solution was added to 17.3 g. of *p*-bromophenol (0.1 mole) in 15 ml. of methanol. After 18 hours at room temperature most of the solvent was removed under reduced pressure. Upon cooling, a crystalline product (3.1 g.) separated and was removed by filtration: m.p. 91–92°, after recrystallization from 95% ethanol. The mother liquor was taken up in 60 ml. of *i*-propyl ether, washed with 60 ml. of 10% aqueous potassium hydroxide and then with water, and dried over sodium sulfate. Upon removal of *i*-propyl ether a solid (2.0 g.) was obtained which melted at 90–92°, after recrystallization from 95% ethanol. The m.p. of neither of the above products was depressed when they were mixed with 3,4-dihydro-3-cyclohexyl-6-bromo-1,3,2H-benzoxazine (m.p. 91–92°); yield 35% based on cyclohexylamine.

The aqueous alkaline fractions were acidified with concentrated aqueous hydrochloric acid and extracted with *i*-propyl ether; removal of the ether resulted in 10.2 g. of a light tan solid; m.p. 63–64°, after recrystallization from carbon tetrachloride. Admixture with *p*-bromophenol (m.p. 64°) did not lower the melting point of the product: recovery of *p*-bromophenol not accounted for as benzoxazine, 71%.

3,4-Dihydro-6-chloro-3,5-dimethyl-8-*i*-propyl-1,3,2H-benzoxazine.—Paraformaldehyde (2.4 g., 0.08 mole) was dissolved in 5 ml. of warm methanol containing 0.1 g. of potassium hydroxide. The solution was cooled in ice and water and 4.96 g. of 25% aqueous methylamine (0.04 mole) was added. After addition of 7.4 g. of *p*-chlorothymol (0.04 mole) in 8 ml. of methanol, the reaction mixture was heated under gentle reflux for three hours. The resulting mixture, which had separated into two layers, was taken up in 40 ml. of benzene, washed three times with 5% aqueous potassium hydroxide and then with water. The benzene extract was dried over sodium sulfate and the benzene removed under reduced pressure. Distillation of the resulting light brown sirup (9 g.) gave 6.8 g. of a light yellow oil; b.p. 120–122° at 0.3 mm.; yield 71%.

Anal. Calcd. for $C_{13}H_{18}ClNO$: C, 65.13; H, 7.57; N, 5.84. Found: C, 65.53; H, 7.55; N, 5.71.

N-Methyl-(5-chloro-2-hydroxy-6-methyl-3-*i*-propylbenzyl)-amine Hydrochloride.—A solution containing 2.2 g. of 3,4-dihydro-6-chloro-3,5-dimethyl-8-*i*-propyl-1,3,2H-benzoxazine, 5 ml. of 20% aqueous hydrochloric acid and 25 ml. of 95% ethanol was distilled. During the course of the distillation formaldehyde was evolved and 30 ml. of 50% aqueous ethanol and 10 ml. of water were added. The distillation was continued until about 20 ml. of liquid remained in the flask. Water (20 ml.) was then added until the residue just became cloudy. Upon cooling a crystalline product (1.1 g.) separated; m.p. 172–174°.

Anal. Calcd. for $C_{12}H_{19}Cl_2NO$: C, 54.55; H, 7.25. Found: C, 54.89; H, 7.23.

N,N-Bis-(4-hydroxy-3,5-dimethoxybenzyl)-cyclohexylamine.—Cyclohexylamine (9.9 g., 0.1 mole) was added with cooling to 50 ml. of dioxane containing 15 ml. of 37% aqueous formaldehyde (0.2 mole). After addition of 30.8 g. of 2,6-dimethoxyphenol (0.2 mole) the reaction mixture was refluxed gently for one and two-thirds hours. Upon concentration of the solution and cooling a crystalline product (28 g., 65% yield) was obtained; m.p. 141°, after recrystallization from propanol-2.

Anal. Calcd. for $C_{24}H_{33}NO_6$: C, 66.80; H, 7.71; active hydrogen, 2.00. Found: C, 66.70; H, 8.04; active hydrogen (Zerewitinoff), 2.06.

N,N-Bis-(4-hydroxy-3,5-dimethoxybenzyl)-methylamine.—This compound was prepared in essentially the same manner as N,N-bis-(4-hydroxy-3,5-dimethoxybenzyl)-cyclohexylamine except that 12.4 g. of 25% aqueous methylamine (0.1 mole) was used in place of the cyclohexylamine. The product (25 g., 69% yield) melted at 137° after recrystallization from propanol-1 and gave a positive test for active hydrogen with methylmagnesium iodide.

Anal. Calcd. for $C_{19}H_{25}NO_6$: N, 3.85. Found: N, 3.70.

Infrared Absorption Spectra.—The infrared absorption spectra reported were determined with a Baird double-beam recording spectrophotometer through the courtesy of Samuel P. Sadtler and Son, Inc. In both cases the sample was mulled in mineral oil.

SALT LAKE CITY 1, UTAH RECEIVED JULY 30, 1951

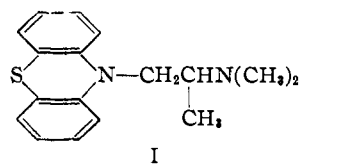
[CONTRIBUTION FROM ABBOTT LABORATORIES]

Histamine Antagonists. IV. C-Methyl Derivatives of 1,4-Disubstituted Piperazines[1]

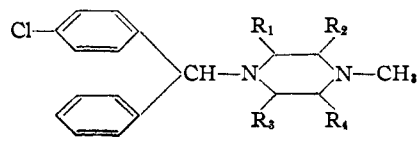
BY KARL M. BECK, K. E. HAMLIN AND ARTHUR W. WESTON

Several analogs of 1-(*p*-chlorobenzhydryl)-4-methylpiperazine (II) containing C-alkyl substituents on the piperazine nucleus have been prepared as antihistaminic drugs. The branching produced by these C-alkyl groups did not improve the antihistaminic activity. The structure of the N-methyl derivative of 2-methylpiperazine, prepared as an intermediate in the synthesis of one of these analogs, has been established as 1,2-dimethylpiperazine by an unequivocal synthesis.

The activity of certain antihistaminic drugs has been enhanced by replacement of the usual ethylenediamine side-chain by a propylenediamine grouping, as illustrated by Phenergan (I). This type of branching also appears in other physiologically active substances, such as Methadone (6-dimethylamino-4,4-diphenyl-3-heptanone) and Amphetamine (α-methylphenethylamine). Previous investigation[2] of 1,4-disubstituted piperazines has led to the development of the useful histaminic drug, Di-Paralene (II).[3] Consequently, a study was undertaken to determine the effect of branching on the antihistaminic activity of II.



I



II, R_1, R_2, R_3, R_4 = H
III, R_1, R_3, R_4 = H; R_2 = CH_3
IV, R_1, R_4 = H; R_2, R_3 = CH_3
V, R_1, R_3 = H; R_2, R_4 = CH_3
VI, R_1, R_2 = H; R_3, R_4 = $CH_2CH_2CH_2CH_2$

The analogs III–VI were prepared from the corresponding C-substituted piperazines by the previously described procedure.[2a] This method

(1) Presented before the Medicinal Division of the American Chemical Society, Cleveland, April 9, 1951.

(2) (a) K. E. Hamlin, A. W. Weston, F. B. Fischer and R. J. Michaels, Jr., THIS JOURNAL, 71, 2731, 2734 (1949); (b) R. Baltzly, S. Du Breuil, W. S. Ide and E. Lorz, *J. Org. Chem.*, 14, 775 (1949).

(3) Di-Paralene is the Abbott Laboratories trade mark for Chlorcyclizine, 1-(*p*-chlorobenzhydryl)-4-methylpiperazine.

TABLE I

DERIVATIVES OF 1,2-DIMETHYLPIPERAZINE

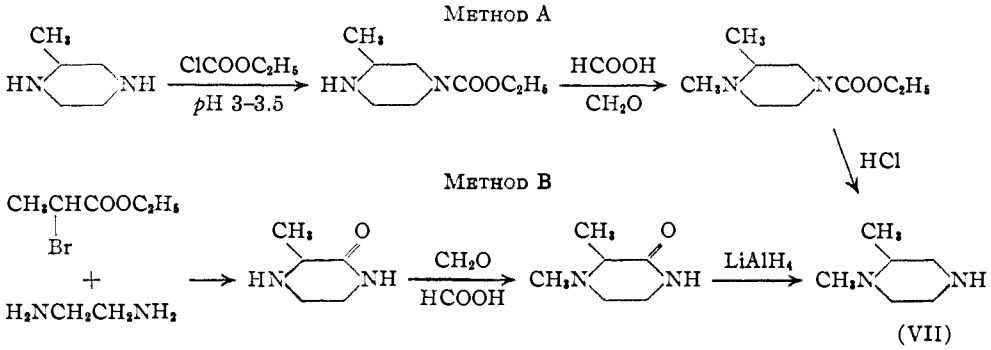
Salt	Formula	M.p., °C., dec., Method A	M.p., °C., dec., Method B	Mixed m.p., °C. dec.	Analyses, % Calcd.	Found Method A	Found Method B
Dipicrate[a]	$C_6H_{14}N_2 \cdot 2C_6H_3N_3O_7$	262	263	261	C, 37.77	C, 37.96	C, 37.99
					H, 3.52	H, 3.40	H, 3.65
Sesquioxalate[b]	$C_6H_{14}N_2 \cdot 1^1/_2C_2H_2O_4$	193–194	198–199	197–198	N, 11.24	N, 11.20	N, 11.37
4-(*p*-Nitrobenzoyl)-hydrochloride[c]	$C_{13}H_{17}N_3O_3 \cdot HCl$	267–268	268	267–268	N, 14.02	N, 14.10	N, 14.13

[a] Formed in ethanol and recrystallized from 60% aqueous ethanol. The melting-points varied over an 8° range depending upon rate of heating. Simultaneous determinations on both samples gave proximate values. [b] Formed with excess ethereal oxalic acid and recrystallized from an ethanol–methanol mixture. [c] Formed in benzene from equimolar amounts of the piperazine and *p*-nitrobenzoyl chloride, and recrystallized from an ethanol–methanol mixture.

involves blocking one nitrogen atom of the piperazine with a carbethoxy group, methylation of the other nitrogen, decarbethoxylation, and, finally, *p*-chlorobenzhydrylation of the nitrogen atom which had been protected.

The two dimethylpiperazines used in the synthesis of IV and V were obtained commercially.[4] The 2-methylpiperazine, used to prepare III, was made by the method of Kitchen and Pollard.[5] This same procedure was employed to synthesize the closely related 2,3-tetramethylenepiperazine, or decahydroquinoxaline, the intermediate for VI. Although this compound has been reported previously,[6] it is now fully identified and characterized.

Carbethoxylation of the unsymmetrical 2-methyl- and 2,6-dimethylpiperazine could give either the 1- or 4-carbethoxy derivative in each case. The method used to establish 1-carbethoxy-3-methylpiperazine as the structure obtained from 2-methylpiperazine is outlined below.



(VII)

Since 2-keto-3-methylpiperazine has only one basic nitrogen to undergo methylation in the Clarke–Eschweiler reaction, the resulting dimethylpiperazine must have the structure VII. Proof that the products obtained by method A and method B were identical was furnished by comparing physical properties[7] and melting points of three solid derivatives, Table I.

Apparently the steric effect of the methyl group upon the nitrogen atom nearest it predominates over any inductive effect,[8] so that reaction with ethyl chloroformate occurs at the second nitrogen atom. As a corollary of this observation, it seems reasonable to assume that the two substituents in 2,6-dimethylpiperazine would exert a similar effect and that V would represent the structure of the final product.

In 1-(*p*-chlorobenzhydryl)-3,4-dimethylpiperazine (III) the branching of the side chain occurs in the same relative position as it does in Phenergan (I). However, neither this compound nor any of the other C-methyl analogs was a better antihistaminic agent than Di-Paralene (II).[9]

Acknowledgment.—The authors are grateful to Messrs. Morris Freifelder and G. R. Stone for conducting the high pressure reactions. We are also indebted to Mr. E. F. Shelberg and his staff for the microanalytical determinations.

Experimental

2-Methylpiperazine.—Cyclization of 55 g. (0.465 mole) of N-(2-hydroxypropyl)-ethylenediamine[10] was effected by heating with 11 g. of Raney nickel and hydrogen at 200 p.s.i. initial pressure at 185–200° for 5 hours. Distillation gave 25.1 g. (54%) of product, b.p. 147–150° at 739 mm. This method was preferred to that employing copper chromite catalyst and dioxane as a solvent.[4]

2-(β-Aminoethylamino)-cyclohexanol.—A solution of 1200 g. (14 moles) of ethylenediamine (69% aqueous) in 1 liter of methanol was stirred and maintained at a temperature of 45–60° by external heating while 200 g. (2 moles) of cyclohexene oxide[11] in 100 cc. of methanol was added dropwise over a period of 4 hours. The mixture was distilled and the product collected as a colorless liquid, b.p. 122–123° at 1.2 mm.; yield 277 g. (84%). The compound solidified after standing a few days.

Anal. Calcd. for $C_8H_{18}N_2O$: C, 60.72; H, 11.46. Found: C, 61.20; H, 11.37.

(4) The authors gratefully acknowledge the gift of samples of 2,5-dimethylpiperazine and 2,6-dimethylpiperazine from Carbide and Carbon Chemical Corporation.

(5) L. J. Kitchen and C. B. Pollard, THIS JOURNAL, **69**, 854 (1947).

(6) M. Mousseron and G. Combes, *Bull. soc. chim. France*, [5] **14**, 82 (1947).

(7) Properties examined included infrared absorption spectra. The spectrograms showed no differences between the two samples.

(8) This is in accordance with Brown's concept of F-strain. H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944); H. C. Brown, *ibid.*, **67**, 374 (1945).

(9) L. W. Roth, R. K. Richards and I. M. Shepperd, *Arch. intern. pharmacodynamie*, **80**, 378 (1949).

(10) L. J. Kitchen and C. B. Pollard, *J. Org. Chem.*, **8**, 342 (1943).

(11) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 185. The intermediate 2-chlorocyclohexanol was prepared by the method of M. S. Newman and C. A. VanderWerf, THIS JOURNAL, **67**, 233 (1945), rather than by the procedure in "Organic Syntheses."

TABLE II: INTERMEDIATE PIPERAZINES, R_5—

R_1	R_2	R_3	R_4	R_5	B.p. °C.	Mm.	Ref. index $n^{25}D$	Yield, %	Formula	Analyses, % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
H	CH_3	H	$COOC_2H_5$	H[a]	120–121	10	1.4689	67	$C_8H_{16}O_2N_2$	55.68	9.37	16.27	56.50	9.16	16.17
H	CH_3	CH_3	$COOC_2H_5$	H	95	1.5	1.4688	45	$C_9H_{18}O_2N_2$	58.04	9.74	15.04	57.82	9.57	14.72
H	CH_3	CH_3	$COOC_2H_5$	$COOC_2H_5$	[b]			9[c]	$C_{12}H_{22}O_4N_2$	55.79	8.59		55.94	8.36	
H	CH_3	H	$COOC_2H_5$	H	86–87	1.3	1.4660	97	$C_9H_{18}O_2N_2$	58.04	9.74		58.19	9.68	
H	H	$CH_2CH_2CH_2CH_2$	$COOC_2H_5$	H	107–109	0.6	1.4968	67	$C_{11}H_{20}O_2N_2$	62.23	9.49		62.42	9.30	
H	CH_3	H	$COOC_2H_5$	CH_3	105–107	8	1.4638	85	$C_9H_{18}O_2N_2$	58.04	9.74		58.38	9.56	
H	CH_3	CH_3	$COOC_2H_5$	CH_3	115–116	12	1.4617	77	$C_{10}H_{20}O_2N_2$	59.97	10.07		59.90	9.96	
H	CH_3	H	$COOC_2H_5$	CH_3	122–125	12	1.4653	94	$C_{10}H_{20}O_2N_2$	59.97	10.07		60.22	9.89	
H	H	$CH_2CH_2CH_2CH_2$	$COOC_2H_5$	CH_3	103–104	0.6	1.4900	89	$C_{12}H_{22}O_2N_2$	63.68	9.80		63.71	9.41	
H	CH_3	H	H	CH_3[d]	147–148	748	1.4645	82	$C_6H_{14}N_2$	63.10	12.36	24.54	63.65	12.41	24.44
H	CH_3	H	H	CH_3[e]	151–152	753	1.4647	48	$C_6H_{12}N_2$	63.10	12.36	24.54	62.18	12.27	25.01
H	CH_3	CH_3	H	CH_3[f]	148	750	1.4574	82	$C_7H_{16}N_2$	65.57	12.58	21.85	65.45	12.49	21.87
H	CH_3	H	H	CH_3[f]	144	740	1.4680	77	$C_7H_{16}N_2$	65.57	12.58	21.85	65.09	12.65	21.38
H	H	$CH_2CH_2CH_2CH_2$	H	CH_3	88–90	8	1.4989	76	$C_5H_{12}N_2$	70.08	11.76		70.21	11.46	

[a] Monooxalate m.p. 131–133°. Calcd. for $C_8H_{16}N_2O_2 \cdot C_2H_2O_4$: C, 45.79; H, 6.92; N, 10.69. Found: C, 45.90; H, 6.77; N, 10.82. [b] M.p. 78°. [c] By-product in preparation of preceding compound. [d] Prepared by method A. [e] Prepared by method B. [f] Dipicrate, m.p. 272° dec. *Anal.* Calcd. for $C_7H_{16}N_2 \cdot 2C_6H_2(NO_2)_3(OH)$: C, 38.91; H, 3.78. Found: C, 38.84; H, 3.96.

The dihydrochloride salt was formed in ether and was recrystallized from absolute ethanol as white needles melting at 229–230° (dec.).

Anal. Calcd. for $C_8H_{18}N_2O \cdot 2HCl$: N, 12.12. Found: N, 12.28.

Decahydroquinoxaline.—Heating 38 g. (0.24 mole) of 2-(β-aminoethylamino)-cyclohexanol, 7.5 g. of Raney nickel and hydrogen at 200 p.s.i. initial pressure at 200° for 6 hours gave a solid reaction product. An ethanol solution of the solid was decolorized with carbon and evaporated to dryness. The residue was recrystallized from low-boiling petroleum ether as white needles, m.p. 150–151°; yield 8 g. (24%).

Anal. Calcd. for $C_8H_{16}N_2$: N, 19.98. Found: N, 20.15.

The dihydrochloride was formed in ether. It was recrystallized from methanol as a white solid, m.p. 365° dec., subliming at 60–70° at 0.2 mm.

Anal. Calcd. for $C_8H_{16}N_2 \cdot 2HCl$: C, 45.08; H, 8.51. Found: C, 45.25; H, 8.22.

1-Carbethoxypiperazines.—The carbethoxypiperazines were prepared by the method of Stewart and co-workers[12] through the reaction of the piperazine with ethyl chloroformate in buffered aqueous solution at a *p*H of 3–3.5. A 1,4-dicarbethoxy derivative was isolated as a by-product from the carbethoxylation of 2,5-dimethylpiperazine, and a similar derivative was obtained from 2-methylpiperazine when the *p*H was not carefully controlled. The properties of the 1-carbethoxypiperazines are summarized in Table II.

1-Carbethoxy-4-methylpiperazines.—The 1-carbethoxypiperazines were methylated with formic acid and formaldehyde by the method of Clarke and co-workers.[13] Since the products are very water soluble, the solutions were concentrated *in vacuo*, made alkaline with 50% alkali, and solid sodium hydroxide was added to achieve more complete separation of the products. These compounds are listed in Table II.

1-Methylpiperazines.—Decarbethoxylation was effected by refluxing the 1-carbethoxy-4-methylpiperazines with a fivefold excess of concentrated hydrochloric acid for 65–75 hours. The products were isolated in the manner outlined above and a e described in Table II.

2-Keto-3-methylpiperazine.—This compound was prepared by the general method for 3-alkyl-2-ketopiperazines.[14] The product upon redistillation was collected at 97–99° at 0.3 mm.; yield 19 g. Recrystallization from dry ether containing about 0.5% of isopropyl alcohol gave a hygroscopic white solid melting at 57–59° but was attended by considerable loss, so that after three recrystallizations only 7 g. of product remained. Analysis[15] indicated partial hydration.

Anal. Calcd. for $C_5H_{10}N_2O \cdot {}^1/_4H_2O$: C, 50.99; H, 8.38; N, 23.63. Found: C, 50.61; H, 8.92; N, 23.62.

The picrate was formed in ethanol and recrystallized from isopropyl alcohol, m.p. 167–168°.

Anal. Calcd. for $C_5H_{10}N_2O \cdot C_6H_2(NO_2)_3(OH)$: C, 38.49; H, 3.82; N, 20.41. Found: C, 38.78; H, 3.92; N, 20.65.

1,2-Dimethyl-3-ketopiperazine.—Methylation was carried out by the method of Clarke, *et al.*,[13] and the product was extracted continuously for 120 hours with ether from a strongly alkaline solution. The product distilled at 97° at 1 mm. as a colorless liquid, solidified and, was recrystallized from low-boiling petroleum ether as white plates, m.p. 79–80°.

Anal. Calcd. for $C_6H_{12}N_2O$: C, 56.22; H, 9.44; N, 21.86. Found: C, 56.63; H, 9.08; N, 21.64.

The hydrochloride formed in ether and was recrystallized from absolute ethanol as a hygroscopic white solid melting at 261–262° dec.

Anal. Calcd. for $C_6H_{12}N_2O \cdot HCl$: N, 17.20. Found: N, 17,23.

1,2-Dimethylpiperazine (Method B).—A mixture of 2.7 g. (0.07 mole) of lithium aluminum hydride and 100 cc. of dry

(12) H. W. Stewart, R. J. Turner and J. J. Denton, *et al.*, *J. Org. Chem.*, **13**, 134 (1948).

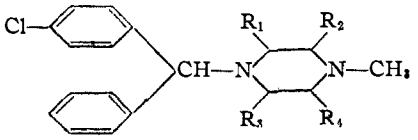
(13) H. T. Clarke, H. B. Gillespie and S. Z. Weisshaus, THIS JOURNAL, **55**, 4571 (1933).

(14) S. R. Aspinall, *ibid.*, **62**, 1202 (1940).

(15) Difficulty was experienced in obtaining satisfactory elemental analyses of some of the piperazine bases. In these cases solid derivatives were prepared which gave acceptable analyses.

TABLE III

1-(*p*-CHLOROBENZHYDRYL)-4-METHYLPIPERAZINES,



No.	R_1	R_2	R_3	R_4	B.p. °C.	Mm.	Yield, %	Formula	Analyses, %[16] Calcd. C	Calcd. H	Found C	Found H	M.p.,[b] °C.	Picrate[a] Calcd. N, %	Found N, %
III	H	CH_3	H	H	152–153	0.3	73	$C_{19}H_{23}ClN_2$	72.48	7.36	72.56	7.08	196–197	14.50	14.38
IV	H	CH_3	CH_3	H	150–160	1	19	$C_{20}H_{25}ClN_2$	73.04	7.66	73.26	7.12	181–182	12.55	12.36
V	H	CH_3	H	CH_3	177–178	1.4	57	$C_{20}H_{25}ClN_2$	73.04	7.66	73.12	7.36	214–215	14.24	14.14
VI	H	H	$CH_2CH_2CH_2CH_3$		193–197	0.6	57	$C_{21}H_{27}ClN_2$	74.45	7.67	75.17[c]	7.74	263	13.78	13.79

[a] All formed dipicrate salts except IV which formed a monopicrate. [b] These compounds melted with decomposition. [c] An attempt was made to improve this analysis by purification of the base through its dipicrate.

ether was refluxed and stirred in a dry nitrogen atmosphere for 1.5 hours. Then a solution of 2.1 g. (0.0164 mole) of 1,2-dimethyl-3-ketopiperazine in 150 cc. of dry ether was added over a period of 15 minutes. After the reaction mixture was stirred and heated for 4.5 hours more, 8 cc. of water was added to destroy the excess lithium aluminum hydride. The inorganic salts were removed by filtration, and the filtrate was distilled. The product boiled at 151–152° at 753 mm.; yield 0.9 g. (48%).

1-(*p*-Chlorobenzhydryl)-4-methylpiperazines.—The previously described method[28] for *p*-chlorobenzhydrylation was used to prepare these compounds. This procedure involves heating equimolar amounts of the N-methylpiperazine, *p*-chlorobenzhydryl chloride, and anhydrous sodium carbonate in refluxing xylene for 32–64 hours, extracting the product from the xylene with 6 *N* hydrochloric acid, basifying the aqueous solution, and collecting the product with ether. These compounds are listed in Table III. They were all high boiling, viscous liquids which were difficult to purify by distillation. Since the hydrochloride salts were hygroscopic, picrates were used to characterize the bases.[16]

(16) Solutions were prepared for pharmacological testing by neutralizing the bases with dilute hydrochloric acid.

NORTH CHICAGO, ILLINOIS RECEIVED JULY 27, 1951

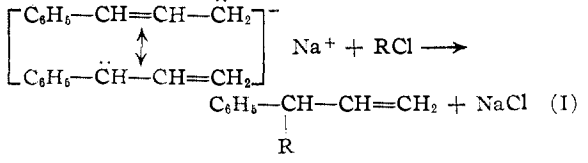
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Allylic Rearrangements. XXXIII. The Reaction of Sodium Allylbenzene with Allylic Halides and Methyl Bromide

BY WILLIAM G. YOUNG, M LTON KOSMIN,[1] R. Y. MIXER[2] AND TOD W. CAMPBELL[3]

The reactions of sodium allylbenzene with allyl bromide, α- and γ-methylallyl chlorides and methyl bromide have been studied in liquid ammonia to determine whether both the primary and secondary carbon atoms of the allylbenzene carbanion are involved in the displacement reaction. It was found that the carbanion attached predominately as the secondary isomer to give the product ($C_6H_5CHRCH{=}CH_2$) but in all cases some of the primary displacement product ($C_6H_5CH{=}CHCH_2R$) was present. It has been shown that both the α- and γ-methylallyl groups retained their configuration during the displacement reaction thus eliminating the possibility of the abnormal bimolecular displacement reaction (S_N2'). In the reaction with methyl bromide it was shown that the product composition varied with the order of addition of methyl bromide *vs.* sodium allylbenzene.

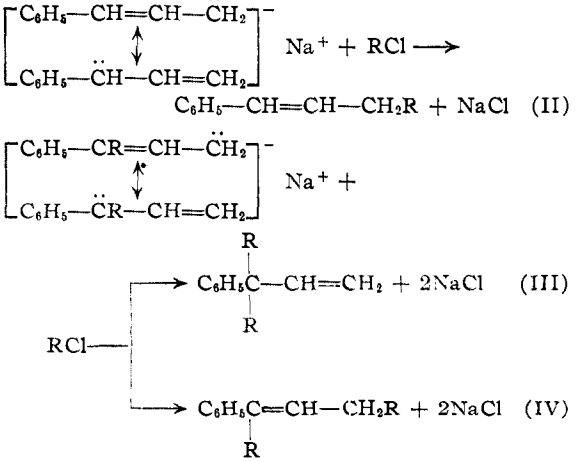
The reaction of allylic halides with sodium allylbenzene (γ-phenylpropenyl sodium) in liquid ammonia has been described by Levy and Cope.[4] Since these workers were primarily interested in the preparation of the secondary-type of reaction product (resulting from reaction I), no special effort was made to isolate other products which



might have been formed in low yields. These other products could arise as a result of attack by the primary carbon atom of the allylbenzene carbanion (reaction II), and by the reaction of the halide with a new carbanion formed by acid–base interchange between sodium allylbenzene and the hydrocarbon formed in reaction (I) (see reactions III and IV).

(1) Monsanto Chemical Co., Dayton, Ohio.
(2) Standard Oil Co. of California Fellow, 1950–1952.
(3) Western Regional Research Laboratory, Albany, California.
(4) H. Levy and A. C. Cope, THIS JOURNAL, **66**, 1684 (1944).

These other products might be expected since Campbell and Young[5] have shown that the reaction



of sodamide with either allyl- or propenylbenzene in liquid ammonia gives the same resonating carbanion system and that the reaction of this system

(5) T. W. Campbell and W. G. Young, *ibid.*, **69**, 688 (1947).