50–60% of the material had reacted after 24 hours.[33] Solid was still forming at a very slow rate but, after three weeks, which included several days of continuous shaking in contact with glass beads, only about 10% additional reaction had occurred.

In working up these reactions, the silver salt was first filtered off, washed with the appropriate organic solvent and the washes combined with the original filtrate. The solid then was washed with water, dried and weighed. Subsequent washing with dilute nitric acid and with aqueous sodium bicarbonate did not change the weight. When acetone was the solvent, it was removed, and the residue, after drying thoroughly in an evacuated desiccator, was dissolved in carbon tetrachloride and titrated for unsaturated acid. The reactions run in acetonitrile[34] were titrated directly.

To show the effect of strong acid on the reactions with silver trifluoroacetate in acetonitrile the following mixture was prepared. *trans*-2-Bromocyclohexanecarboxylic acid, 0.259 g. (0.00125 mole), was dissolved in 5 ml. of acetonitrile along with 0.453 g. of trifluoroacetic acid (0.00397 mole). To this was added 0.276 g. of silver trifluoroacetate (0.00125 mole) in 10–15 ml. of acetonitrile. This was approximately the condition of the actual run after solid stopped precipitating. On mixing, no solid formed and after standing for three days, there was only a very slight cloudiness in the solution. To this solution then was added 0.470 g. of pyridine (0.00594 mole); the solution was acid to moist litmus. Solid began to form at once, but slowly, and, after one week, 0.145 g. of silver bromide (0.000773 mole, 61.8% of theory) had precipitated.

Results.—Data are summarized in Tables I, II and III.

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[34] Eastman Kodak Co. spectro grade. A blank titration in the presence of this acetonitrile was less than 1% in error.

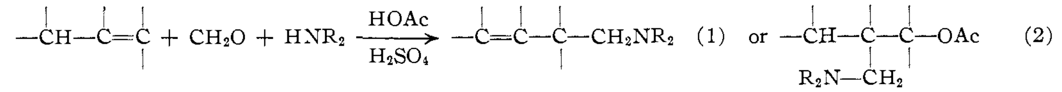
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Reaction of Formaldehyde and Secondary Amines with Some Olefins

BY G. F. HENNION, CHARLES C. PRICE[1a] AND VERNON C. WOLFF, JR.[1b]

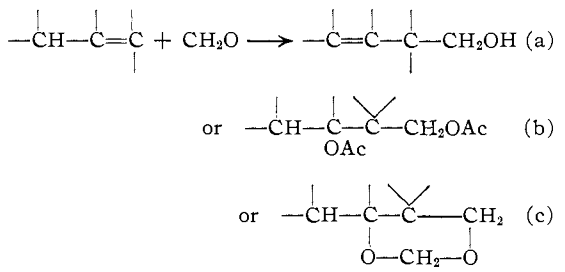
RECEIVED DECEMBER 3, 1954

α-Methylstyrene and *β*-pinene have been found to condense with formaldehyde and secondary amines in acetic acid–sulfuric acid according to reaction 1. Anethole under similar conditions reacted principally by equation 2 while styrene, cyclohexene and 1,1-diphenylethylene failed to react.



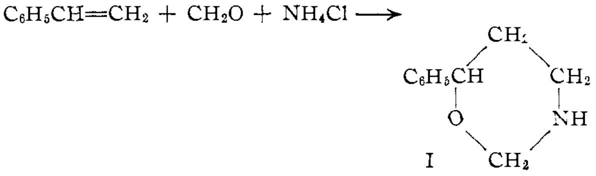
$$-\overset{|}{C}H-\overset{|}{C}=\underset{|}{\overset{|}{C}} + CH_2O + HNR_2 \xrightarrow[H_2SO_4]{HOAc} -\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}-CH_2NR_2 \quad (1) \quad \text{or} \quad -\overset{|}{C}H-\underset{R_2N-CH_2}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-OAc \quad (2)$$

The Prins[2] reaction of formaldehyde with olefins has been shown to result in three major types of products, depending on the olefin and/or the reaction conditions employed.



The course of these reactions may well all involve a common intermediate.[2b,3] The proposal that the formation of *β*,*γ*-unsaturated alcohols (a) proceeded through a pseudocyclic intermediate[3] has been supported by the work of Bain[4] and of Arnold.[5]

Meisel, Hartough and Dickert[6] recently have reported an extension of the Prins type reaction to the preparation of amino compounds.



In addition to 6-phenyltetrahydro-1,3-oxazine (I), its N-bis-methylene derivative or its N-methyl derivative could be obtained by modifying the conditions for the reaction. The authors indicated that the reaction failed for secondary amines.

The work reported herein was undertaken in the hope that olefins more reactive than styrene toward formaldehyde might be induced to condense with secondary amines.

Experimental[7]

Reagents and products were fractionally distilled through a 35 × 1.2-cm. Vigreux column wrapped with aluminum foil (A) or a 40 × 1-cm. electrically heated spiral-packed column (B). Infrared spectra were recorded on a Baird (AB-1-178) or a Perkin–Elmer (model 21) spectrophotometer by Richard Boyle, Anthony Verbiscar or George Svatos and the curves are reproduced in the Ph.D. Dissertation of Vernon C. Wolff, Jr., Science Library, University of Notre Dame.

Dow Chemical Co. *α*-methylstyrene, Eastman Kodak Co. anethole and Hercules Powder Co. *β*-pinene were redistilled before use. The *β*-pinene, after three distillations through column B (15.8-plates) boiled at 56.5–57° (17 mm.), n^{25}_D 1.4752.

Methiodides were prepared by stirring a well-cooled solution of the amine in ethyl acetate while three equivalents of methyl iodide were added dropwise. The copious white precipitate was washed with ethyl acetate and recrystallized, usually from ethyl acetate–absolute ethanol.

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[1] (a) Department of Chemistry, University of Pennsylvania, Phila. 4, Pa.; (b) Eli Lilly and Co. Fellow, 1952–1954. Abstracted from the Ph.D. Dissertation of V.C.W.

[2] See, *e.g.*, (a) H. J. Prins, *Proc. Acad. Sci. Amsterdam.*, **22**, 51 (1919); (b) C. C. Price, F. L. Benton and C. J. Schmidle, THIS JOURNAL, **71**, 2860 (1949).

[3] C. C. Price, "Mechanisms of Reactions at the Carbon–Carbon Double Bond," Interscience Publishers, Inc., New York, N. Y., 1946, p. 45.

[4] J. P. Bain, THIS JOURNAL, **68**, 639 (1946).

[5] R. T. Arnold and J. F. Dowdall, *ibid.*, **70**, 2590 (1948).

[6] S. L. Meisel, H. D. Hartough and J. J. Dickert, U. S. Patent 2,647,117, 2,647,118, and 2,652,429 (*C. A.*, **48**, 4826 (1954)).

[7] Nitrogen analyses by G. M. Maciak, W. L. Brown, H. L. Hunter and W. J. Schenck, Eli Lilly and Co., Indianapolis, Ind.; carbon and hydrogen analyses by Micro-Tech Laboratories, Skokie, Ill.

TABLE I

2-PHENYL-4-AMINO-1-BUTENES

4-Amino group	Yield, %	B.p. °C.	Mm.	$n^{25}D$	Analyses, % Calcd. C	H	Found C	H
$(CH_3)_2N$-	43	110–114	12	1.5226–1.5228	82.23	9.78	82.31	10.25
$(C_2H_5)_2N$-	8.9	82–85	0.3	1.5131–1.5149	82.70	10.41	82.83	10.57
Piperidino-	28.5	115–116	0.20–0.25	1.5375–1.5385	83.66	9.83	82.83	9.77
Pyrrolidino-	6.0	96–97	0.4	1.5401	83.53	9.51	83.65	9.50
Morpholino-	32.4	98–101	0.2–0.3	1.5421–1.5422	77.38	8.81	77.12	8.85

Hydrochlorides were prepared by passing dry hydrogen chloride into the amine in dry ether. The precipitate was recrystallized from ethyl acetate–absolute ethanol.

2-Phenyl-4-dimethylamino-1-butene.—A solution of 10 ml. of sulfuric acid in 300 ml. of glacial acetic acid in a flask equipped with stirrer, reflux condenser and nitrogen inlet tube was cooled in an ice-bath while 140 g. (1.25 moles) of 40% aqueous dimethylamine was added. This was followed by 34.5 g. (1.15 moles) of paraformaldehyde and 118 g. (1.0 mole) of α-methylstyrene. The air was flushed out for five minutes with nitrogen and the mixture then heated under reflux for three hours. After one-half hour of refluxing the reaction mixture became a transparent, homogeneous pale yellow. The reaction mixture was cooled in ice and the chilled solution neutralized with sodium hydroxide (230 g. in 600 ml. of water). The amine layer was taken up in 200 ml. of ether and the aqueous layer washed with two additional 100-ml. portions of ether. The combined ether extracts were washed with water, dried over potassium carbonate and distilled to yield 88 g., b.p. 110–113° (13 mm.), $n^{25}D$ 1.5212. Redistillation yielded 77 g. (43%) of **2-phenyl-4-dimethylamino-1-butene**, b.p. 110–114° (12 mm.), $n^{25}D$ 1.5226–1.5228.

Anal. Calcd. for $C_{12}H_{17}N$: C, 82.23; H, 9.78. Found: C, 82.31; H, 10.25.

TABLE II

2-PHENYL-4-AMINO-1-BUTENE METHIODIDES

4-Amino group	M.p., °C.	Nitrogen, % Calcd.	Found
$(CH_3)_2N$-	162–163	4.42	4.46
Piperidino-	131–133	3.92	3.73
Morpholino-	123–125	3.90	3.56

TABLE III

2-PHENYL-4-AMINO-1-BUTENE HYDROCHLORIDES

4-Amino group	M.p., °C.	Nitrogen, % Calcd.	Found
Et_2N-	120–122	5.84	5.86
Piperidino-	205-206	5.56	5.47
Pyrrolidino-	117–119	5.89	5.73
Morpholino-	177–179	5.52	5.45

An attempt to utilize phosphoric acid in place of sulfuric acid in the preparation of the piperidine analog led to two fractions, one the expected 2-phenyl-4-piperidino-1-butene (15%), the other being dipiperidinomethane (10%), b.p. 118° (22 mm.), $n^{25}D$ 1.4800 (lit.[8] b.p. 115° (15 mm.), $n^{15}D$ 1.4883).

Hydrogenation of 2-Phenyl-4-dimethylamino-1-butene.—A suspension of 5 g. of Raney nickel in a solution of 35 g. of the unsaturated amine in 80 ml. of 95% ethanol was shaken with hydrogen at an initial pressure of 60 p.s.i. After two hours, no further pressure drop occurred. Filtration and distillation yielded 28.0 g. of 3-phenyl-1-dimethylaminobutane, b.p. 112–113° (19 mm.), $n^{25}D$ 1.4940.

The infrared spectrum showed the 6.25 μ benzene band, but not the 6.15 μ double bond nor the 6.35 μ conjugated benzene bands of the original butene. The properties of the other hydrogenated amines are summarized in Table IV, together with the properties of the corresponding hydrochlorides.

Dimerization of 2-Phenyl-4-dimethylamino-1-butene.—Attempts to hydrate 52.5 g. of the butene by slow addition to 117 g. of concentrated sulfuric acid cooled to 5° yielded, after several washings and distillations, 25 g., b.p. 190–192° (2 mm.), $n^{25}D$ 1.5478–1.5480. The product was soluble in dilute hydrochloric acid and showed no indication of hydroxyl or of carbon–carbon double bond absorption in the infrared. These observations, together with the analysis, indicate the structure to be that of the dimer, **1,3-bis-(dimethylaminomethyl)-1-methyl-3-phenylhydrindane.**

Anal. Calcd. for $C_{24}H_{34}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 81.85; H, 9.47; N, 8.80.

Cyclohexene, styrene and 1,1-diphenylethylene were recovered in 65, 80 and 90% yields, respectively, when subject to condensation with paraformaldehyde and piperidine in acetic acid containing 15% sulfuric acid. In the former case, a substantial fraction of dipiperidinomethane also was obtained.

β-Pinene was successfully condensed with formaldehyde and several secondary amines. The results are summarized in Table V. Since Bain[4] has used the name "*nopol*" for the alcohol obtained from β-pinene and formaldehyde, 2-(2-hydroxyethyl)-6,6-dimethyl(1,1,3)bicyclo-2-heptene, we would like to use the term "*nopyl*" for the corresponding radical. Thus, we would call the amine from β-pinene, formaldehyde and piperidine **N-nopylpiperidine.**

TABLE IV

3-PHENYL-1-AMINOBUTANES

Amino group	B.p. °C.	Mm.	$n^{25}D$	Analyses, % Calcd. C	H	Found C	H	Hydrochlorides M.p., °C.	Nitrogen, % Calcd.	Found
$(CH_3)_2N$-	112–113	19	1.4940[a]	81.30	10.80	81.71	11.00	165–167[b]	6.55	6.42
Et_2N-	68–70	0.3	1.4910–1.4915	81.89	11.29	82.80	11.34	115–116	5.79	5.63
Piperidino-	109–112	.3	1.5130–1.5135	82.89	10.67	82.57	10.78	168–170	5.52	5.46
Pyrrolidino-	75–76	.3	1.5132	82.70	10.41	82.32	10.06	137–139	5.84	5.82
Morpholino-	95–96	.25	1.5153	76.67	9.65	76.04	9.56	177–179[c]	5.48	5.48

[a] D. J. Cram, THIS JOURNAL, **74**, 2140 (1952), reported $n^{25}D$ 1.4933. [b] Methiodide, m.p. 134–136°; calcd. N, 4.39; found N, 4.23. [c] Mixture with the corresponding butene hydrochloride melted at 165–170°.

Oxidation with potassium permanganate produced benzoic acid in good yield.

The methiodide crystallized from absolute ethanol, m.p. 162–163°.

Anal. Calcd. for $C_{13}H_{20}IN$: N, 4.42. Found: N, 4.46.

The hydrochloride was an oil which could not be crystallized.

Results for the similar preparation of other aminobutenes are summarized in Table I.

Reduction to the corresponding dihydronopylamines was accomplished by hydrogenation at 1000 p.s.i. at 100° in ethanol with palladium-on-charcoal catalyst. Results are summarized in Table VI.

Nopylpiperidine from Nopol.—Attempts to prepare nopyl chloride from nopol and thionyl chloride led to a mixture of unpleasant smelling material containing sulfur. Nopol

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(8) E. Knoevenagel, *Ber.*, **31**, 2586, note 1 (1899).

TABLE V

NOPYLAMINES

	Yield, %	B.p.			Analyses, %				Hydrochlorides		
					Calcd.		Found			Nitrogen, %	
		°C.	Mm.	$n^{25}D$	C	H	C	H	M.p., °C.	Calcd.	Found
Piperidine[a]	47.5	101–102	0.4	1.4967–1.4970	82.34	11.66	82.18	11.75	253–255	5.19	5.13
Pyrrolidine	20	82–83	.3	1.4946–1.4949	82.13	11.49	82.13	11.54	229–231	5.48	5.39
Morpholine	30	104–106	.3	1.4991–1.5020	76.54	10.71	76.26	10.80	218–220	5.15	5.19

[a] $\alpha^{20}D$ −22.3 to −24.8°; methiodide, m.p. 201–202°; methsulfate, m.p. 145–148°. *Anal.* Calcd. for $C_{18}H_{33}NO_4S$: N, 3.90; Found: N, 3.92.

TABLE VI

DIHYDRONOPYLAMINES

	Yield, %	B.p.			Analyses, %				Hydrochlorides		
					Calcd.		Found			Nitrogen, %	
		°C.	Mm.	$n^{25}D$	C	H	C	H	M.p., °C.	Calcd.	Found
Piperidine[a]	55	95–96	0.35	1.4929–1.4934	81.63	12.42	81.17	12.91	277–282	5.15	4.86
Pyrrolidine	71	89–93	.3	1.4911	81.38	12.29	81.63	12.22	235–237	5.43	5.43

[a] Methiodide, m.p. 221–223°; calcd. N, 3.71; found N, 4.02. Methsulfate, m.p. 171–173°, calcd. N, 3.87; found N, 4.01.

(16.6 g., 0.1 mole) dissolved in 80 ml. of pyridine and cooled to 5° was treated with 20.7 g. of *p*-toluenesulfonyl chloride. After standing overnight at 5°, ice, water and 200 ml. of ether were added. The ether layer was washed with two portions of dilute hydrochloric acid, with water and then dried over magnesium sulfate. The ether was evaporated and the crude nopyl tosylate was heated to reflux with 25 g. of piperidine in 80 ml. of acetone for two hours. After standing overnight, 200 ml. of ether was added, precipitating 20.5 g. of **piperidine *p*-toluenesulfonate**. Recrystallized from ethyl acetate–absolute ethanol, it melted at 130–132° and did not depress an authentic sample prepared from *p*-toluenesulfonic acid and piperidine.

The ether–acetone filtrate was treated slowly with 50 ml. of concentrated hydrochloric acid, precipitating 22.5 g. of the **hydrochloride** of **nopylpiperidine**. After two recrystallizations from water, it melted at 252–255° (sealed tube, dec.). There was no depression in melting point when mixed with the hydrochloride prepared from β-pinene. The free base recovered from the hydrochloride, b.p. 93–95° (0.3 mm.), $n^{25}D$ 1.4952–1.4960, $\alpha^{20}D$ (1 dm., neat), −18.80°, had an infrared spectrum virtually identical with the base from β-pinene.

Dihydronopylpiperidine was prepared similarly from dihydronopyl tosylate, b.p. 100–104° (0.4 mm.), 95–96° (0.3 mm.), $n^{25}D$ 1.4935–1.4937, and showed an infrared spectrum virtually identical with the sample from β-pinene.

1-(*p*-Methoxyphenyl)-2-methyl-3-piperidino-1-propyl Acetate.—A solution of anethole (148 g., 1.0 mole), paraformaldehyde (37.5 g., 1.25 moles) and 10 ml. of concentrated sulfuric acid in 400 ml. of glacial acetic acid, was warmed gently to reflux and boiled for 9.5 hours. After 150 ml. of acetic acid was removed by distillation at 15 mm., 500 ml. of ether was added. This solution was cooled in an ice-bath and treated dropwise with 185 g. of sodium hydroxide in 600 ml. of water with vigorous stirring. The ether layer was separated and the aqueous layer extracted with an additional 300 ml. of ether. The combined ether layers were washed with water, dried and distilled to yield 85 g. of crude product, b.p. 130–157° (0.3 mm.). Two further redistillations gave 30 g. (9.8%), b.p. 146–147° (0.4 mm.), $n^{25}D$ 1.5140.

Anal. Calcd. for $C_{18}H_{27}NO_3$: C, 70.78; H, 8.91. Found: C, 70.92; H, 8.93.

The infrared spectrum showed a strong ester band at 5.78 and a phenyl band at 6.18 μ.

On standing, the above liquid partially crystallized and, after several recrystallizations from aqueous ethanol, the solid portion melted at 53–54°.

Anal. Found: C, 70.38, 70.44; H, 8.80, 8.60.

Since the analysis and the infrared spectrum of the liquid and solid were identical, they presumably represent the two diastereoisomeric pairs resulting from the two asymmetric carbon atoms in **1-*p*-(methoxyphenyl)-2-methyl-3-piperidino-1-propyl acetate**.

The liquid and crystalline materials gave the same **hydrochloride**, m.p. 173–174° dec., both samples giving a sharp ester band at 5.80 μ.

Anal. Calcd. for $C_{18}H_{28}ClNO_3$: N, 4.10. Found: N, 3.96.

A second preparation from anethole gave material, b.p. 160° (0.5 mm.), $n^{25}D$ 1.5169–1.5172, which had an infrared spectrum identical to the first sample but which failed to crystallize, and, in fact, slowly dissolved a seed crystal of the isomer, m.p. 53–54°.

Oxidation of the acetate with alkaline potassium permanganate yielded ***p*-anisic acid**, m.p. 182–184°, proving that reaction had occurred in the side chain and not the nucleus of the anethole.

Hydrolysis of the acetate was accomplished by refluxing with potassium hydroxide in aqueous ethanol. Dilution with water precipitated an oil which was taken up in ether, washed and dried over anhydrous potassium carbonate. Addition of dry ethereal hydrogen chloride gave a gummy precipitate which, after washing with ethyl acetate and recrystallizing from acetone, melted at 170–172°. **This hydrochloride** of **1-*p*-methoxyphenyl-2-methyl-3-piperidino-1-propanol** showed a strong sharp hydroxyl band at 3.05 μ and no ester band.

When a sample of the acetate hydrochloride was allowed to stand in acetone–ethyl acetate for several weeks, a small quantity of material separated in two crystal forms, needles and prisms. These were separated by hand and the prisms melted at 120–121°, the needles at 172–174°. The mixture melted from 119–160°. The two crystals showed the same infrared spectrum with a strong hydroxyl band at 3.05 μ and no ester band. Evidently the acetate ester hydrolyzed under these conditions and the two diastereoisomeric alcohol hydrochlorides crystallized separately.

1-(*p*-Methoxyphenyl)-2-methyl-3-piperidino-1-propanone Hydrochloride.—A solution of 3.32 g. of the alcohol and 1.24 g. of sodium dichromate in 35 ml. of acetic acid was heated slowly to 80°, chilled, covered with ether and treated with 50 g. of sodium hydroxide in 100 ml. of water. The ethereal layer was separated, washed and dried. Addition of ethereal hydrogen chloride precipitated a semi-solid gum, recrystallized from acetone-absolute ethanol, m.p. 173–175° (sealed tube, dec.), lit.[9] 177°. A mixture with an authentic sample prepared from *p*-methoxypropiophenone, formaldehyde and piperidine[9] showed no depression. The infrared spectra of the two samples were identical and showed a conjugated carbonyl (6.05 μ), phenyl (6.25 μ) and conjugated phenyl (6.35 μ) bands.

Discussion

The mechanism which appears most reasonable for the course of the reactions described above is outlined below and resembles very closely those proposed for the Prins reaction[3] and by Alexander and Underhill[10] for the Mannich reaction.

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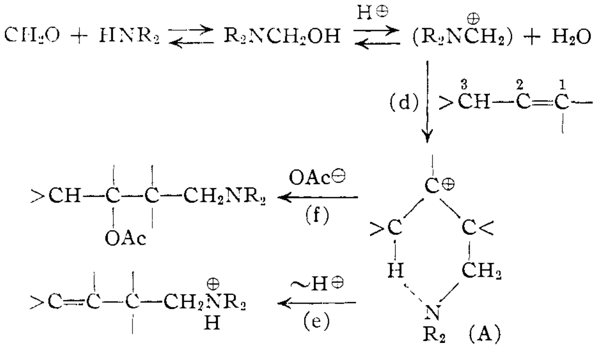
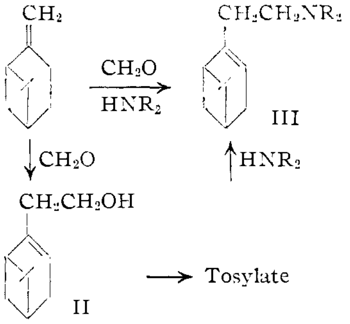
[9] C. Mannich and D. Lammering, *Ber.*, **55**, 3510 (1922).

[10] E. R. Alexander and E. J. Underhill, THIS JOURNAL, **71**, 4014 (1949).



That the migration of the double bond in fact occurs as suggested in step (e) above is amply demonstrated for the case of β-pinene.

The structure of nopol (II) has been demonstrated by Bain[4] and we have found that the amine III produced from nopol through the tosylate is in fact identical with that directly produced from β-pinene. The absence of carbon skeleton rearrangements suggests that the steps (d) and (e) must proceed virtually simultaneously since a free carbonium ion of the type represented by the intermediate (A) would be highly susceptible to carbon migration.



Evidence for assigning the α-methylstyrene product the structure of 2-phenyl-4-piperidino-1-butene is based principally on the similarity of the infrared spectra of our compound to that of 2-phenyl-1-butene, rather than 2-phenyl-2-butene.[11]

For anethole, the intermediate (A) would be most stable if the positive charge could be on the carbon alpha to the aromatic ring and there would thus be no hydrogen on carbon 3 so that step (e) could not occur and acetate ion would add instead by step (f).

(11) D. J. Cram, THIS JOURNAL, **74**, 2140 (1952).

PHILADELPHIA, PENNA.
NOTRE DAME, IND.

[CONTRIBUTION FROM THE ROHM & HAAS CO.]

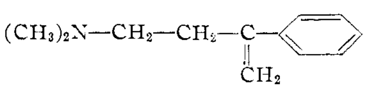
The Aminomethylation of Olefins. I. The Reaction of Secondary Amines, Formaldehyde, and Olefins

BY CLAUDE J. SCHMIDLE AND RICHARD C. MANSFIELD

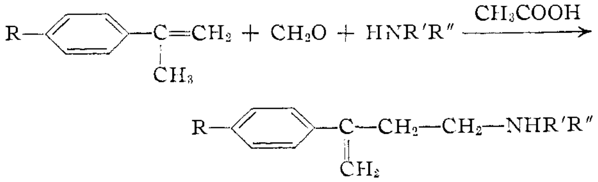
RECEIVED APRIL 2, 1955

New syntheses of 3-aryl-3-butenylamines, substituted cinnamylamines and 1-aryl-3-aminopropanols by the reaction of substituted styrenes, formaldehyde and secondary amines in acetic acid are reported. Unsaturated tertiary amines have been obtained from the reaction of several terpenes, formaldehyde and secondary amines.

The facility with which α-methylstyrene reacts with formaldehyde in acetic acid solution[1] suggested the possibility that this olefin would react with formaldehyde and secondary amines under comparable conditions. The reaction of α-methylstyrene, dimethylamine and paraformaldehyde was found to proceed readily in acetic acid solution to yield N,N-dimethyl-3-phenyl-3-butenylamine (I).


I

The structure of I was established by hydrogenation to N,N-dimethyl-3-phenylbutylamine[2] and the infrared spectrum which showed a strong absorption of 11.17 μ and had a close resemblance to that of 2-phenyl-1-butene[2] indicating that the double bond is in the terminal position. A series of 3-aryl-3-butenylamines prepared from α-methylstyrene and p,α-dimethylstyrene is given in Table I.



Unsaturated tertiary amines were also obtained from α- and β-pinene, camphene and limonene. These are listed in Table II. The amines from β-pinene, like the corresponding alcohol, nopol, exhibit optical activity.

This reaction may be represented by a combina- of Wagner's[3] hypothesis relating other acid-catalyzed reactions of secondary amines and formaldehyde with that of Price[4] concerning the reaction of formaldehyde with olefins.

Tertiary aminoalcohols were obtained from the reaction of p-methoxystyrene, anethole and isosafrole with formaldehyde and secondary amines un-

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(1) C. C. Price, F. L. Benton and C. J. Schmidle, THIS JOURNAL, **71**, 2860 (1949).

(2) D. J. Cram, *ibid.*, **74**, 2137 (1952).

(3) E. C. Wagner, *J. Org. Chem.*, **19**, 1862 (1954).

(4) C. C. Price, "Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 45.