilled in vacuum. There was received 43 g. of dimethylamino-1-pentin-2-yl-5-*p*-thiocresyl ether (X). The yield was 30% of the theoretical amount. Its physical constants are: b. p. 156–158° at 0.5 mm.; d^{20}_4 1.0151; n^{20}_D 1.5620; MR (calcd.), 73.09; MR (obsd.), 74.44.

Anal. Calcd. for $C_{14}H_{19}NS$: N, 6.01. Found: N, 6.18.

The Addition of Methanol to (II).—The amine (2.25 moles) and absolute methanol (2.47 moles) in which sodium (0.22 mole) was dissolved were heated in an autoclave at 100° for twelve hours. The reaction product was poured into a large volume of water, and the water-insoluble material was separated, dried and vacuum distilled. There was received 125 g. of product corresponding in composition to the addition of one molecule of methanol to (II). The product (yield 40%) had a powerful fish-like odor. Its constants are: b. p. 69–71° at 1 mm.; d^{20}_4 0.8987; n^{20}_D 1.5400; MR (obsd.), 48.82.

Anal. Calcd. for $C_8H_{15}NO$: N, 9.93. Found: N, 10.52.

Attempts to establish the structure of this compound by permanganate oxidation were unsuccessful; the amine was completely destroyed. Attempts to add two molecules of methanol to (II) were unsuccessful; the products obtained were tar-like and were for the most part undistillable *in vacuo.*

Exhaustive Methylation of (II).—Exhaustive methylation of (II) with methyl iodide and potassium hydroxide or silver oxide gave for the most part a tar, but a hydrocarbon—presumably pentatetraene $(CH_2{=}C{=}C{=}C{=}CH_2)$—was obtained in poor yields. It absorbed oxygen rapidly and when heated it gelled and finally exploded violently.

The most convenient method for carrying out the methylation consists in treating the methyl iodide quaternary salt of (II) (m. p. 182–184°) with an excess of freshly precipitated silver oxide in aqueous suspension. The quaternary salt (97 g.) in 300 cc. of water was agitated with silver oxide (100 g.) at 45°. When the test for the presence of ionic iodide in the aqueous solution was negative, the silver iodide was filtered off and the filtrate was vacuum distilled. From the condensate there was received 4 g. of hydrocarbon. The residue consisted entirely of tar. The product appeared to boil from 80–90° when distilled immediately; n^{20}_D 1.4778.

Anal. Calcd. for C_5H_4: C, 93.75; H, 6.25. Found: C, 91.97; H, 6.74.

Summary

The reaction between vinylacetylene, paraformaldehyde and secondary aliphatic amines yields α-dialkylaminomethyl-β-vinylacetylenes. Several transformation products of typical members of this new class of amines are described.

WILMINGTON, DELAWARE RECEIVED JULY 17, 1935