chloride were used to rinse the magnesium sulfate plug and were added to the tube. The nmr spectrum (20%) showed no extraneous peaks; a spectrum (19%) of unreacted allylbenzene was used for comparison of peak ratios. After nmr analyses, both tubes were sealed under vacuum and submitted for total deuterium analyses. The reacted allylbenzene (in carbon tetrachloride solution) showed 1.85 atom % excess deuterium; the protio solution gave 0.04 (compared to benzoic acid).

The collected *trans*-propenylbenzene, 0.319 g, was filtered through a 5-g plug of silica gel and flash distilled. Part of the distillate was diluted with carbon tetrachloride; nmr analysis of the resulting solution (24%) was compared to a 23% solution of protio olefin. The remainder of the distillate was submitted for total deuterium analysis. The pertinent vpc, nmr, and deuterium analysis data for this experiment appear in the Results section.

***cis*-Propenylbenzene at 97.7°.** The olefin, 0.226 g, was added to a clean, dry 18 × 150 mm test tube that had been constricted to facilitate sealing and swept thoroughly with pure nitrogen. The tube was again swept briefly with purified nitrogen and capped with a serum cap. With a clean, dry 10-ml syringe that had been purged with nitrogen, 10.0 ml of *t*-butyl alcohol-O-*d* (0.99 atom of deuterium per molecule), 0.394 *M* in potassium *t*-butoxide, was added to the tube. The tube was immediately fixed on the vacuum line; the contents was frozen with a Dry Ice–acetone bath and exposed to vacuum, and the tube was sealed. The contents was thawed in the constant-temperature bath; when all solid had melted the tube was shaken thoroughly and totally immersed in the bath, and the timer was started. After 90 min the tube was removed from the oil bath and immersed in a 600-ml beaker filled with water. The outside of the tube was cleaned, the tube opened, and 0.1 ml of the contents was removed and worked up (procedure B) for vpc analysis. The remaining reaction solution was added to a separatory funnel filled with 100 ml of pentane, 150 ml of water, and 15 ml of saturated brine. The isolation procedure was on a scale of one-half of that used in the allylbenzene exchange experiment. The reaction mixture was subjected to preparative vpc (column A, 88°, 10 psi). The recovered starting material, 67 mg, was transferred from the collector to an nmr tube by the method used for starting material in the allylbenzene exchange experiment. The nmr solution (15%) of reacted olefin was integrated against a 15% solution of authentic protio olefin. After nmr analysis the two tubes were sealed and submitted for total deuterium analysis. The pertinent analytical data appear in the Results section.

***trans*-Propenylbenzene at 97.7°.** This experiment was performed in the same way as the above experiment involving *cis*-propenylbenzene. The sample of *trans*-propenylbenzene used (270 mg) contained *ca.* 0.06% *cis*-propenylbenzene and less than 0.01% allylbenzene by vpc analysis. The *t*-butyl alcohol-O-*d* (0.99 atom of deuterium per molecule) contained 0.394 *M* potassium *t*-butoxide. The contents of the tube was melted in the 75° bath, and only when the contents were melted and mixed was the tube immersed in the 97.7° bath for 30 min. Starting material was recovered by preparative vpc (column A, 90°, 10 psi); the 131 mg collected was passed through a 6-g column of silica gel with pentane as eluent and flash distilled at aspirator pressure. The solution prepared for nmr analysis (33%) was integrated against a 33% solution of unreacted olefin. The pertinent analytical data appear in the tables.

Control Runs. Allylbenzene at 25°. Allylbenzene, *ca.* 10 mg, and *t*-butyl alcohol, *ca.* 0.25 ml that had been distilled from molecular sieves, were mixed in a 6-mm o.d. tube that had been swept with purified nitrogen. The tube was sealed under vacuum and placed in the 25° bath for 90 hr. It was then opened and the contents subjected to isolation by procedure B (no added base). Analysis demonstrated the presence of less than 0.2% of either of the propenylbenzenes.

***cis*-Propenylbenzene at 98°.** A mixture of *cis*-propenylbenzene and 3-phenylpentane, *ca.* 3 mg, and *ca.* 0.2 ml of *t*-butyl alcohol that had been distilled from molecular sieves, was placed in a 6-mm tube that had been swept with purified nitrogen. The tube was sealed under vacuum and placed in the 98° bath for 22 hr. The tube was then opened and the contents worked up by procedure B (but with no added base). Analysis showed 4.0% *trans*-propenylbenzene and less than 0.05% allylbenzene. Analysis of the starting mixture showed that less than 0.1% *trans*-propenylbenzene was present. It was not rigorously demonstrated that the 4% of the *trans* isomer did not arise by ionic catalysis from trace amounts of acid introduced in the mixing, sealing, or isolation processes.

ortho-Substitution Rearrangement of 2- and 4-Substituted Benzyltrimethylammonium Ions Having Functional Substituents[1]

Karl P. Klein, Rann L. Vaulx, and Charles R. Hauser

Contribution from the Department of Chemistry, Duke University, Durham, North Carolina. *Received July 25, 1966*

Abstract: *ortho*-Substitution rearrangements of 2- and 4-substituted benzyltrimethylammonium ions in which the substituent contained a carbinol, amide, ketone, or olefin group were effected by means of potassium amide in liquid ammonia. Generally the reagent reacted initially with an active hydrogen of the substituent to form monoanions, which underwent rearrangement with excess reagent through appropriate dianions. Certain of the rearranged amines from the 4-substituted quaternary ions were further rearranged through their methiodides. An earlier method for preparation of the 4-substituted benzyldimethylamines required for their methiodides was improved and extended. Theoretical and synthetic aspects of the rearrangement are considered.

Ring-substituted benzyltrimethylammonium ions have previously been observed to undergo the *ortho*-substitution rearrangement with sodium amide or potassium amide in liquid ammonia when the 2, 3, or 4 substituent was methyl,[2,3] methoxy,[3] or chloro[3] and the 3 substituent was benzyl,[4] but not when the 2 or 4 substituent was benzyl,[4] the 3 substituent bromo or trifluoromethyl,[3b] and the 4 substituent cyano.[3a] With the possible exception of the 3-benzyl quaternary ion, none of these quaternary ions underwent an initial reaction with the reagent involving the ring substituents and yet exhibited the rearrangement with excess reagent. Recently,[5] however, two such examples were reported.

---

(1) Supported by the Army Research Office (Durham) and by the National Science Foundation.

(2) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951).

(3) (a) W. Q. Beard, Jr., and C. R. Hauser, *J. Org. Chem.*, **25**, 334 (1960); (b) W. Q. Beard, Jr., D. N. Van Eenam, and C. R. Hauser, *ibid.*, **26**, 2310 (1961).

(4) C. R. Hauser, W. Q. Beard, Jr., and F. N. Jones, *ibid.*, **26**, 4790 (1961).

(5) R. L. Vaulx, G. C. Jones, and C. R. Hauser, *ibid.*, **27**, 4385 (1962).

Table I. Rearrangements of Quaternary Ions of Type III to Form Amines of Type IV

Quat Ion	Rearranged amine	Yield, %	Mp or bp (mm), °C
IIIa	2-(3-Dimethylaminomethyl)-2-methylphenyl-1,1-diphenylethanol (IVa)	92	82–83.5[c]
IIIb	3-(Dimethylaminomethyl)-2-methyl-N-phenylbenzamide (IVb)	86 (92)[a]	129.5–130.5[d]
IIIc	3-(Dimethylaminomethyl)-2-methylbenzyl phenyl ketone (IVc)	70 (91)[a]	141–144 (0.15)
IIId	3-(Dimethylaminomethyl)-2-methylbenzophenone (IVd)	65	142–145 (0.4)
IIIe	3-(2,2-Diphenylvinyl)-2-N,N-trimethylbenzylamine (IVe)	36[b] (77)[a,b]	240–241[e,f]

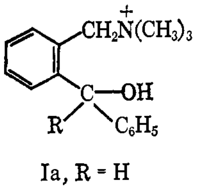
[a] Yield based on amount of quaternary salt used minus that recovered. [b] Yield of methiodide. [c] Recrystallized from hexane. [d] Recrystallized from hexane–ethanol. [e] Melting point of methiodide. [f] Recrystallized from acetonitrile–ether.

Table II. Spectra and Analyses for Rearranged Amines IVa–e from Quaternary Ions IIIa–e

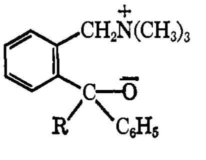
		Nmr data,[a] cps ± 1									
		Protons									
Product	ν, cm^{-1}	N-Methyl[b]	2-Methyl[b]	N-Benzyl[b]	Aromatic[e]	Other[b]	Empirical formula		C, %	H, %	N, %
IVa	848, 806, 763, 699	124	117	214	400–446	136,[f] 193[g]	$C_{24}H_{27}NO$	Calcd			4.05
								Found			4.25
IVb	1653, 1541, 1285, 848, 807, 758, 697	165[c]	136	255[d]	415–450		$C_{17}H_{20}N_2O$	Calcd	76.08	7.51	10.44
								Found	76.15	7.39	10.26
IVc	1681, 850, 775, 757, 692						$C_{18}H_{21}NO$[h]	Calcd	80.66	7.92	5.24
								Found	80.93	8.27	5.13
IVd	1666, 848, 777, 730, 709	130	134	202	422–470		$C_{17}H_{19}NO$[i]	Calcd	80.57	7.56	5.53
								Found	80.41	7.44	5.43
IVe							$C_{25}H_{28}IN$[j]	Calcd	63.96	6.01	2.98
								Found	63.76	6.03	2.95

[a] Determined in carbon tetrachloride, except where noted. [b] Singlet. [c] Determined in trifluoroacetic acid. [d] Doublet centered at this value. [e] Multiplet. [f] Hydroxyl proton. [g] Benzylic protons. [h] The picrate of IVc, after two recrystallizations from ethanol, melted at 157–158°. *Anal.* Calcd: C, 58.06; H, 4.87; N, 11.29. Found: C, 58.18; H, 4.73; N, 11.58. [i] The picrate of IVd, after two recrystallizations from ethanol, melted at 150–152°. *Anal.* Calcd: C, 57.26; H, 4.60; N, 11.61. Found: C, 57.00; H, 4.56; N, 11.78. [j] Analyzed as methiodide.

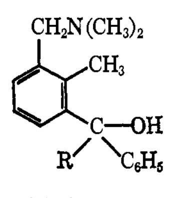
These were the carbinol quaternary ions Ia and Ib, with which the initial reaction produced alkoxide quaternary ions I′a and I′b and the rearrangement tertiary amines IIa and IIb, respectively.



Ia, R = H
b, R = C_6H_5



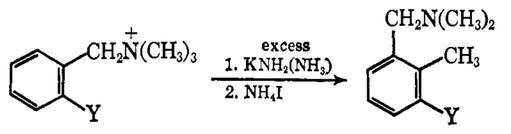
I′a, R = H
b, R = C_6H_5



IIa, R = H
b, R = C_6H_5

In the present investigation various 2- and 4-substituted benzyltrimethylammonium ions having functional substituents were found to undergo the rearrangement.

Results with 2-Substituted Benzyltrimethylammonium Ions. Quaternary ions IIIa–d were rearranged by means of 3 equiv of potassium amide in liquid ammonia, and quaternary ion IIIe by 1 equiv, to form tertiary amines IVa–e, respectively (eq 1). Amine IVe was isolated as its methiodide. The yields were generally good to excellent (Table I).



(1)

IIIa, Y = $CH_2C(C_6H_5)_2OH$
b, Y = $CONHC_6H_5$
c, Y = $CH_2COC_6H_5$
d, Y = COC_6H_5
e, Y = $CH{=}C(C_6H_5)_2$

IVa, Y = $CH_2C(C_6H_5)_2OH$
b, Y = $CONHC_6H_5$
c, Y = $CH_2COC_6H_5$
d, Y = COC_6H_5
e, Y = $CH{=}C(C_6H_5)_2$

The structures of the rearranged amines were supported by analyses and spectral data (Table II).[6] The infrared spectra of amines IVa–d showed peaks ascribable to the aromatic dimethylaminomethyl group (at 848–850 cm^{-1}),[3a] to three adjacent aromatic hydrogens (at 775–807 cm^{-1}),[7] and to five adjacent aromatic hydrogens (at 730–763 and 692–709 cm^{-1}).[7] The spectrum of amide amine IVb exhibited a secondary amide peak at 1653 cm^{-1},[8] and the spectra of keto amines IVc and IVd carbonyl peaks at 1681 and 1666 cm^{-1}, respectively.[9] The nmr spectra of the rearranged amines IVa, IVb, and IVd showed chemical shifts in the calculated ratios for the N-methyl, 2-methyl, and aromatic protons (see Table II).

The structure of keto amine IVd was confirmed by oxidation, followed by cyclization to form anthraquinone acid V, which was independently synthesized from benzanthrone[10] (Scheme I).

The structure of unsaturated amine IVe was established by independent synthesis involving dehydration of rearranged carbinolamine IVa (eq 2).

Similar to the quaternary ions Ia,b studied earlier,[5] quaternary ions IIIa–c underwent an initial reaction with the reagent involving an active hydrogen of the ring substituent to form monoanions III′a–c, respectively. This was demonstrated by lack of appreciable rearrangement on treatment of IIIa–c with 1.1 equiv of

---

(6) The spectra of the carbinolamine(s) exhibited strong hydroxyl peaks but they are not listed because they may have been due, partly, to moisture.

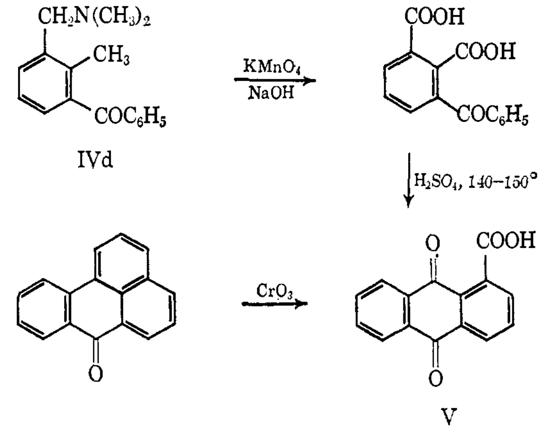
(7) See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, pp 76–79.

(8) See ref 7, p 211.

(9) See ref 7, p 137.

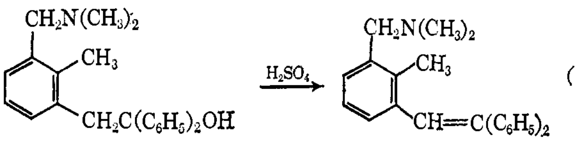
(10) A. G. Perkin, *J. Chem. Soc.*, 117, 696 (1920).

Scheme I



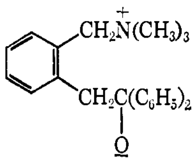
IVd

V

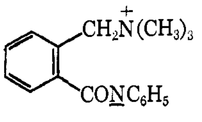


IVa IVe (2)

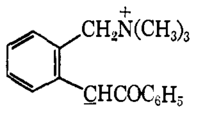
the reagent and, usually, recovery of the starting quaternary ions.



III'a

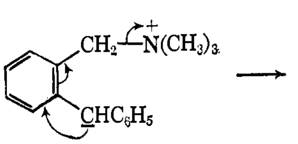


III'b

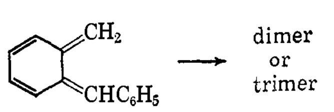


III'c

The stability of monocarbanion III'c is of particular interest, since the related monocarbanion VI is known to eliminate trimethylamine under similar conditions to form an *exo*-methylene derivative which polymerizes (eq 3).[4] The lack of such an elimination with monocarbanion III'c appears ascribable to its more weakly basic nature because of resonance involving the carbonyl group.

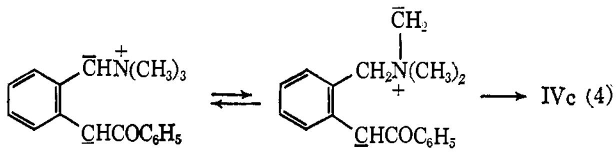


VI



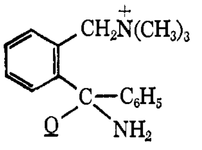
(3)

The rearrangement of intermediate monoanions III'a–c (see eq 1) presumably involved the further intermediate formation of dianions; for example, that of monoanion III'c involved dianion III''c and, in equilibrium, dianion III'''c which underwent the rearrangement to form IVc (eq 4).

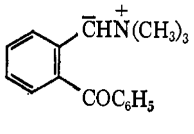


III''c III'''c (4)

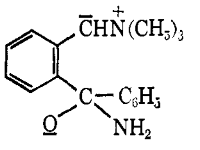
Also quaternary ion IIId evidently underwent an initial reaction with the reagent involving the ring substituent, since 1.1 equiv of the reagent failed to produce appreciable rearrangement and IIId was recovered. This might have involved either addition of the alkali amide to the carbonyl group of IIId to form III'd or ionization of a benzylic hydrogen of IIId to give carbanion III''d. If the benzyl carbanion III''d were formed, its failure to rearrange may be ascribed to its lack of effective equilibration with the methyl carbanion (see eq 4) because of resonance with the carbonyl group. Rearrangement with excess reagent may then be explained by formation of dianion III'''d, in which the benzyl carbanion can equilibrate with the methyl carbanion because the resonance with the carbonyl group has now been destroyed.



III'd



III''d



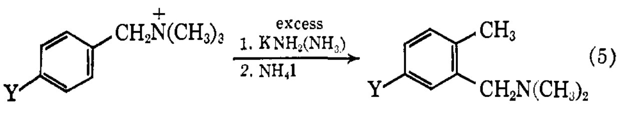
III'''d

The reaction of quaternary ion IIId with excess reagent produced, besides rearranged amine IVd (65%), some (11%) 2-methylbenzyldimethylamine, which appeared to arise mainly through cleavage of the rearranged amine IVd; moreover, some benzamide, which was the other cleavage product, was isolated.

However, quaternary ion IIIe underwent rearrangement evidently without involving the olefinic group of the ring substituent since the conversion yield was good with only 1 equiv of the reagent (see Table I). In fact, excess reagent produced polymer which appeared to arise from attack of the reagent on the olefinic group of the rearranged amine IVe.

It should be mentioned that, in contrast to the ketone quaternary ion IIId, the 2-cyanobenzyltrimethylammonium ion reacted with excess reagent to product tarry material, which was not further investigated.

Results with 4-Substituted Benzyltrimethylammonium Ions. Quaternary ions VIIa–e were rearranged by means of 3 equiv of potassium amide in liquid ammonia to form the tertiary amines VIIIa–e, respectively (eq 5). The yields were good (Table III).



(5)

VIIa, Y = CH_2OH	VIIIa, Y = CH_2OH
b, Y = $C(CH_3)_2OH$	b, Y = $C(CH_3)_2OH$
c, Y = $C(C_6H_5)_2OH$	c, Y = $C(C_6H_5)_2OH$
d, Y = COC_6H_5	d, Y = COC_6H_5
e, Y = $NHCOC_6H_5$	e, Y = $NHCOC_6H_5$

The structures of the rearranged amines were supported by analyses and spectral data (Table IV).[6] The infared spectra of amines VIIIa–e showed peaks ascribable to the aromatic dimethylaminomethyl group (at 840–845 cm^{-1}),[3a] to one free aromatic hydrogen (at 885–900 cm^{-1}),[7] and to two adjacent aromatic hydrogens (at 820–845 cm^{-1}).[7] Peaks in the regions 725–759 and 692–701 cm^{-1} appeared in the spectra of VIIIc–e and are in accord with the structure having five adjacent aromatic hydrogens.[7] The spectra of amide amine VIIIe showed three peaks attributable to a secondary amide[8] and that of keto amine VIIId a peak

Table III. Rearrangements of Quaternary Ions of Type VII to Form Amines of Type VIII

Quat Ion	Rearranged amine	Yield, %	Mp or bp (mm), °C
VIIa	3-(Dimethylaminomethyl)-4-methylbenzyl alcohol (VIIIa)	62	106–110 (0.6)
VIIb	3-(Dimethylaminomethyl)-α,α,4-trimethylbenzyl alcohol (VIIIb)	64	106–110 (0.6)
VIIc	3-(Dimethylaminomethyl)-4-methyltriphenylmethanol (VIIIc)	61	89.5–91[a]
VIId	3-(Dimethylaminomethyl)-4-methylbenzophenone (VIIId)	66	157–161 (1.5)
VIIe	N-(3-Dimethylaminomethyl-4-methylphenyl)benzamide (VIIIe)	61	135.5–136[b]

[a] Recrystallized from hexane. [b] Recrystallized from cyclohexane.

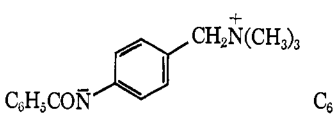
Table IV. Spectra and Analyses for Rearranged Amines VIIIa–e from Quaternary Ions VIIa–e

		Nmr,[a] cps ± 1									
		Protons									
Product	ν, cm⁻¹	N-Methyl[b]	2-Methyl[b]	N-Benzyl[b]	Aromatic[c]	Other[b]	Empirical formula		C, %	H, %	N, %
VIIIa	900, 843, 823	124	135	195	423–430	265[d]	$C_{11}H_{17}NO$[f]	Calcd	44.85	6.28	4.36
						307[e]		Found	45.20	6.35	4.11
VIIIb	900, 841,826						$C_{13}H_{21}NO$	Calcd	75.31	10.21	6.76
								Found	75.46	10.09	6.84
VIIIc	887, 840, 826, 759, 701	121	136	193	415–430	181[e]	$C_{23}N_{25}NO$	Calcd	83.34	7.60	4.23
								Found	83.51	7.85	4.49
VIIId	1658, 887, 845, 740, 699						$C_{18}H_{22}INO$[g,h]	Calcd	54.71	5.57	3.55
								Found	55.04	5.57	3.36
VIIIe	1661, 1520, 1282, 885, 846, 820, 725, 692	134	138	202	426–480		$C_{17}H_{20}N_2O$	Calcd	76.08	7.51	10.44
								Found	76.35	7.45	10.31

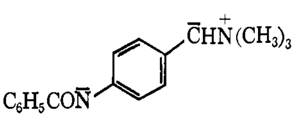
[a] Determined in carbon tetrachloride, except VIIIe which was run in deuteriochloroform. [b] Singlet. [c] Multiplet. [d] Benzylic protons. [e] Hydroxyl proton. [f] The methiodide of VIIIa, recrystallized from acetonitrile–ether, melted at 197.5–198°. *Anal.* Calcd for $C_{12}H_{20}INO$: C, 73.70; H, 9.56. Found: C, 73.37; H, 9.55. [g] Analyzed as the methiodide which, after recrystallization from acetonitrile–ether, melted at 191–192°. [h] The picrate of VIIId, recrystallized from absolute ethanol, melted at 167–168°. *Anal.* Calcd for $C_{23}H_{22}N_4O_8$: C, 56.92; H, 5.57; N, 11.54. Found: C, 57.27; H, 5.50; N, 11.53.

ascribable to the carbonyl group.[9] The nmr spectra of amines VIIIa, VIIIc, and VIIIe showed chemical shifts in the calculated ratios for the N-methyl, 2-methyl, and aromatic protons (see Table IV).

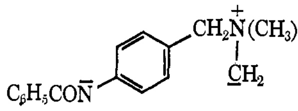
The rearrangements of quaternary ions VIIa–e (see eq 5) presumably involved intermediate formation of the corresponding mono- and dianions; for example, that of VIIe involved monoanion VII′e and dianions VII″e and VII‴e. The stability of the intermediate monoanion VII′e is to be contrasted with the instability of the more strongly basic monocarbanion IX, which is known to eliminate trimethylamine accompanied by polymerization under similar conditions.[4]



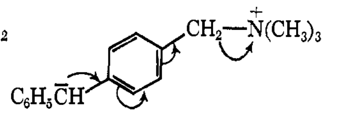
VII′e



VII″e



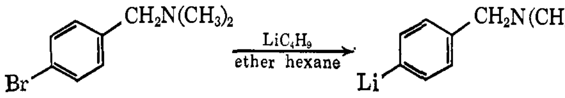
VII‴e



IX

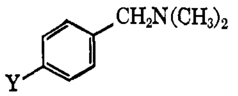
It should be mentioned that the previously reported[3a] failure of the 4-cyanobenzyltrimethylammonium ion to undergo appreciable rearrangement with excess reagent under the usual conditions has now been confirmed.

In connection with the synthesis of quaternary ions VIIa–d, the recent method[11] for preparing 4-lithiobenzyldimethylamine (X)[12] involving a halogen–metal interchange (eq 6) was improved and extended significantly. Thus, lithioamine X was condensed not only with benzophenone to form solid adduct XIc (instead of the oil reported earlier)[11] but also with other appropriate electrophilic compounds to give XIa,b,d and XI (Tables V and VI). Only carbinolamine XIa appears to have been prepared previously by another route, for which no yield was reported;[13] the present method seems superior. Ketone amine XId was reduced by the Wolff–Kishner procedure to afford 4-benzylbenzyldimethylamine. Compounds XIa–d were readily converted to their methiodides but carbinoldiamine XII failed to afford a satisfactory di-

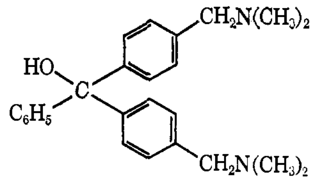


(6)

X



XIa, Y = CH_2OH
b, Y = $C(CH_3)_2OH$
c, Y = $C(C_6H_5)_2OH$
d, Y = COC_6H_5



XII

---

(11) F. N. Jones and C. R. Hauser, *J. Org. Chem.*, 27, 4389 (1962).

(12) The possible isomerization of this 4-lithioamine to 2-lithiobenzyldimethylamine, which may be stabilized by chelation, evidently did not occur even at 48° in ether–benzene (45 hr) since treatment of the resulting reaction mixture with acetone afforded only the 4 adduct XIb. For the isomerization of α-lithiobenzyldimethylamine to 2-lithioamine see W. H. Puterbaugh and C. R. Hauser, *J. Am. Chem. Soc.*, 85, 2467 (1963).

(13) M. Charpentier-Morize and B. Tchoubar, *Compt. Rend.*, 233, 1621 (1951).

Table V. Condensations of Lithioamine X with Electrophilic Compounds

Electrophilic compd	Condensation product	Mp or bp (mm), °C	Yield,[a] %
Formaldehyde	4-(Dimethylaminomethyl)benzyl alcohol (XIa)	132–135 (4)[d,e]	52[f]
Acetone	4-(Dimethylaminomethyl)-α,α-dimethylbenzyl alcohol (XIb)	112–115 (2)	68
Benzophenone	4-(Dimethylaminomethyl)phenyldiphenylmethanol (XIc)	97–99[b]	72 (74)[c]
Benzonitrile	4-(Dimethylaminomethyl)benzophenone (XId)	167–170 (1.5)	65
Methyl benzoate	4,4′-Bis(dimethylaminomethyl)triphenylmethanol (XII)	124.5–125.5[b]	54

[a] The yield was based on the starting amine. [b] Recrystallized from hexane. [c] The interchange reaction time was 4 hr. [d] Lit.[13] bp 140–143° (8 mm). [e] The methiodide, recrystallized from acetonitrile–ether, melted at 144–146°; lit.[13] mp 145–147°. [f] Some (8%) benzyldimethylamine (identified by vpc), bp 54–57° (8 mm), was obtained.

Table VI. Analyses and Infrared Data of Condensation Products and Melting Points and Analyses of Methiodides

Condn product	ν,[a] cm⁻¹	Empirical formula		C, %	H, %	N, %	Methiodide mp, °C	Empirical formula		C, %	H, %	N, %
XIb	3333, 813	$C_{12}H_{19}NO$	Calcd			7.25	157–159[d]	$C_{13}H_{22}INO$	Calcd	46.57	6.61	4.18
			Found			7.02			Found	46.26	6.50	4.32
XIc	3375, 813	$C_{22}H_{23}NO$	Calcd	83.24	7.30	4.41	238.5–239.5[b,c]	$C_{23}H_{26}INO$	Calcd	60.12	5.70	3.05
	768, 704		Found	83.05	7.43	4.69			Found	60.13	5.71	3.21
XId	1655, 823	$C_{16}H_{17}NO$	Calcd			5.85	207–209[d]	$C_{17}H_{20}INO$	Calcd	53.55	5.29	3.67
	747, 702		Found			5.81			Found	53.77	5.11	3.89
XII	3390, 806	$C_{25}H_{30}N_2O$	Calcd	80.17	8.07	7.48						
	769, 699		Found	80.15	7.89	7.62						

[a] For infrared peaks of the dimethylaminomethyl group see Table VII. [b] Recrystallized from acetonitrile. [c] Lit.[11] mp 229–230°. Infrared spectra of this sample and authentic sample (ref 11) were superimposable. [d] Recrystallized from acetonitrile–ether.

methiodide, which would have been of interest because of a possible twofold rearrangement with alkali amide.

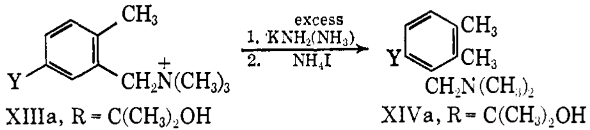
It should be pointed out that, whereas the infrared spectra of benzyldimethylamine and a number of substituted or polysubstituted derivatives show only a single peak (strong) for the aromatic dimethylaminomethyl group in the region 837–853 cm⁻¹,[3a] the spectra of nine out of ten 4-substituted benzyldimethylamines studied exhibit two peaks that appear attributable to the aromatic dimethylaminomethyl group, a weak peak in the previously observed region and a strong peak in the region 855–869 cm⁻¹ (see Table VII).

Table VII. Infrared Peaks of the Dimethylaminomethyl Group of 4-Substituted Benzyldimethylamines

4-Substituted benzyldimethylamine	ν, cm⁻¹ Region 855–869[a]	Region 833–850[b]
$(CH_3)_2C(OH)$– (compare with XIb)	862	844
$(C_6H_5)_2C(OH)$– (compare with XIc)	862	845
$C_6H_5C(=O)$– (compare with XId)	866	840
$(CH_3)_2NCH_2C_6H_4C(C_6H_5)(OH)$– (compare with XII)	866	848
Bromo	859	833
Chloro	859	834
Fluoro	855	839
Methoxy	862	835
Trifluoromethyl	869	850
Methyl	859	...

[a] Strong peak. [b] Weak peak.

Further Rearrangements. Two of the rearranged amines, VIIIb and VIIIc, were converted to their methiodides, XIIIa and XIIIb, which were further rearranged with excess potassium amide in liquid ammonia to afford XIVa and XIVb in yields of 43 and 69%, respectively (eq 7).



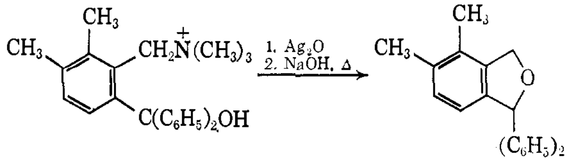
(7)

XIIIa, R = $C(CH_3)_2OH$
b, R = $C(C_6H_5)_2OH$

XIVa, R = $C(CH_3)_2OH$
b, R = $C(C_6H_5)_2OH$

The structures of the rearranged amines were supported by analyses and spectral evidence. Their infrared spectra showed peaks for the dimethylaminomethyl group and two adjacent aromatic hydrogens. Their nmr spectra exhibited chemical shifts in the calculated ratios assignable to the N-methyl, the ring methyl, the benzylic, and the aromatic protons.

The structure of amino alcohol XIVb was confirmed by cyclization of its methiodide XV to produce phthalan XVI (eq 8). The structure of this cyclic ether was substantiated by analysis and infrared and nmr spectra.



(8)

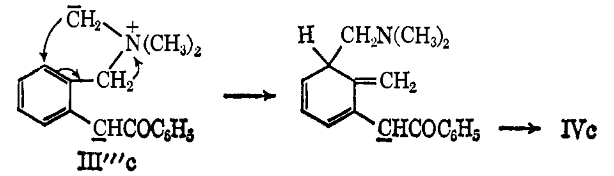
XV XVI

The rearrangements of quaternary ions XIIIa,b (see eq 7) presumably involved intermediate formations of the corresponding mono- and dianions. Interestingly, these rearrangements did not appear to be retarded appreciably by the presence of the bulky tertiary group on the carbon adjacent to the position at which $CH_2N(CH_3)_2$ becomes attached to the ring or by the negative charge on the oxygen of the tertiary group in the intermediate monoanion.

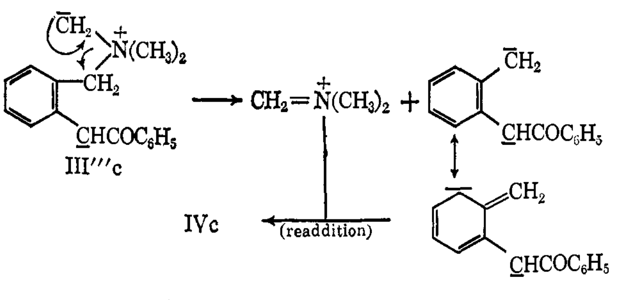
Discussion

The above rearrangements of intermediate dianions, for example, that of dianion III‴c (see eq 4), might have involved either the original cyclic mechanism[2] or an elimination–readdition process[14] as illustrated by Schemes II and III, respectively.

Scheme II



Scheme III



Although neither of these mechanisms has been established,[15] we prefer the cyclic process (Scheme II) at the present time for such rearrangements in liquid ammonia at $-33°$ since facile elimination of a dianion (Scheme III) seems less likely at this relatively low temperature. Moreover, the rearrangement of such a quaternary ion as XIIIb appears better accounted for by the cyclic mechanism because the intermolecular readdition process might be expected to be more affected by steric hindrance.

Incidentally, the elimination–readdition mechanism appears more suitable to the Stevens 1,2 shift[16] since not only is the 1,2 shift favored over the *ortho*-substitution rearrangement by elevation of temperature,[17] but also interference with the five-atom transition state for the latter sometimes favors the 1,2 shift even at $-33°$. Thus, whereas the dibenzyldimethylammonium ion undergoes the *ortho* rearrangement with sodium amide in liquid ammonia,[2] the more complex benzhydrylbenzyldimethylammonium ion exhibits the 1,2 shift with sodium amide under similar conditions.[17b] However, the elimination mechanism might be common to both rearrangements at higher temperatures.[14]

The present results extend considerably the scope of the *ortho*-substitution rearrangement. The method should be successful not only with the corresponding 3-substituted benzyltrimethylammonium ions and some other benzyl types of quaternary ions, but also with quaternary ions having certain other functional groups.

Although only two further rearrangements were effected, others could probably be realized; indeed, starting with a 2-substituted benzyltrimethylammonium ion, further rearrangements all the way around the aromatic ring are possible since this has been accomplished where the 2 substituent was methyl.[2] Furthermore, the functional substituent in the rearranged tertiary amine may be converted to another group leading to various derivatives.

Experimental Section[18]

2-Substituted Benzyltrimethylammonium Iodides. Quaternary ammonium iodides IIIa and IIId were prepared as described previously.[19] Amide quaternary iodide IIIb was prepared from the amide amine[19a] in 85% yield by treatment in ethanol with methyl iodide. After recrystallization from acetonitrile IIIb melted at 180–181°. *Anal.* Calcd for $C_{17}H_{21}IN_2O$: C, 51.52; H, 5.34; N, 7.07. Found: C, 51.85; H, 5.30; N, 6.88.

Similarly, ketone quaternary iodide IIIc was prepared from the corresponding ketone amine[19a] in 65% yield. After three recrystallizations from ethanol IIIc melted at 168–169°. *Anal.* Calcd for $C_{18}H_{22}INO$: C, 54.69; H, 5.61; N, 3.54. Found: C, 54.46; H, 5.67; N, 3.55.

Olefin quaternary iodide IIIe, prepared from the corresponding amine[19b] in nearly quantitative yield (98%), was recrystallized from acetonitrile–ether, mp 221–223°. *Anal.* Calcd for $C_{24}H_{26}IN$: C, 63.32; H, 5.71; N, 3.08. Found: C, 63.12; H, 5.73; N, 2.91.

Rearrangement of Quaternary Ions IIIa–e with Excess Potassium Amide to Form IIIa–e. The appropriate methiodide (0.05 mole) was added to a stirred solution of 0.15 mole of potassium amide in 300–600 ml of anhydrous liquid ammonia. After 6 hr, the reaction mixture was neutralized with 0.15 mole of ammonium iodide. The ammonia was evaporated on the steam bath as 200–300 ml of ether was added. The ether solution was decanted from the solid residue and extracted with several portions of 4 *M* hydrochloric acid to remove the basic products. The acidic extracts were combined and made strongly basic with potassium hydroxide (cooled and stirred), and the resulting mixture was extracted with ether. The ether extract was dried and the solvent removed. The residual basic fraction was distilled or recrystallized. In Tables I and II are summarized the yields and physical constants of the rearranged amines IVa–e.

In several experiments some of the starting methiodide was recovered by triturating the ether-insoluble solid residue with acetonitrile, cooling the filtered supernatant, and adding ether; the recovered methiodide was taken into account in calculating the conversion yields of rearranged amines given in parentheses in Table I.

In the experiment with methiodide IIId, hexane was added to the reaction product to precipitate benzamide (0.20 g), mp and mmp 125–127°. Distillation of the basic fraction afforded 1.0 g (11%) of 2-methylbenzyldimethylamine and 9.90 g (65%) of rearranged ketone amine IVd. The 2-methylbenzyldimethylamine was identified by comparison of infrared spectra and by mixture melting point of the picrates employing authentic samples.

Oxidation and cyclization of the rearranged ketone amine IVd to anthraquinone-1-carboxylic acid (V) was accomplished as described previously for 3-(dimethylaminomethyl)-2-methylbenzhydrol.[5] A mixture melting point of V with an authentic sample prepared by oxidation of benzanthrone[10] was undepressed. Moreover, the infrared spectra of the two samples were identical.

A blank experiment was performed with the rearranged ketone amine IVd (8.15 g, 0.032 mole) and 0.065 mole of potassium amide in 250 ml of anhydrous ammonia; the reaction mixture was

---

(14) D. J. Cram ("Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 223–238) has suggested that this mechanism might be common to both the *ortho*-substitution rearrangement and the Stevens 1,2 shift.

(15) Possibly these two mechanisms could be distinguished by a study of appropriate 3-substituted or 3,5-disubstituted benzyltrimethylammonium ions since, whereas the cyclic mechanism involves a nucleophilic attack on the aromatic ring, the other process, after elimination, involves an electrophilic attack.

(16) The Stevens 1,2 shift has been suggested to involve a frontward or sideward displacement (SNi); see C. R. Hauser and S. W. Kantor, *J. Am. Chem. Soc.*, 73, 1437 (1951). If, however, an elimination mechanism operates, the resulting ion pair must be closely associated since the reaction occurs with retention of configuration; see J. H. Brewster and M. W. Kline, *ibid.*, 74, 5179 (1952). Also, see R. K. Hill and T. Chan, *ibid.*, 88, 866 (1966).

(17) (a) G. Wittig and H. Strieb, *Ann.*, 584, 1 (1953); (b) C. R. Hauser, R. M. Manyik, W. R. Brasen, and P. L. Bayless, *J. Org. Chem.*, 20, 1119 (1955).

(18) Melting points and boiling points are uncorrected. Elemental analyses were performed by Ilse Beetz, Kronach, West Germany, and Janssen Pharmaceutica, Beerse, Belgium. Vapor phase chromatography was carried out on an F and M Model 500 gas chromatograph using a 5-ft Apiezon L and 6-ft silicone gum rubber columns. Infrared spectra were taken on Perkin-Elmer Infracords, Models 137 and 237, using the potassium bromide pellet method for solids and the neat liquid between sodium chloride plates for liquids. Nmr spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as internal reference.

(19) (a) F. N. Jones, R. L. Vaulx, and C. R. Hauser, *J. Org. Chem.*, 28, 3461 (1963); (b) R. L. Vaulx, F. N. Jones, and C. R. Hauser, *ibid.*, 29, 1387 (1964).

worked up to give a basic fraction (7.42 g) which, as indicated by vpc, consisted of 92% starting ketone amine IVd and 8% 2-methylbenzyldimethylamine.

In the experiment with methiodide IIIe under the usual conditions, polymer was produced. However, when the reaction was repeated employing only 1.1 molecular equiv of the reagent, the basic fraction consisted of a viscous liquid, which was treated with excess methyl iodide in acetonitrile to give 5.05 g (36%) of the methiodide of rearranged amine IVe. Also, part (33%) of the starting methiodide IIIe was recovered from the original ether-insoluble solid residue of the reaction product.

Independent synthesis of IVe was effected by refluxing 6.90 g (0.020 mole) of alcohol amine IVa for 18 hr in 20% H_2SO_4. The reaction mixture was cooled and made strongly basic to liberate the olefin amine IVe. Treatment of this viscous liquid with excess methyl iodide afforded 5.50 g (84%) of the methiodide of IVe, mp 236–237°, undepressed on admixture with a sample of the methiodide from IVe prepared from the rearrangement of methiodide IIIe.

Treatment of Quaternary Ions IIIa–d with 1.1 Molecular Equiv of Potassium Amide. To a stirred suspension of 0.055 mole of potassium amide in liquid ammonia was added 0.05 mole of quaternary iodides IIIa, IIIc, and IIId. Work-up as described above afforded a negligible amount of basic fraction and the starting quaternary iodides were recovered in yields of 91, 85, and 82%, respectively.

Treatment of 0.05 mole of quaternary ion IIIb with 0.055 mole of potassium amide in refluxing dry tetrahydrofuran for 4 hr yielded a negligible basic fraction. Aqueous work-up precluded any recovery of starting quaternary ion IIIb.

4-Substituted Benzyldimethylamines. To 0.05 mole of 4-bromobenzyldimethylamine[11] in a 250-ml erlenmeyer flask was added 0.06 mole of *n*-butyllithium in hexane.[20] The flask was filled completely with anhydrous ether, tightly stoppered, and allowed to stand at room temperature (25–30°) for 1 hr.[21] The solution, which was assumed to contain 0.05 mole of 4-lithiobenzyldimethylamine (X), was then used for the condensations described below, the results of which are summarized in Tables V and VI.

(A) With Benzophenone, Acetone, and Methyl Benzoate. To a boiling solution of the ketone (10% excess over the *n*-butyllithium used to prepare X) or ester (0.035 mole) in 200 ml of anhydrous ether in a 500-ml erlenmeyer flask was added the ether–hexane solution of X (0.05 mole). The resulting mixture was allowed to stand at room temperature for 4 hr, then hydrolyzed by careful addition of water. The two layers were separated, and the ether layer was extracted twice with 4 *N* hydrochloric acid. The acid extracts were made basic with excess 6 *N* sodium hydroxide. The resulting mixture was extracted three times with ether. The combined ethereal solution was dried over anhydrous magnesium sulfate and the solvent removed. The residue was distilled or recrystallized.

(B) With Formaldehyde. Gaseous formaldehyde, generated by heating paraformaldehyde in a stream of nitrogen, was passed over a stirred ether–hexane solution of lithioamine X (0.05 mole) for 15 min (transient purple color.) After stirring for 3 hr the resulting yellow-green suspension was worked-up as described above under A to give a light yellow oil, which was distilled.

(C) With Benzonitrile. To a stirred ether–hexane solution of lithioamine X (0.05 mole) in a three-necked flask (which had been flushed with dry nitrogen) was added dropwise 0.18 mole of benzonitrile in ether. After refluxing under nitrogen for 6 hr the red mixture was cooled and 25 ml of water was added, followed by 10 ml of glacial acetic acid. The layers were separated. The ether was combined with two ether extracts of the aqueous layer and the solution was dried over anhydrous magnesium sulfate. The solvent was removed and the residue (brown oil) was stirred and refluxed with 250 ml of 6 *M* hydrochloric acid for 72 hr. After cooling, the solution was extracted with ether to remove neutral materials. The aqueous layer was made basic with sodium hydroxide pellets and extracted three times with ether. The solvent was removed from the combined ethereal extracts, and the residual brown oil was distilled.

Reduction of amine ketone XId was effected by the Haung-Minlon[22] modification of the Wolff–Kishner procedure to afford a 59% yield of 4-(dimethylaminomethyl)diphenylmethane, bp 124–129° (1 mm). The methiodide, recrystallized from acetonitrile–ether, melted at 176–177.5°, lit.[4] mp 178–179°. A mixture melting point of this sample and an authentic sample[4] melted at 176–178°. The infrared spectra of the two samples were superimposable.

4-Substituted Benzyltrimethylammonium Iodides. Amines XIa–d were treated with excess methyl iodide in acetonitrile to form in nearly quantitative yields the corresponding methiodides which were recrystallized (see Table VI; also footnote *e*, Table V).

Amide quaternary iodide VIIe was prepared from α-chloro-*p*-nitrotoluene by treatment with dimethylamine, followed by reduction of the nitro group with tin and hydrochloric acid. After benzoylation of the primary amine group with benzoyl chloride, treatment with excess methyl iodide yielded VIIe as a hygroscopic solid melting at 249–250° in an over-all yield of 30%, which could probably be improved.

Anal. Calcd for $C_{17}H_{21}IN_2O$: N, 7.07. Found: N, 7.29.

Rearrangement of Quaternary Ions VIIa–e with Excess Potassium Amide to Form Amines VIIIa–e. To a stirred solution of 0.06–0.15 mole of potassium amide in 300–600 ml of anhydrous ammonia was added 0.02–0.05 mole of the appropriate methiodide. After 1–2 hr, the reaction mixture was neutralized with excess ammonium iodide. The ammonia was evaporated on the steam bath as 200–300 ml of ether was added. The ether solution was filtered from the solid residue and dried over magnesium sulfate, and the solvent was removed. The residue was recrystallized or distilled. In Tables III and IV are summarized the yields and physical constants of the rearranged amines VIIIa–e.

Conversion of Rearranged Amines VIIIb–c to Methiodides XIIIa–b. The rearranged carbinolamine VIIIa (0.02 mole) was treated with excess methyl iodide in acetonitrile to form methiodide XIIIa in 98% yield; after three recrystallizations from acetonitrile–ether, XIIIa melted at 178–179°.

Anal. Calcd for $C_{14}H_{24}INO$: C, 48.14; H, 6.93; N, 4.01. Found: C, 48.09; H, 6.99; N, 4.13.

The rearranged carbinolamine VIIIc (0.02 mole) was similarly converted to its methiodide in 96% yield; after two recrystallizations from acetonitrile–ether the methiodide melted at 204.5–206°.

Anal. Calcd for $C_{24}H_{28}INO$: C, 60.89; H, 5.96; N, 2.96. Found: C, 60.59; H, 5.99; N, 3.03.

Further Rearrangement of Quaternary Ions XIIIa and b to Form Carbinolamines XIVa and b. These reactions were carried out as described for quaternary ions VIIa–e. Removal of the solvent afforded an oil which was treated as described below.

The oil obtained from 6.05 g (0.017 mole) of methiodide XIIIa and 0.55 mole of potassium amide was distilled to give 1.65 g (43%) of 2-(dimethylaminomethyl)-α,α,3,4-tetramethylbenzyl alcohol (XIVa), bp 105–107 (1.3 mm). The infrared spectrum[6] of XIVa had a peak at 844 cm^{-1}, characteristic of the aromatic dimethylaminomethyl group,[3a] and a peak at 818 cm^{-1}, consistent with a structure having two adjacent aromatic hydrogens.[7] The nmr spectrum[23] of XIVa exhibited singlets at 86, 133, 22, and 426 ± 1 cps, assigned to the α,α-dimethyl, dimethylamino and ring methyl, benzylic, and hydroxyl protons, respectively. The aromatic multiplet was centered at 410 ± 1 cps.

Anal. Calcd for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33. Found: C, 76.02; H, 10.52; N, 6.34.

A sample of rearranged carbinolamine XIVa was converted to its picrate which, after three crystallizations, melted at 187.5–188.5°.

Anal. Calcd for $C_{20}H_{26}N_4O_8$: C, 53.30; H, 5.82; N, 12.44. Found: C, 53.30; H, 5.66; N, 12.36.

The oil obtained from 9.35 g (0.02 mole) of methiodide XIIIb and 0.06 mole of potassium amide was crystallized by cooling to −80° in methanol. The solid was recrystallized from ethanol to give 4.75 g (68%) of 2-(methylaminomethyl)-3,4-dimethyltriphenylmethanol (XIVb), mp 159–161°. The infrared spectrum[6] of XIVb had a peak at 846 cm^{-1}, ascribable to the aromatic dimethylaminomethyl group,[3a] and peaks at 833, 755, and 699 cm^{-1}, consistent with the structure having two and five adjacent aromatic hydrogens.[7] The nmr spectrum of XIVb exhibited singlets at 128, 134, and 180 ± 1 cps, assignable to the dimethylamino, ring methyl, and benzylic protons, respectively. The aromatic multiplet was centered at approximately 405 cps.

Anal. Calcd for $C_{24}H_{27}NO$: C, 83.44; H, 7.88; N, 4.05. Found: C, 83.66; H, 8.03; N, 4.26.

A sample of rearranged carbinolamine XIVb was converted to

---

[20] Obtained from the Foote Mineral Co., New Johnsonville, Tenn., as an approximately 1.6 *M* solution.

[21] The original procedure for the halogen–metal interchange involved the use of a 200% excess of *n*-butyllithium in ether for 4 hr.

[22] See Haung-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

[23] These spectra were determined in carbon tetrachloride.

its methioide which, after two recrystallizations from acetonitrile-ether, melted at 263–264°.

Anal. Calcd for $C_{25}H_{30}INO$: C, 61.60; H, 6.20; N, 2.87. Found: C, 61.77; H, 6.13; N, 2.93.

Cyclization of methiodide XV was effected by treating 9.75 g (0.02 mole) of XV with silver oxide essentially as described for the methiodide of 2-(dimethylaminomethyl)triphenylmethanol.[24] The oily residue resisted crystallization and was chromatographed on alumina eluted with hexane. Removal of solvent afforded, after recrystallization from hexane, 1.15 g (20%) of 3,4-dimethyl-1,1-diphenylphthalan (XVI), mp 105.5–106.5°. The infrared spectrum of XVI exhibited a peak for a cyclic ether[25] at 1010 cm^{-1} and peaks at 813, 759, and 799 cm^{-1}, consistent with the structure having two and five adjacent aromatic hydrogens.[7] The nmr spectrum of XVI showed singlets at 126 and 134 ± 1 cps, assigned to the ring methyl protons, and at 303 ± 1 cps, assigned to the benzylic protons. The aromatic multiplet was centered at approximately 430 cps.

Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found: C, 88.00; H, 6.67.

---

[24] R. L. Vaulx, R. N. Jones, and C. R. Hauser, *J. Org. Chem.*, 29, 505 (1964).

[25] See ref 7, p 119.

The Migration Aptitude of Substituted Benzyl *vs.* Methyl in Carbonium Ion Reactions of the 2,2-Dimethyl-3-aryl-1-propyl System. The Question of Alkyl Participation[1]

John R. Owen and William H. Saunders, Jr.

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. *Received August 8, 1966*

Abstract: A series of 2,2-dimethyl-3-(*p*-X-phenyl)-1-propyl *p*-toluenesulfonates (X = CH_3O, CH_3, H, Cl, CF_3) was prepared and subjected to solvolysis in acetic and formic acids. The rates of solvolysis were determined along with the yields of methyl- and benzyl-migrated products. Methyl migrated faster than benzyl in all cases, but the methyl: benzyl migration aptitude (corrected for the statistical factor) varied from 4.6 for X = CF_3 down to 1.4 for X = CH_3O in acetic acid at 109.58°, and a similar variation was noted in formic acid. The rates also varied with the substituent, being about four times faster for X = CH_3O than for X = CF_3. The rates, migration aptitudes, and partial rate factors for methyl and benzyl migration all follow the Hammett equation. Earlier results on the migration aptitude of unsubstituted benzyl were shown to be too high. Whether the ionization and rearrangement are concerted or stepwise is discussed. While firm conclusions cannot be drawn, the concerted process seems more likely.

We undertook a study of relative migration aptitudes of methyl and substituted benzyl groups as a continuation of earlier work on methyl *vs.* benzyl[2] and methyl *vs.* phenyl[3] migration aptitudes in neopentyl-like systems. The substituted benzyl group offered the opportunity of varying the electronic character of an alkyl group without simultaneously changing its steric requirements. We also hoped that a careful study of the relation between rate and migration aptitude would permit a decision on whether the ionization and migration were stepwise or concerted.

Results

The starting materials (I; see Scheme I) were easily prepared from the appropriate benzyl halide and methyl isobutyrate with sodium hydride,[2,4] followed by reduction and tosylation. The major synthetic task was preparation of reference samples of the expected products.

The esters IV and V are expected from capture of solvent by the carbonium ions II and III, and our earlier work[2] revealed that VIII is also produced, presumably by addition of solvent to the conjugated olefin from II. The alcohols corresponding to IV, V, and VIII were obtained by Grignard additions which, in most cases, employed readily available starting materials. Details are given in the Experimental Section.

Our former studies on Ic employed analysis of the rearranged olefin mixture as a part of the determination of product proportions.[2] Reduction of the olefins to the alkylbenzenes VI and VII had seemed a very attractive way of simplifying the analytical problem, but we found no way of separating VI and VII. In the present work, we found several gas chromatographic columns capable of separating VI and VII (see the Experimental Section). Authentic samples were readily prepared by dehydrating the alcohols corresponding to IV and V and hydrogenating the resulting olefin mixtures.

Some difficulty was encountered in preparing VId and VIId, for the hydrogenation conditions (palladium on charcoal in ethanol) partially dechlorinated the aromatic ring. A pure sample of VId was obtained by gas chromatography and of VIId by Wolff–Kishner reduction of 3-methyl-1-(*p*-chlorophenyl)-2-butanone. Rather than suffer the complication of a four-component hydrocarbon mixture, however, we usually converted the olefin mixture obtained in the solvolyses to VIc and VIIc by hydrogenation over palladium on charcoal in alkaline ethanol. This procedure gives quantitative dechlorination.

---

[1] This work was supported by the U. S. Army Research Office (Durham). J. R. O. received an American Cyanamid Fellowship in 1963–1964, and an Eastman Kodak Award in 1963.

[2] P. Warrick, Jr., and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **84**, 4095 (1962).

[3] W. H. Saunders, Jr., and R. H. Paine, *ibid.*, **83**, 882 (1961).

[4] B. E. Hudon and C. R. Hauser, *ibid.*, **62**, 2457 (1940).