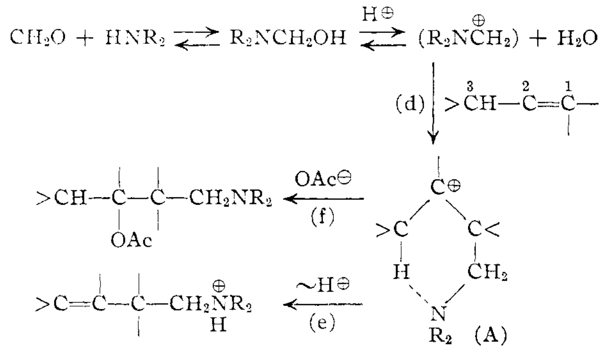
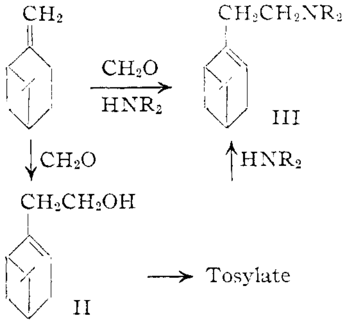


That the migration of the double bond in fact occurs as suggested in step (e) above is amply demonstrated for the case of β-pinene.

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).

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[CONTRIBUTION FROM THE ROHM & HAAS CO.]

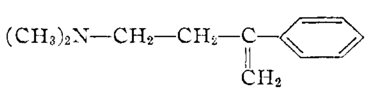
The Aminomethylation of Olefins. I. The Reaction of Secondary Amines, Formaldehyde, and Olefins

BY CLAUDE J. SCHMIDLE AND RICHARD C. MANSFIELD

RECEIVED APRIL 2, 1955

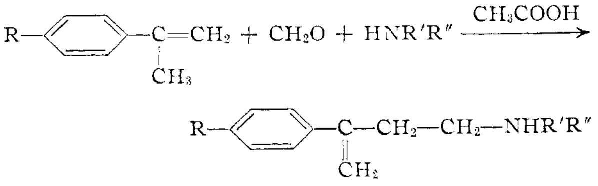
New syntheses of 3-aryl-3-butenylamines, substituted cinnamylamines and 1-aryl-3-aminopropanols by the reaction of substituted styrenes, formaldehyde and secondary amines in acetic acid are reported. Unsaturated tertiary amines have been obtained from the reaction of several terpenes, formaldehyde and 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 combination 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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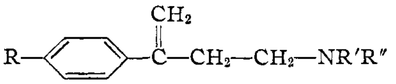
[1] C. C. Price, F. L. Benton and C. J. Schmidle, THIS JOURNAL, **71**, 2860 (1949).

[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.

TABLE I

3-ARYL-3-BUTENYLAMINES, 

R	-NR'R''	Time, hr.	Yield, %	B.p. °C.	Mm.	$n^{25}D$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
H	$N(CH_3)_2$	16[a]	60	65–70	0.5	1.5225	$C_{12}H_{17}N$	82.23	82.22	9.78	10.01	7.99	7.99
H	$N(C_2H_5)_2$	5[b]	33	145–146	25	1.5126	$C_{14}H_{21}N$	82.70	82.32	10.41	10.47	6.89	6.90
H	NC_4H_8O[c]	16[b]	30	175–180	15	1.5439	$C_{14}H_{19}NO$	77.38	77.20	8.81	8.87	6.45	6.47
H	$C_6H_5CH_2NCH_3$	16[b]	39	140–150	1	1.5615	$C_{18}H_{21}N$	86.01	85.31	8.42	8.48	5.57	5.48
CH_3	$N(CH_3)_2$	6[d]	56	115–120	6	1.5209	$C_{13}H_{19}N$	82.48	82.10	10.12	10.26	7.40	7.36
CH_3	$N(C_2H_5)_2$	16	34	110–115	2	1.5156	$C_{15}H_{23}N$	82.89	82.40	10.67	10.90	6.44	6.44
CH_3	NC_4H_8O[c]	16[b]	51	160–165	4	1.5407	$C_{15}H_{21}NO$	77.87	78.40	9.15	9.23	6.06	5.86
CH_3	$N(CH_2)_4CH_2$	16[b]	32	145–148	4	1.5363	$C_{16}H_{23}N$	83.78	83.27	10.11	10.42	6.11	5.82
CH_3	$N(CH_2)_3CH_2$	16[b]	18	125–130	2	1.5384	$C_{15}H_{21}N$	83.66	83.03	9.83	9.76	6.51	6.30

[a] N,N,N',N'-Tetramethyldiaminomethane used as the source of amine and one-half of the required formaldehyde. [b] One equiv. of phosphoric acid added. [c] 4-Morpholinyl. [d] Dimethylamine sulfate used as the source of amine and one equivalent of sulfuric acid.

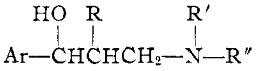
TABLE II

REACTION OF TERPENES, FORMALDEHYDE AND SECONDARY AMINES

Terpene	Secondary amine	Time, hr.	Yield, %	B.p. °C.	Mm.	$n^{25}D$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
α-Pinene	$H\text{-}N(CH_3)_2$	30	33	120–130	18	1.4819	$C_{13}N_{23}N$	80.76	80.13	11.99	11.34	7.25	7.3
β-Pinene	$H\text{-}N(CH_3)_2$	2	65	133–143	20	1.4771	$C_{13}N_{23}N$	80.76	80.05	11.99	12.32	7.25	7.6
Camphene	$H\text{-}N(CH_3)_2$	16	21[a]	55–65	0.3	1.4789	$C_{13}H_{23}N$	80.76	80.13	11.99	12.12	7.25	7.05
d-Limonene	$H\text{-}N(CH_3)_2$	16[b]	24	70–80	0.3	1.4809	$C_{13}H_{23}N$	80.76	79.58	11.99	12.12	7.25	7.24
Dipentene	$HN(CH_2)_4CH_2$	16	22	105–114	0.75	1.5000	$C_{16}H_{27}N$	82.33	80.70	11.67	11.53	6.00	5.86
β-Pinene	$HN(CH_2)_4CH_2$	16	28	115–125	2	1.4977	$C_{16}H_{27}N$	82.33	81.90	11.67	11.64	6.00	6.05
Camphene	HNC_4H_8O[c]	16	24	87–97	0.6	1.5025	$C_{15}H_{25}NO$	76.54	76.00	10.71	10.72	5.95	5.93
β-Pinene	HNC_4H_8O[c]	16	44	170–180	10	1.4985	$C_{15}H_{25}NO$	76.54	74.32	10.71	10.51	5.95	6.16
d-Limonene	HNC_4H_8O[c]	16	18	100–110	0.3	1.5030	$C_{15}H_{25}NO$	76.54	75.28	10.71	10.82	5.95	5.78

[a] 26% yield with dimethylamine sulfate. [b] Dimethylamine sulfate used as the source of amine and one equivalent of sulfuric acid. [c] Morpholine.

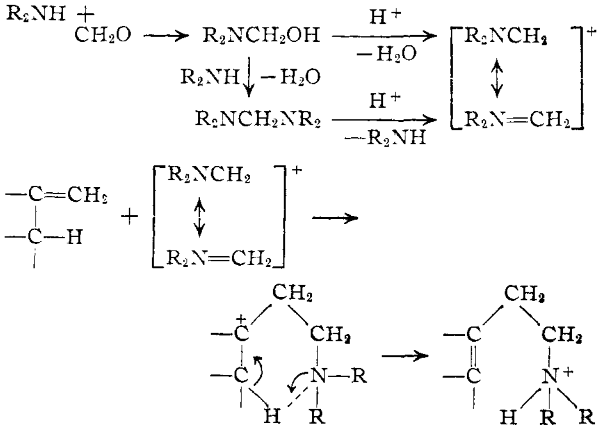
TABLE III

AMINO ALCOHOLS 

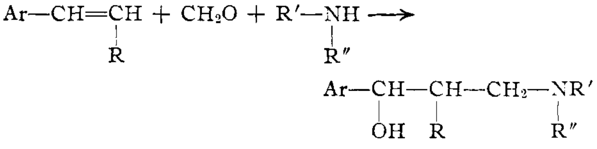
$Ar\text{—}\underset{|}{\overset{HO}{C}}H\underset{}{\overset{R}{C}}HCH_2\text{—}\overset{R'}{N}\text{—}R''$

Ar	R	NR'R''	Time, hr.	Yield, %	B.p. °C.	Mm.	$n^{25}D$	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
p-Anisyl	H	NC_4H_8O[a]	1	36	175–185	2.0	1.5328	$C_{14}H_{21}NO_3$	66.90	66.96	8.42	8.06	5.57	5.30
p-Anisyl	CH_3	$N(CH_3)_2$[b]	8	42	130–140	1.2	1.5144	$C_{13}H_{21}NO_2$	69.92	69.75	9.48	9.44	6.27	6.34
3,4-Methylene-dioxyphenyl	CH_3	$N(CH_3)_2$[c]	8	34	125–135	0.4	1.5241	$C_{13}H_{19}NO_3$	65.80	65.88	8.07	8.17	5.90	5.78

[a] 4-Morpholinyl. [b] N,N,N',N'-Tetramethyldiaminomethane used as the source of amine and one-half of the formaldehyde. [c] Dimethylamine sulfate used as the source of amine and one equivalent of sulfuric acid.



der reaction conditions sufficiently mild to avoid dehydration.



$$Ar\text{—}CH{=}\underset{R}{\underset{|}{C}}H + CH_2O + R'\text{—}\underset{R''}{\underset{|}{N}}H \longrightarrow Ar\text{—}\underset{OH}{\underset{|}{C}}H\text{—}\underset{R}{\underset{|}{C}}H\text{—}CH_2\text{—}\underset{R''}{\underset{|}{N}}R'$$

These are listed in Table III.

The reaction of *p*-methoxystyrene, formaldehyde and dimethylamine sulfate in acetic acid gave, after 18 hours refluxing, a 30% yield of N,N-dimethyl-*p*-methoxycinnamylamine (II).

N,N-Dimethyl-3,3-di-*p*-anisylallylamine (III) was obtained from the reaction of 1,1-bis-*p*-methoxyphenylethylene, formaldehyde and dimethylamine sulfate in acetic acid.

N,N-Dimethyl-3-*p*-anisyl-3-phenylbutylamine (IV) was obtained from the reaction of N,N-dimethyl-3-phenyl-3-butenylamine (I) with anisole in the presence of zinc chloride.

Acknowledgments.—To Dr. J. D. Stroupe for spectroscopic data and physical-chemical interpretation. To Dr. D. J. Cram for supplying infrared data for the phenylbutenes prior to their publication. To Mr. C. W. Nash and Mr. Thomas Callan, with their staffs, for analytical data reported.

Experimental

The Reaction of Secondary Amines, Formaldehyde and Olefinic Compounds.—The following general procedure was employed to prepare the compounds listed in Tables I, II and III. One mole of the amine was dissolved in 400 g. (6.6 moles) of acetic acid and 31.6 g. (1 mole, 95% assay) of paraformaldehyde was added. The mixture was heated until a clear solution was obtained and one mole of the olefinic compound was added. The mixture was stirred and refluxed for the length of time indicated. After cooling, the mixture was poured into 1.5 l. of water and extracted with benzene. The aqueous layer was made basic with excess sodium hydroxide solution. The amine was taken up in benzene, dried and distilled.

N,N,N′,N′-Tetramethyldiaminomethane was employed in some cases as the source of dimethylamine and one-half of the required formaldehyde. The addition of one equivalent of sulfuric acid or phosphoric acid per mole of amine before the olefin was added appeared to be advantageous with the less reactive systems. The more conveniently handled dimethylamine sulfate was successfully employed in several instances. These variations are indicated in the tables.

N,N-Dimethyl-3-phenylbutylamine.—Reduction of 75 g. of N,N-dimethyl-3-phenylbutenylamine (I) in 175 ml. of ethanol at 100 atm. and 100° using 7 g. of Raney nickel gave 59.5 g. (78%) of N,N-dimethyl-3-phenylbutylamine,[2] b.p. 110–113° (20 mm.), n^{25}D 1.4940.

Anal. Calcd. for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.10; H, 10.85; N, 7.83.

N,N-Dimethyl-*p*-methoxycinnamylamine (II).—A mixture of 70 g. (0.28 mole, 76% assay) of technical dimethyl[5] amine sulfate solution, 13 g. (0.41 mole, 95% assay) of paraformaldehyde, 52 g. (0.39 mole) of *p*-methoxystyrene and 72 g. (1.2 moles) of acetic acid was stirred and refluxed for 18 hours. After cooling, the mixture was poured into 500 ml. of water and extracted with benzene. The aqueous layer was made basic with excess sodium hydroxide solution. The amine was taken up in benzene, dried and distilled to give 48 g. (64%), b.p. 110–135° (3 mm.). This was redistilled to give 22 g. (30%) of N,N-dimethyl-*p*-methoxycinnamylamine, b.p. 120–125° (3 mm.).

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.28; H, 9.29; N, 7.3.

N,N-Dimethyl-3,3-di-*p*-anisylallylamine (III).—A mixture of 9 g. (0.28 mole) of paraformaldehyde, 120 g. (2 moles) of acetic acid, 61.5 g. (0.25 mole) of dimethylamine sulfate (76% assay) was stirred and heated until a clear solution was obtained. Sixty grams (0.25 mole) of 1,1-bis-*p*-methoxyphenylethylene[6] was added. The mixture was stirred and refluxed 16 hr. The amine was isolated as in the previous examples and distilled to give 36 g. (12%) of N,N-dimethyl-3,3-di-*p*-anisylallylamine, b.p. 195–205° (2.2 mm.) n^{25}D 1.5853.

Anal. Calcd. for $C_{19}H_{23}NO_2$: C, 76.71; H, 7.79; N, 4.74. Found: C, 75.79; H, 7.47; N, 4.65.

N,N-Dimethyl-3-anisyl-3-phenylbutylamine (IV).—Hydrogen chloride was passed into a solution of 87.5 g. (0.5 mole) of N,N-dimethyl-3-phenyl-3-butenylamine (I) in 216 g. (2 moles) of anisole with stirring and cooling to form the amine hydrochloride. The mixture was heated to 80° to effect solution of the amine salt and 70 g. of anhydrous zinc chloride was added slowly. An exothermic reaction took place and the temperature rose to 105°. Hydrogen chloride was passed into the solution for one hour, during which period the temperature rose to 110° and then fell to 80°. The mixture was then heated at 120° for 2 hours. After cooling, the mixture was mixed with 1 l. of water and 100 g. of concentrated hydrochloric acid. The unreacted anisole was separated from the aqueous layer which was then made basic with 500 ml. of 50% sodium hydroxide solution. The amine was taken up in benzene, dried, and distilled to give 103 g. (72%) of N,N-dimethyl-3-anisyl-3-phenylbutylamine, b.p. 185–195° (4.5 mm.), n^{25}D 1.5564.

Anal. Calcd. for $C_{19}H_{25}NO$: C, 80.52; H, 8.89; N, 4.94. Found: C, 80.26; H, 8.60; N, 4.95.

PHILADELPHIA, PA.

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[5] R. Quelet, *Bull. soc. chim.*, **7**, 196 (1940).

[6] R. Quelet and J. Allard, *ibid.*, **7**, 215 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PENNSYLVANIA STATE UNIVERSITY]

The Stereochemistry of Radical–Olefin Addition Reactions. Reactions of *cis*- and *trans*-2-Butenes with Bromotrichloromethane

BY PHILIP S. SKELL AND ROBERT C. WOODWORTH[1]

RECEIVED JANUARY 3, 1955

The light-initiated free-radical chain reactions of *cis*- and *trans*-2-butene with bromotrichloromethane have been examined in detail to elucidate the relative rates of the successive reactions and the structure of the chain-carrying 3-trichloromethyl-2-butyl radical. The reaction of *cis*- or *trans*-2-butene with bromotrichloromethane produces a mixture of identical quantities of the two diastereomeric 1:1 addition products. These results indicate that the addition of a trichloromethyl radical to *cis*- or *trans*-2-butene produces the same mixture of diastereomeric 3-trichloromethyl-2-butyl radicals, $CH_3—CH(CCl_3)—\dot{C}H—CH_3$. There is no evidence in support of a three-atom ring structure for this radical. It seems likely that all aliphatic free radicals have the conventional open-chain structure. The addition of a $\cdot CCl_3$ radical to either of the 2-butenes proceeds at comparable rates: $k_c/k_t = 2.4$. The rate of interconversion of the diastereomeric 3-trichloromethyl-2-butyl radicals by rotation about the C_2–C_3 bond must be greater than the rate of reaction of these radicals with bromotrichloromethane. The rate of reaction of the diastereomeric radicals with bromotrichloromethane must be greater than the rate of dissociation of the radicals to $\cdot CCl_3$ and C_4H_8. A pyramidal structure for the trivalent carbon of the 3-trichloromethyl-2-butyl radical is suggested.

It is a well-known experimental fact that in polar media addition of bromine to olefins proceeds by a stereospecific course resulting in *trans* addition to the double bond. These facts have been explained by assuming a positively charged three-atom ring intermediate which formally derives from the placement of a Br^+ at a position approximately equidistant from the doubly bound atoms and above the plane of the double bond. This intermediate then acquires the equivalent of a Br^- which approaches from the free side of the double bond plane, thus resulting in the *trans* attachment of the two bromine atoms.

The experimental basis for a similar discussion of the addition of radicals to olefins has not lent itself

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[1] National Science Foundation Fellow.