tetroxide. The reaction is rapid and exothermic and produces nitrogen as well as nitric oxide. This reaction is probably one source of the nitrogen gas which is found as a reaction product in the isobutylene reaction. The aldehyde is rather more stable, permitting it to be isolated if desired. When held at 60° for about an hour in the presence of nitric acid, the aldehyde is oxidized to the acid.

Another reaction intermediate is a compound having an infrared absorption at 6.45 μ. This was detected in the oil obtained from the tubular reactor, but the compound itself could not be isolated. It disappeared at a first-order rate from the neutral oil, as detected by changes in the infrared spectrum. The only major change observed in the infrared spectrum, other than the disappearance of the 6.45 μ absorption, was a corresponding increase at 5.48 μ, where α-nitratoisobutyric anhydride absorbs. Thus the 6.45 μ band is thought to be an intermediate in the formation of the anhydride. Absorption at 6.45 μ is characteristic of nitro or nitroso groups,[16] indicating that the compound contains nitrogen–oxygen bonds, but little else is known of its nature. No anhydride could be found in the N_2O_4 oxidation products of isobutyraldoxime or of α-nitratoisobutyraldehyde, and it is therefore suspected that the 6.45 μ absorbing material occurs from a reaction of N_2O_4 with isobutylene nitrosonitrate in a reaction that is competitive with isomerization to the oxime. The relation of these reactions is shown in Fig. 1.

Acknowledgments.—Elizabeth McElhill, Charles E. Dills and John O. H. Peterson contributed to the experimental work reported here.

(16) John F. Brown, Jr., THIS JOURNAL, **77**, 6341 (1955).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Alkylation of Amines with *t*-Acetylenic Chlorides. Preparation of Sterically Hindered Amines[1]

BY G. F. HENNION AND ROBERT S. HANZEL[2]

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Aliphatic *prim*- and *sec*-amines are alkylated slowly at room temperature, in good yield, by *t*-acetylenic chlorides. The reaction is catalyzed by cuprous chloride. Catalysis is needed only in the case of aromatic amines; otherwise the latter react poorly. Many of the acetylenic amines produced have been hydrogenated to the corresponding allylic and saturated derivatives. A large number of new sterically hindered amines are described.

Discussion

The successful alkylation of *prim*- and *sec*-amines by *t*-acetylenic chlorides was first reported in a previous paper in this series.[3] The present study was undertaken to determine if this reaction is applicable to amines RNH_2 and $RR'NH$ of varied basicities and steric features; if the acetylenic amines, $R^1R^2C(NR^3R^4)C{\equiv}CH$, so produced are amenable to semi- and full hydrogenation without hydrogenolysis; and thus to ascertain if a new general route to sterically hindered amines of various types is available.

The simple reaction involved, namely

$$R^1R^2C(Cl)C{\equiv}CH + 2R^3R^4NH \longrightarrow R^1R^2C(NR^3R^4)C{\equiv}CH + R^3R^4NH{\cdot}HCl$$

succeeded in all cases studied and thus appears to be notably insensitive to steric features, except for rate. Thus *t*-butylamine, morpholine and piperidine reacted substantially as well as did ethylamine and *n*-propylamine. While an excess of R^3R^4NH ordinarily was used to serve as the HCl acceptor, triethylamine, potassium carbonate and potassium hydroxide often served equally well for this purpose, permitting use of R^3R^4NH in minimum amounts. In view of the mechanism previously proposed[3,4] for the reaction, it was surprising to observe that it is catalyzed by copper and by cuprous salts. When the amine subjected to alkylation was a strong base, catalysis ordinarily was not needed. With weakly basic compounds (aromatic amines) cuprous salt catalysis was necessary in order to obtain the products in good yields within a reasonable reaction time. While the mechanistic role of cuprous salts is not known, it may be that the dipolar ion intermediate[3,4] A is made more reactive in the form of the acetylide structure B. Alternatively, the *t*-acetylenic chloride used may form its acetylide C in the alkaline reaction mixture, subsequently leading to B and/or A as the species responsible for alkylation.

$$\underset{\text{A}}{R^1R^2\overset{\oplus}{C}-C{\equiv}C^{\ominus}} \qquad \underset{\text{B}}{R^1R^2C^{\oplus}-C{\equiv}C-Cu} \qquad \underset{\text{C}}{R^1R^2C(Cl)-C{\equiv}C-Cu}$$

That elimination of HCl from the *t*-acetylenic chloride with formation of an eneyne hydrocarbon intermediate and subsequent addition of amine to the latter is not involved in the reaction mechanism was clearly shown by the fact that amines did not react with isopropenylacetylene, $CH_2{=}C(CH_3)C{\equiv}CH$, under any of the conditions which succeeded when chlorides were used.

Catalytic hydrogenation of the new compounds $R^1R^2C(NHR^3)C{\equiv}CH$ readily afforded the corresponding allylic and saturated derivatives ($-CH{=}CH_2$ and $-CH_2CH_3$, respectively, in place of $-C{\equiv}CH$). Semi-hydrogenation was achieved with either 5% Pd/$BaCO_3$ or 10% Pd/C in petroleum

(1) Paper no. 71 on substituted acetylenes; previous paper, G. F. Hennion and F. X. O'Shea, *J. Org. Chem.*, **23**, 662 (1958).

(2) Eli Lilly Co. Fellow, 1957–1959. Abstracted from a portion of the Ph.D. Dissertation of R.S.H.

(3) G. F. Hennion and K. W. Nelson, THIS JOURNAL, **79**, 2142 (1957).

(4) G. F. Hennion, *et al.*, *ibid.*, **73**, 4735 (1951); **75**, 1653 (1953).

TABLE I

ACETYLENIC AMINES, $(CH_3)_2C(NR^1R^2)C{\equiv}CH$

Compd.	R^1	R^2	Molecular formula	M.p., °C.	B.p. °C.	B.p. Mm.	$n^{25}D$	Yield,[a] %	Method	Nitrogen, % Calcd.	Nitrogen, % Obsd.	Hydrochlorides: Molecular formula	M.p., °C.	Carbon, % Calcd.	Carbon, % Obsd.	Hydrogen, % Calcd.	Hydrogen, % Obsd.	Nitrogen, % Calcd.	Nitrogen, % Obs
I	CH_3-	H-	$C_6H_{11}N$	−5	96–98		1.4234	59	C	14.42	14.29	$C_6H_{12}NCl$	216–217	53.96	54.10	8.99	9.08	10.49	10.73
II	CH_3CH_2-	H-	$C_7H_{13}N$	50–51	108–109		....	44	A	12.60	12.02	$C_7H_{14}NCl$	183–185	56.94	56.49	9.56	9.89	9.49	9.31
								42	C										
III	$CH_2{=}CHCH_2-$	H-	$C_8H_{13}N$	31	130		....	43	A	11.37	11.26	$C_8H_{14}NCl$	194–195	60.18	60.62	8.84	8.76	8.77	8.85
								34	B										
IV	n-C_3H_7-	H-	$C_9H_{15}N$	32	129		....	55	A	11.19	10.89	$C_9H_{16}NCl$	171–173	59.43	59.53	9.98	9.94	8.66	8.75
V	i-C_3H_7-	H-	$C_9H_{15}N$	28	117		1.4179[b]	58	A		[d]	$C_9H_{16}NCl$	204–206	59.43	59.30	9.98	9.94	8.66	8.55
								56	A[c]										
VI	n-C_4H_9-	H-	$C_9H_{17}N$	24	151		1.4279	64	A	10.06	10.29	$C_9H_{18}NCl$	183–184	61.52	61.23	10.33	10.34	7.97	7.92
								19	D										
VII	i-C_4H_9-	H-	$C_9H_{17}N$	19	140–142		1.4232	50	A	10.06	9.94	$C_9H_{18}NCl$	215–216	61.52	61.45	10.33	10.46	...	...
VIII	s-C_4H_9-	H-	$C_9H_{17}N$	−11	139		1.4250	55	A	10.06	10.00	$C_9H_{18}NCl$	181–183	61.52	61.78	10.33	10.36	7.97	7.86
								50	B										
								49	B[e]										
IX	t-C_4H_9-	H-	$C_9H_{17}N$	24	135–136		1.4292	52	A[f]	10.06	10.24	$C_9H_{18}NCl$	221–223	61.52	61.27	10.33	10.00	7.97	8.16
								28	B[g]										
								34	B[e,g]										
								14	C										
X	$-(CH_2)_2O(CH_2)_2-$		$C_9H_{15}NO$	78–79	97	30	....	33	A	9.14	8.71	$C_9H_{16}NOCl$	189–190	56.98	57.11	8.50	8.89	7.39	7.28
								79	C										
								75	D										
XI	$CH_3OCH_2CH_2CH_2-$	H-	$C_9H_{17}NO$	...	53	2	1.4369	52	B	9.02	8.99	$C_9H_{18}NOCl$	165–166	56.39	56.09	9.46	9.23	7.31	7.27
XII	$-CH_2(CH_2)_3CH_2-$		$C_{10}H_{17}N$	56–57	74	18	....	46	A	9.26	9.20	$C_{10}H_{18}NCl$	188–189	63.98	63.82	9.66	9.54	7.46	7.55
								68	C										
								50	D										
XIII	p-ClC_6H_4-	H-	$C_{11}H_{12}NCl$	...	98–99	0.4	1.5538	46	D	7.27	7.35	$C_{11}H_{13}NCl_2$	155–156	57.41	57.90	5.69	6.05	6.09	6.06
XIV	C_6H_5-	H-	$C_{11}H_{13}N$	49–50	76–78	0.2	....	56	C	8.80	8.67	$C_{11}H_{14}NCl$	169–170	67.51	67.15	7.21	7.18	...	...
								59	D										
XV	$C_6H_{11}-$[h]	H-	$C_{11}H_{19}N$	32	91	20	....	55	A	8.48	8.29	$C_{11}H_{20}NCl$	236–237	65.49	65.47	9.99	10.02	6.94	7.17
XVI	n-$C_8H_{17}-$	n-C_3H_7-	$C_{11}H_{21}N$	...	74	19	1.4362	28	A	8.37	8.32	$C_{11}H_{22}NCl$	208–209	64.84	65.01	10.89	10.99	6.87	7.01
XVII	$C_6H_5CH_2-$	H-	$C_{12}H_{15}N$	42–43	79	0.3	....	46	A	8.09	7.99	$C_{12}H_{16}NCl$	246–247	68.72	68.66	7.69	7.69	6.68	6.67
XVIII	C_6H_5-	CH_3-	$C_{12}H_{15}N$	...	72	.5	1.5210	44	D	8.09	8.38	$C_{12}H_{16}NCl$	149–150	68.72	69.16	7.69	7.72	6.68	6.61
XIX	p-$CH_3OC_6H_4-$	H-	$C_{12}H_{15}NO$	...	110–111	.3	1.5391	55	D	7.40	7.46	$C_{12}H_{16}NOCl$	169–170	63.85	64.22	7.15	7.17	6.20	6.22
XX	$(C_2H_5)_2N(CH_2)_2-$	H-	$C_{12}H_{26}N_2$	...	83	3.5	1.4479	41	B	14.27	13.98	$C_{12}H_{26}N_2Cl_2$	190–191	53.52	53.54	9.73	9.79	10.41	10.17

[a] Yields are for twice distilled material of 3° boiling range or less. [b] Undercooled. [c] No water added; 7 days at room temperature. [d] Calcd. for $C_8H_{15}N$: C, 76.74; H, 12.08. Obsd.: C, 76.57; H, 12.19. [e] With potassium carbonate instead of potassium hydroxide. [f] Nineteen days at room temperature. [g] Thirty-seven days at room temperature. [h] Cyclohexyl.

TABLE II

ACETYLENIC AMINES, $R^1R^2C(NR^3R^4)C{\equiv}CH$

Compd.	R^1	R^2	R^3	R^4	Molecular formula	B.p., °C.	Mm.	M.p., °C.	$n^{25}D$	d^{25}	Yield,[a] %	Method	Nitrogen, % Calcd.	Nitrogen, % Obsd.	Molecular formula	M.p., °C.	Carbon, % Calcd.	Carbon, % Obsd.	Hydrogen, % Calcd.	Hydrogen, % Obsd.	Nitrogen, % Calcd.	Nitrogen, % Obsd.
XXI	CH_3–	C_2H_5–	H–	$C_8H_{15}N$	75–76	110		1.4320	0.803[b]	23	A	8.18	8.41	$C_8H_{16}NCl$	181–182	59.43	59.65	9.98	9.97	8.66	8.63
										57	C										
XXII	CH_3–	C_2H_5–	i-C_3H_7–	$C_9H_{17}N$	79	90		1.4268	....	38	A	10.06	9.90	$C_9H_{18}NCl$	194–196	61.52	61.86	10.33	10.27	7.97	8.05
										23	C										
XXIII	CH_3–	C_2H_5–	t-C_4H_9–	$C_{10}H_{19}N$	65	35		1.4369	0.805	46	A[d]	9.14	9.07	$C_{10}H_{20}NCl$	204–205	63.30	63.24	10.63	10.63	7.38	7.58
										31	B[e]										
XXIV	CH_3–	C_2H_5–	C_2H_5–	$C_{10}H_{19}N$	162–164			1.4398	....[c]	21	C	...	...								
XXV	CH_3–	C_4H_9–	C_4H_9–	$C_{12}H_{23}N$	96	1	31	....	....	46	C	8.09	8.07	$C_{12}H_{24}NCl$	162–163	68.72	69.14	7.69	7.83	6.68	6.85
										68	D										
XXVI	C_2H_5–	C_2H_5–	C_2H_5–	$C_9H_{17}N$	83	70		1.4380	0.813	27	A	10.06	9.89	$C_9H_{18}NCl$	205–207	61.52	61.27	10.32	10.13	7.97	7.88
										49	C										
XXVII	C_2H_5–	C_2H_5–	i-C_3H_7–	$C_{10}H_{19}N$	84	50		1.4342	.805	29	A	9.14	9.12	$C_{10}H_{20}NCl$	222–223	63.30	63.58	10.63	10.80	7.38	7.40
XXVIII	C_2H_5–	C_2H_5–	t-C_4H_9–	$C_{11}H_{21}N$	74	20		1.4415	.816	21	A^f	8.37	8.33	$C_{11}H_{22}NCl$	267–268	64.84	64.94	10.89	10.83	6.87	6.75
XXIX	C_2H_5–	C_2H_5–	C_6H_5–	$C_{14}H_{17}N$	101	1		1.5372	....	40	D	7.48	7.35	$C_{14}H_{18}NCl$	156–157	69.78	69.99	8.11	8.05	6.26	6.39
XXX	$-CH_2(CH_2)_3CH_2-$		C_2H_5–	$C_9H_{17}N$	79	15	32	1.4492	0.887	48	A	9.26	9.25	$C_9H_{18}NCl$	219–220	63.98	63.96	9.66	9.69	7.46	7.42
										28	C										
XXXI	$-CH_2(CH_2)_3CH_2-$		i-C_3H_7–	$C_{11}H_{19}N$	85	18	32	....	....	47	A	8.18	8.41	$C_{11}H_{20}NCl$	225–226[g]	65.49	65.78	9.99	10.08	6.94	6.93
XXXII	$-CH_2(CH_2)_3CH_2-$		i-C_4H_9–	$C_{12}H_{21}N$	92	13	41	....	....	56	A^e	7.81	7.64	$C_{12}H_{22}NCl$	223–224[g]	66.79	67.04	10.28	10.57	6.49	6.62
XXXIII	$-CH_2(CH_2)_3CH_2-$		C_6H_5–	$C_{14}H_{17}N$	.....	..	96–97	....	....	60	D	7.03	7.02	$C_{14}H_{18}NCl$	199–200[g]	71.32	71.04	7.69	7.41	5.94	6.08

[a] Yields are for twice distilled material of 3° boiling range or less. [b] 3-Diethylamino-3-methyl-1-pentyne; lit. b.p. 77–78° at 120 mm., $n^{25}D$ 1.4318, d^{25} 0.802 (C. F. Hennion and E. C. Teach, THIS JOURNAL, **75**, 4297 (1953)). [c] 3-Diethylamino-3-methyl-1-pentyne; lit. b.p. 103–105° at 120 mm., $n^{25}D$ 1.4397 (note *b*). [d] Sixteen days at room temp. [e] Thirty-nine days at room temp. [f] Twenty-two days at room temp. [g] Melts with decomposition.

ether.[5] Hydrogenation to saturation was equally well accomplished with use of mildly active Raney nickel in ethanol.[6] In two instances, however (compounds XXVIII and XXXII, Table II), hydrogenation with Raney nickel self-terminated at the olefin stage, indicating steric hindrance to further reaction. In these cases the saturated compounds were not prepared.[7]

All of the amines prepared were examined by way of their infrared spectra. The acetylenic compounds (Tables I and II) showed acetylenic hydrogen strongly at about 3.05 μ and the ethynyl group weakly near 4.7 μ. Those having the vinyl group (Table III) had absorption bands near 6.1 and 11 μ as required. The saturated compounds (Table IV) had no infrared bands indicative of unsaturation.

The pK_a's of five of the new amine hydrochlorides were measured in the Lilly Research Laboratories, Indianapolis. The following results (in 66% dimethylformamide at 25°) were reported.[8] 3-*t*-Butylamino-3-methyl-1-butyne (compd. IX, Table I), 8.2; 3-*t*-butylamino-3-methyl-1-butene (compd. XXXVI, Table III), 10.0; 2-*t*-butylamino-2-methylbutane (compd. XLVIII, Table IV), 10.6; 1-*t*-butylamino-1-ethynylcyclohexane (compd. XXXII, Table II, 8.2; 1-*t*-butylamino-1-vinylcyclohexane (compd. XLV, Table III), 10.2. It will be noted that the electron-withdrawing ethynyl group sharply reduces basicity relative to the corresponding allylic and saturated compounds and that two bulky groups on nitrogen provide essentially no steric hindrance to basicity. *t*-Butyl-*t*-amylamine (XLVIII) is a remarkably strong base.

Further work is in progress to explore more adequately the chemistry of sterically hindered amines.

Experimental

The *t*-acetylenic chlorides were prepared from the carbinols as described previously.[3]

Four procedures (methods A–D) were used for the alkylation reactions with only minor variations in the various applications. These methods are illustrated by the following examples.

Preparation of 3-Isopropylamino-3-methyl-1-butyne (Method A).—To 44.3 g. (0.75 mole) of isopropylamine was added with cooling and shaking 25 ml. of water in 5-ml. portions. 3-Chloro-3-methyl-1-butyne (25.5 g., 0.25 mole) was then added in one portion and the solution was allowed to stand at room temperature for 7 days. The mixture, now two layers, was then poured into 200 ml. of ether and 200 ml. of water. The ethereal layer was washed with two 100-ml. portions of water, dried superficially with anhydrous potassium carbonate and finally overnight with potassium hydroxide pellets. Distillation gave a series of fractions, b.p. 110–121°, $n^{25}D$ 1.4180–1.4209, wt. 20 g. (64% yield). Redistillation with use of a 30-cm. Vigreux column gave 18 g. (58% yield), b.p. 115–118°, m.p. 27°, $n^{25}D$ (undercooled) 1.4189.

Preparation of 3-(3′-Diethylaminopropylamino)-3-methyl-1-butyne (Method B).—A cold solution of potassium hydroxide (22.4 g., 0.4 mole in 25 ml. of water) was added slowly with cooling to a solution of 39 g. (0.3 mole) of freshly

(5) G. F. Hennion, *et al.*, *J. Org. Chem.*, **21**, 1142 (1956).

(6) The amount and activity of nickel catalyst used are critical. Very rapid hydrogenation, especially with nickel catalysts, results in extensive hydrogenolysis perhaps due in large measure to rapid rise in temperature.

(7) A private communication from Dr. Nelson R. Easton, The Lilly Research Laboratories, Indianapolis, Ind., advised that complete hydrogenation of XXVIII and XXXII (as well as others) was achieved by hydrogenation of the acetylenic amine hydrochlorides in ethanol with use of platinum oxide as the catalyst.

(8) Private communication from Dr. E. C. Korufeld.

TABLE III

ALLYL AMINES, $R^1R^2C(NHR^3)CH{=}CH_2$

Compd.	R^1	R^2	R^3	Molecular formula	B.p. °C.	B.p. Mm.	$n^{25}D$	d^{25}	Yield,[a] %	Method	Nitrogen, % Calcd.	Nitrogen, % Obsd.	Hydrochlorides: Molecular formula	M.p., °C.	Carbon, % Calcd.	Carbon, % Obsd.	Hydrogen, % Calcd.	Hydrogen, % Obsd.	Nitrogen, % Calcd.	Nitrogen, % Obsd.
XXXIV	CH_3–	CH_3–	C_2H_5–	$C_7H_{15}N$	110		1.4156	0.758	73	E										
									54	F	12.37	12.02	$C_7H_{16}NCl$	138–140	56.17	56.48	10.78	10.54	9.36	9.33
XXXV	CH_3–	CH_3–	i-C_3H_7–	$C_8H_{17}N$	122		1.4172	...	81	E	11.01	10.87	$C_8H_{18}NCl$	115–116	58.70	58.89	11.08	11.13	8.56	8.48
XXXVI	CH_3–	CH_3–	t-C_4H_9–	$C_9H_{19}N$	140		1.4294	0.778	54	E	9.92	9.90	$C_9H_{20}NCl$	203–204	60.82	60.87	11.34	11.42	7.88	7.96
									44	F										
XXXVII	CH_3–	C_2H_5–	C_2H_5–	$C_8H_{17}N$	77	110	1.4272	0.779	89	E	11.01	11.27	$C_8H_{18}NCl$	114–117	58.70	58.54	11.08	11.14	8.56	8.37
XXXVIII	CH_3–	C_2H_5–	i-C_3H_7–	$C_9H_{19}N$	84	90	1.4278	...	63	E	9.92	10.13	$C_9H_{20}NCl$	116–117	60.82	60.67	11.34	11.05	7.88	8.01
XXXIX	CH_3–	C_2H_5–	t-C_4H_9–	$C_{10}H_{21}N$	67	25	1.4372	0.793	66	E	9.02	9.06	$C_{10}H_{22}NCl$	164–166	62.64	62.50	11.57	11.59	7.30	7.38
									73	F										
XL	C_2H_5–	C_2H_5–	C_2H_5–	$C_9H_{19}N$	84	70	1.4356	.794	73	F	9.92	10.34	$C_9H_{20}NCl$	167–169	60.82	60.94	11.34	11.25	7.88	7.79
XLI	C_2H_5–	C_2H_5–	i-C_3H_7–	$C_{10}H_{21}N$	89	50	1.4360	.796	74	E	9.02	9.29	$C_{10}H_{22}NCl$	196–198	62.64	62.84	11.57	11.79	7.30	7.41
									50	G										
XLII	C_2H_5–	C_2H_5–	t-C_4H_9–	$C_{11}H_{23}N$	78	18	1.4432	.810	62	G	8.27	8.11	$C_{11}H_{24}NCl$	183–184	64.20	64.32	11.76	11.50	6.81	6.87
XLIII	$-CH_2(CH_2)_3CH_2$–	C_2H_5–		$C_{10}N_{19}N$	82	18	1.4662	.865	77	F	9.14	9.35	$C_{10}H_{20}NCl$	181–183	63.30	63.14	10.63	10.18	7.38	7.33
XLIV	$-CH_2(CH_2)_3CH_2$–	i-C_3H_7–		$C_{11}H_{21}N$	93	20	1.4649	.860	49	F	8.37	8.38	$C_{11}H_{22}NCl$	172–174	64.84	65.11	10.89	10.97	6.87	6.91
XLV	$-CH_2(CH_2)_3CH_2$–	t-C_4H_9–		$C_{12}H_{23}N$	91	13	1.4670	.867	72	E	7.73	7.84	$C_{12}H_{24}NCl$	165–166	66.18	66.46	11.11	11.44	6.43	6.50
									48	G										

[a] Yields are for twice distilled material of 2° boiling range or less.

TABLE IV

SATURATED AMINES, $R^1R^2C(NHR^3)CH_2CH_3$

Compd.	R^1	R^2	R^3	Molecular formula	B.p. °C.	B.p. Mm.	$n^{25}D$	d^{25}	Yield,[a] %	Nitrogen, % Calcd.	Nitrogen, % Obsd.	Hydrochlorides: Molecular formula	M.p., °C.	Carbon, % Calcd.	Carbon, % Obsd.	Hydrogen, % Calcd.	Hydrogen, % Obsd.	Nitrogen, % Calcd.	Nitrogen, % Obsd.
XLVI	CH_3–	CH_3–	C_2H_5–	$C_7H_{17}N$	115		1.4053	...	78	12.16	12.40	$C_7H_{18}NCl$[b]	160–161	55.43	55.70	11.96	11.85	9.24	9.03
XLVII	CH_3–	CH_3–	i-C_3H_7–	$C_8H_{19}N$	127		1.4080	...	73	10.84	10.72	$C_8H_{20}NCl$	131–132	57.98	57.93	12.17	11.85	8.45	8.21
XLVIII	CH_3–	CH_3–	t-C_4H_9–	$C_9H_{21}N$	144		1.4179	0.767	42	9.78	9.75	$C_9H_{22}NCl$	218–219[c]	60.14	60.24	12.34	12.26	7.79	7.82
XLIX[d]	CH_3–	CH_3–	C_6H_5–	$C_{11}H_{17}N$	121	25	1.5250	...	68										
L	CH_3–	C_2H_5–	C_2H_5–	$C_8H_{19}N$	81	110	1.4185	...	66	10.84	11.12	$C_8H_{20}NCl$	164–166	57.98	57.61	12.17	11.90	8.45	8.44
LI	CH_3–	C_2H_5–	i-C_3H_7–	$C_9H_{21}N$	87	90	1.4210	.774	59	9.78	9.99	$C_9H_{22}NCl$	194–196	60.14	60.36	12.34	12.18	7.79	7.84
LII	CH_3–	C_2H_5–	t-C_4H_9–	$C_{10}H_{23}N$	70	25	1.4290	.787	37	8.91	9.33	$C_{10}H_{24}NCl$	195–196	61.99	62.06	12.48	12.25	7.23	7.43
LIII[e]	CH_3–	C_2H_5–	C_6H_5–	$C_{12}H_{19}N$	124	18	1.5255	...	69										
LIV	C_2H_5–	C_2H_5–	C_2H_5–	$C_9H_{21}N$	88	70	1.4269	.786	57	9.78	10.22	$C_9H_{22}NCl$	189–191	60.14	60.36	12.34	12.44	7.79	7.80
LV	$-CH_2(CH_2)_3CH_2$–	C_2H_5–		$C_{10}H_{21}N$	81	15	1.4540	...	68	9.02	9.11	$C_{10}H_{22}NCl$	190–191	62.64	62.52	11.57	11.48	7.31	7.35
LVI	$-CH_2(CH_2)_3CH_2$–	i-C_3H_7–		$C_{11}H_{23}N$	85	15	1.4580	...	68	8.27	8.44	$C_{11}H_{24}NCl$	200–201	64.20	64.09	11.76	11.61	6.81	6.83

[a] Yields are for twice distilled material of 2° boiling range or less. [b] 2-Ethylamino-2-methylbutane hydrochloride; lit. m.p. 155° (J. Bewad, *J. Russ. Phys.-Chem. Soc.*, **32**, 490 (1900); *Chem. Zentr.*, **71** II, 945 (1900)). [c] Melts with decomposition. [d] 2-Phenylamino-2-methylbutane; lit. b.p. 112–114° at 25 mm. (W. J. Hickinbottom, *J. Chem. Soc.*, 951 (1933)). [e] 3-Phenylamino-3-methylpentane; lit. b.p. 121–122° at 17.5 mm. (note *d*).

distilled 3-diethylaminopropylamine in 25.5 g. (0.25 mole) of 3-chloro-3-methyl-1-butyne. The two-layer mixture was allowed to stand at room temperature for 6 days and then was poured into 200 ml. of ether and 100 ml. of water. The ethereal layer was worked up as described above. Distillation gave 27 g. (55% yield), b.p. 99–135° at 30 mm. Redistillation yielded 20 g. (41%), b.p. 83–86° at 4.5 mm., $n^{25}D$ 1.4275.

Preparation of 3-Piperidino-3-methyl-1-butyne (Method C).[9]—A mixture of 127.5 g. (1.5 moles) of piperidine, 100 ml. of ether, 50 ml. of water, 0.3 g. of cuprous chloride and 0.3 g. of copper bronze powder was prepared under nitrogen in a three-neck flask equipped with mechanical stirrer. 3-Chloro-3-methyl-1-butyne (51 g., 0.5 mole) dissolved in 50 ml. of ether was then added dropwise with stirring (1.5 hours) under nitrogen while maintaining an inside temperature of 17-20°. After stirring for an additional 2 hours at room temperature, the mixture was poured into 200 ml. of ether and 100 ml. of water. The ethereal layer was washed with cold water, dried for 15 minutes with anhydrous potassium carbonate, filtered, redried with potassium hydroxide pellets overnight and then distilled. Two distillations gave 51.5 g. (68% yield), b.p. 83° at 35 mm., m.p. 56–57°.

Preparation of 3-Phenylamino-3-methyl-1-butyne (Method D).[9]—A mixture of 27.9 g. (0.3 mole) of aniline, 40.5 g. (0.4 mole) of triethylamine, 100 ml. of ether, 25 ml. of water, 0.3 g. of cuprous chloride and 0.3 g. of copper bronze powder was prepared under nitrogen in a three-neck flask equipped with mechanical stirrer. 3-Chloro-3-methyl-1-butyne (25.5 g., 0.25 mole) dissolved in 25 ml. of ether was added dropwise with stirring (1 hour) while maintaining an inside temperature of 16–20°. After stirring for an additional 2 hours at room temperature, the mixture was poured into 200 ml. of ether and 100 ml. of water. The ethereal layer was treated as described immediately above. Two distillations yielded 23.5 g. (59% yield), b.p. 76–78° at 0.2 mm., m.p. 49–50°. The analytical sample was purified by sublimation.

Hydrogenation of Acetylenic Amines.—Three procedures (methods E, F and G) were employed. Typical applications are recited below.

Semi-hydrogenation of 3-Isopropylamino-3-methyl-1-butyne (Method E).—A solution of 12.8 g. (0.1 mole) of 3-isopropylamino-3-methyl-1-butyne in 50 ml. of petroleum ether (Skellysolve B) containing 0.010 g. 10% palladium-on-activated charcoal was subjected to hydrogenation at room temperature under an initial pressure of 41 p.s.i.g. The pressure dropped by 6.8 p.s.i.g. within 1.5 hours and by 8.8 p.s.i.g. after 5.5 hours, corresponding to hydrogen uptake for semi-hydrogenation. After removal of the catalyst by filtration, two distillations gave 9.2 g. (71% yield) of 3-isopropylamino-3-methyl-1-butene, b.p. 121–122°, $n^{25}D$ 1.4172.

Semi-hydrogenation of 3-*t*-Butylamino-3-methyl-1-pentyne (Method F).—A solution of 15.3 g. (0.1 mole) of 3-*t*-butylamino-3-methyl-1-pentyne in 50 ml. of petroleum ether containing 0.075 g. of 5% palladium-on-barium carbonate was hydrogenated at room temperature under an initial pressure of 44 p.s.i.g. as described above. The theoretical amount of hydrogen was absorbed in less than 2 hours. Two distillations gave 10 g. (64% yield) of 3-*t*-butylamino-3-methyl-1-pentene, b.p. 66° at 25 mm., $n^{25}D$ 1.4372.

Hydrogenation of 3-Ethylamino-3-methyl-1-butyne (Method G).—A solution of 11.1 g. (0.1 mole) of 3-ethylamino-3-methyl-1-butyne in 50 ml. of 95% ethanol containing 2 g. (wet with alcohol) of Raney nickel[6] was hydrogenated at room temperature under an initial pressure of 40 p.s.i.g. The pressure dropped by 22.5 p.s.i.g. within 2 hours and 10 minutes. The catalyst was removed by filtration and the alcoholic solution was acidified (cold) by dropwise addition of concentrated hydrochloric acid. The alcohol was then distilled, the last portion *in vacuo*. The pasty residue was dissolved in 100 ml. of water and the aqueous solution was extracted with two 100-ml. portions of ether (discarded). The amine was then released from the aqueous solution by slow addition of cold 40% sodium hydroxide solution. The amine layer was removed and the aqueous solution was extracted twice with 75-ml. portions of ether. The amine and ether extracts were combined, dried and distilled. Two distillations gave 9.0 g. (78% yield) of 2-ethylamino-2-methylbutane, b.p. 112–115°, $n^{25}D$ 1.4055–1.4051.

Amine hydrochlorides were precipitated in substantially quantitative yields by addition of dry ethereal hydrogen chloride to solutions of the amines in anhydrous ether and were purified by crystallization from a mixture of anhydrous ethanol and ethyl acetate. Melting points listed in Tables I, II, III and IV, were determined in sealed capillaries and are uncorrected.

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(9) Caution must be exercised during the first distillation of product when this method is used. In several instances vigorous decomposition of still residue occurred while distillation was in progress. Redistillations were not troublesome.

[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORP., RICHMOND, CALIF.]

The Alkali Metal Catalyzed Alkylation of Toluene with Propylene

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The alkylation of toluene with propylene in the presence of lithium, sodium and potassium catalysts was studied over a range of temperatures from 100 to 300°. The principal product is isobutylbenzene, but abnormal addition to form *n*-butylbenzene is an important side reaction. At the higher temperatures hydrogen transfer reactions to form propane and "coke" are also important. Catalyst activity increases in the order lithium < sodium < potassium. Product composition also varies with the alkali metal used. Reaction mechanisms consistent with the observed kinetics and product distribution are presented. With the active potassium catalyst at low temperatures the reaction is suitable for the preparation of butylbenzenes in high yield.

The alkylation of alkylaromatics with olefins employing an alkali metal catalyst has been previously reported.[1-8] Aromatic alkylation with acid-type catalysts results in alkylation of the benzene ring. The alkali metal catalyzed reaction usually results in alkylation of the side chain, although

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