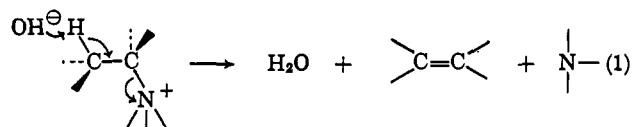# Mechanism of the Hofmann Elimination Reaction: An Ylide Intermediate in the Pyrolysis of a Highly Branched Quaternary Hydroxide[1]

BY ARTHUR C. COPE AND ANIL S. MEHTA[2]

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Mass spectrometric analysis of the trimethylamine formed on pyrolysis of the highly branched quaternary base N,N,N-trimethyl-2-t-butyl-3,3-dimethylbutylammonium hydroxide-2-d_1 showed that this decomposition proceeded principally by an ylide mechanism.

The decomposition of a quaternary ammonium hydroxide to an olefin and an amine has been generally described as an E2 reaction involving the concerted elimination of a β-proton by hydroxide ion and the removal of a tertiary amine.[3] One of the requirements of the E2 mechanism is that the β-proton and the leaving nitrogen moiety be coplanar and in the trans conformation (eq. 1). Other pathways which have been considered[3,4] are the two-step β-carbanion mechanism

(E1cb, eq. 2), the α-elimination (eq. 3) and the cis-ylide mechanism (eq. 4).
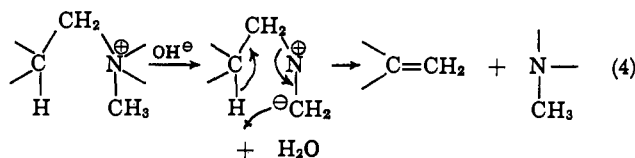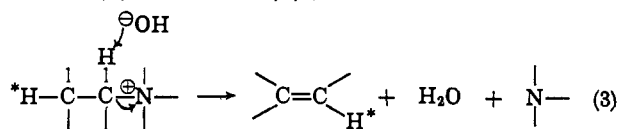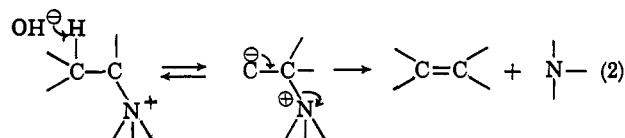
Conclusive evidence has been presented in support of the E2 mechanism for the Hofmann elimination in simple alkyl ammonium hydroxides[4,5] having a β-hydrogen atom that can become trans to the amino function in the transition state. However, Hofmann eliminations for compounds having only a cis-β-hydrogen atom are also known. For example, trans-2-phenylcyclohexyltrimethylammonium hydroxide gave only 1-phenylcyclohexene and no 3-phenylcyclohexene.[6] In this case there is experimental evidence for a direct cis-elimination,[7,8] and further recent work[9] has eliminated the possibility of the ylide mechanism and supports the E1cb route. This example, however, represents a special case due to the presence of the phenyl group which increases the acidity of the β-

hydrogen atom and stabilizes the carbanion formed by its removal.

In this paper evidence is presented for a Hofmann elimination proceeding by the cis-ylide mechanism in a case where steric factors favor a cis over a trans elimination and where the β-hydrogen is activated only by the quaternary nitrogen atom. Earlier work from this Laboratory had reported[10] a comparative study of the Hofmann decomposition of quaternary hydroxides of the type $R_2CH-CH_2-\overset{+}{N}(CH_3)_3OH^-$ with the observation that an unusually high yield of the olefin 1,1-di-t-butylethylene ($R = t-C_4H_9$) was obtained. Molecular models show that this hydroxide cannot adopt the requisite conformation for a trans E2 elimination; in fact, the conformation required for a cis elimination is favored.[10]

In order to determine whether or not the ylide mechanism accounted for the elimination in this case, N,N,N-trimethyl-2-t-butyl-3,3-dimethylbutylammonium hydroxide-2-d_1 (1) was synthesized and decomposed thermally. The presence of substantial amounts of deuterium in the trimethylamine formed would support the postulation of the ylide intermediate 2 in the reaction as shown in eq. 5.
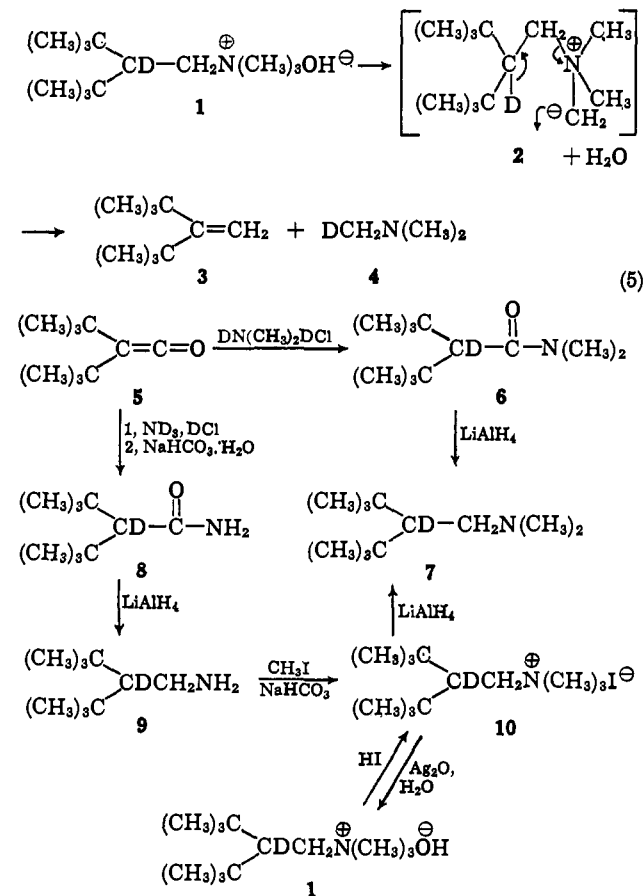
(1) Supported in part by the Army Research Office (Durham) under Grant No. DA-ARO-D-31-124-G240.

(2) James Flack Norris Memorial Fellow, 1961–1962.

(3) A. C. Cope and E. R. Trumbull in "Organic Reactions," Vol. XI, John Wiley and Sons, Inc., New York, N. Y., 1960, p. 317.

(4) V. G. Shiner and M. L. Smith, J. Am. Chem. Soc., 80, 4095 (1958).

(5) A. C. Cope, N. A. LeBel, P. T. Moore and W. R. Moore, ibid., 83, 3861 (1961).

(6) R. T. Arnold and P. N. Richardson, ibid., 76, 3649 (1954).

(7) J. Weinstock and F. G. Bordwell, ibid., 77, 6706 (1955).

(8) A. C. Cope, G. A. Berchtold and D. L. Ross, ibid., 83, 3859 (1961).

(9) G. Ayrey, E. Buncel and R. N. Bourns, Proc. Chem. Soc., 458 (1961).

(10) A. C. Cope and D. L. Ross, J. Am. Chem. Soc., 83, 3854 (1961).

Hexamethylacetone was converted to di-t-butylketene (5) by the method of Newman, Arkell and Fukunaga.[11] Addition of dimethylamine-N-d_1[12] to the ketene 5 gave the N,N-dimethylamide 6. Attempts to reduce 6 with lithium aluminum hydride gave very low yields of the tertiary amine 7. Combustion analysis of the amine isolated from a reduction using di-n-butyl ether as solvent showed that no deuterium was lost under the drastic conditions used (115°, 107 hours), even though the deuterium atom is α to the amide carbonyl group.

An alternative procedure leading to the quaternary hydroxide in satisfactory yields was the following: addition of deuterioammonia to the ketene 5 followed by removal of any deuterium in the amino group by equilibration gave the amide 8. Combustion analysis of the amide showed 1.01 atoms of deuterium per molecule and was in agreement with mass spectrometric analysis (2.4% d_0, 97.6% d_1). Di-t-butylacetamide-2-d_1 (8) was reduced with lithium aluminum hydride in 48% yield to the primary amine 9. In contrast to the reduction of the dimethylamide 6, this reduction resulted in about a 7–10% loss of deuterium according to combustion analysis (0.904 atom of deuterium per molecule). The primary amine 9 was converted to the quaternary hydroxide 1 via the methiodide 10. Lithium aluminum hydride reduction of the methiodide afforded the tertiary amine 7 which by mass spectrometric analysis consisted of 6.5% d_0-species, 93.4% d_1-species and 0.1% d_2-species and by combustion analysis contained 0.923 atom of deuterium per molecule. From these data as well as from the combustion analysis of the primary amine 9 it followed that the quaternary hydroxide consisted of 90–93% monodeuterated species and that the remainder was undeuterated.

The hydroxide was decomposed and the trimethylamine from each fraction was collected by gas chromatography and analyzed for deuterium by mass spectrometry. The results, summarized in Table I, indicate that 65–70% of the trimethylamine was monodeuterated. Since the starting hydroxide consisted of 90–93% d_1-species, the major pathway (75 ± 3%) of the reaction was through the ylide intermediate 2.

The presence of small amounts (1–4%) of dideuterated trimethylamine can be explained by exchange into the α-methyl groups of the quaternary hydroxide of the deuterium from any DOH formed. In support of this, the decomposition was stopped before completion and the recovered hydroxide was converted to the tertiary amine 7 via the methiodide. The increase in deuterium content of this sample of 7 relative to the one obtained from the starting methiodide paralleled the amount of dideuterio species present in the trimethylamine. The olefin formed in the pyrolysis was found to be deuterium-free.

Interpretation of the Mass Spectra. Trimethylamine.—Trimethylamine cannot be accurately analyzed for deuterium by comparison of the spectra of nondeuterated and partially deuterated samples, because preferential loss of hydrogen from the molecule on electron impact gives rise to an intense peak at m/e 58 (M-1, of even higher intensity than the molecular ion peak). Peaks due to loss of two and three hydrogen atoms further complicate the situation, making it impossible[13] to extrapolate from the spectrum of non-

(11) M. S. Newman, A. Arkell and T. Fukunaga, *J. Am. Chem. Soc.*, **82**, 2498 (1960).

(12) N. A. LeBel, Ph.D. Thesis, Massachusetts Institute of Technology, 1957.

(13) The probability of fragmentation of a C–D bond is not necessarily the same as that of the corresponding C–H bond. For examples, see K. Bie-

deuterated trimethylamine to that of the pure monodeuterated species required for the analysis. Reduction of the ionizing potential from 70 e.v. to slightly above the ionization potential of trimethylamine is of no use in this case because of the similarly low appearance potential of the $C_3H_8N^+$ ion (M-1)$^+$.

Therefore, trimethylamine-d_1 was synthesized to obtain its true mass spectrum. The spectrum of dideuteriotrimethylamine was then approximated by linear extrapolation of the spectra of the pure d_0- and d_1-species rather than by undertaking its synthesis. This was justifiable because the low intensity of the m/e 62 peak in the amine from pyrolysis indicated a low concentration (if any) of dideuterated species. Even an appreciable discrepancy between the true spectrum and the extrapolated one would not affect the results appreciably.

Using these data the mass spectra of the samples of trimethylamine from the pyrolysis experiments were analyzed as ternary mixtures of components of known mass spectrum. The peaks at m/e 58, 59 and 60 (rather than the molecular ion peaks at m/e 59, 60 and 61) were used as "analytical peaks" because of their intensity. Thus the only assumption made in the analytical procedure (in addition to the assumption of validity of the extrapolation just discussed to obtain the spectrum of trimethylamine-d_2) is that the ionization efficiency of labeled and unlabeled molecules is the same. This is based on analogy with cases in which these values were measured.[14,15]

MASS SPECTROMETRIC ANALYSIS^a FOR DEUTERIUM IN TRIMETHYLAMINE FRACTIONS FROM THE HOFMANN DECOMPOSITION^{b,c}

Fraction	% d_0	% d_1^{d}	% d_2	Elapsed time, min.	Extent of pyrolysis,^{e} %
1	30.3	68.4	1.3	1	0.3
2	29.0	70.8	0.2	2	5
3	34.2	63.9	1.9	3.5	38
4	29.7	67.2	3.1	4.5	73
5^f	27.5	68.5	4.0	6	100

^{a} For details see A. S. Mehta, Ph.D. Thesis, M.I.T., 1963. ^{b} The figure after the decimal point is not significant. ^{c} The decomposition was carried out under a nitrogen atmosphere at 130–135° (bath temperature) and 6 mm. pressure. ^{d} Calculation on the basis of a binary (d_0,d_1) mixture rather than a ternary (d_0,d_1,d_2) mixture gave the following values for % d_1 for the five fractions: 69.4, 71.0, 65.3, 70.1, 71.1. ^{e} The extent of pyrolysis is calculated for the nth fraction as 100 times the amount of trimethylamine collected in fractions 1 to n divided by the total amount collected in all fractions. ^{f} The 1,1-di-t-butylethylene collected from this fraction had a mass spectrum identical (within 1%) with that of an authentic non-deuterated sample.

Methyl-d_1 p-toluenesulfonate (11), prepared by the reaction of formaldehyde with lithium aluminum deuteride followed by decomposition of the resulting aluminum salt with p-toluenesulfonyl chloride in basic solution, was treated with anhydrous dimethylamine to give trimethylamine-d_1 (4) isolated as the hydrochloride. Mass spectrometric analysis of the tosylate 11 showed it to consist of 4.94% d_0-species, 94.8% d_1-species and 0.22% d_2-species. Using a large excess of formaldehyde gave a tosylate with a still larger percentage of d_0-species. Since the lithium aluminum deuteride was isotopically pure, some equi-

mann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 207 and references cited therein.

(14) For a discussion see ref. 13, pp. 213–214.

(15) The error due to "M + 1" peaks originating from ion–molecule collisions was shown to be negligible. The intensity of this peak was found to be very low (0.2–1.2% of the M$^+$ peak, in excess of the calculated isotope peak) and not to vary significantly over the pressure range employed to determine the mass spectra of the various samples.

libration, presumably of the type shown, took place during the reaction. Combustion analysis of the picrate of the trimethylamine-d_1 obtained from the methyl-d_1 p-toluenesulfonate containing 94.8% d_1-

species showed 0.954 atom of deuterium per molecule, a result in agreement with the mass spectrometric analysis of the p-toluenesulfonate. Thus, from the mass spectrum of this synthetic trimethylamine-d_1 and its established composition (5% d_0, 95% d_1, essentially 0% d_2), the mass spectrum of isotopically pure trimethylamine-d_1 for use in the analyses of trimethylamine from the quaternary hydroxide decomposition was deduced.[16]

Amine 7.—The molecular ion peak (m/e 185) of this amine was of very low intensity, so a fragment peak at m/e 128 (formed by loss of one t-butyl group) was used. The peak at m/e 127 (loss of $-CH_2-N-(CH_3)_2$) was only 2.7% of the m/e 128 peak and hence did not interfere with the analysis.

Experimental[17]

Di-t-butylketene.[11]—1,1-Di-t-butylethanol was prepared in 84% yield from hexamethylacetone and two equivalents of methylmagnesium iodide. Dehydration with thionyl chloride in pyridine gave 1,1-di-t-butylethylene, shown by gas chromatography (silicone oil, 114°, γ-methyl-γ-nitropimelonitrile, 36°) to be 95% pure, the remainder being hexamethylacetone. No trace of the previously reported[11] rearranged olefin was found. The subsequent steps were carried out as described previously[11] and gave di-t-butylketene in an over-all yield of 17% from hexamethylacetone.

N,N-Dimethyl-2,2-di-t-butylacetamide-2-d_1 (6).—Lithium dimethylamide, prepared from butyllithium and dimethylamine, was decomposed with deuterium oxide to give dimethylamine-N-d_1. Deuterium chloride was prepared by heating a stirred mixture of benzoyl chloride and deuterium oxide at 140° and dissolving the liberated gas in benzene. A mixture of 6.2 g. of di-t-butylketene in 80 ml. of dry benzene, 34 ml. of dimethylamine-N-d_1 and 0.75 ml. of 0.35 N deuterium chloride in benzene in a glass-lined pressure vessel was heated at 200° and 1500 p.s.i. of nitrogen for 168 hours. Milder conditions or shorter periods of time gave incomplete reaction. The resulting solution was concentrated under reduced pressure and the residue was dissolved in ether and washed with sodium bicarbonate solution. Evaporation of the dried ether solution gave a crystalline residue which was sublimed at 70–85° (3 mm.) to give 5.5 g. (68%) of N,N-dimethyl-2,2-di-t-butylacetamide-2-d_1, m.p. 85–87°. An analytical sample, after a second sublimation, had m.p. 86–87°.

Anal. Calcd. for $C_{12}H_{24}DNO$: C, 71.94; H + D, 12.58; N, 6.99. Found: C, 72.06; H + D, 12.57; N, 6.79; deuterium,[18] 0.73 atom per molecule.

N,N-Dimethyl-2,2-di-t-butylethylamine-2-d_1 (7).—In a typical preparation the amide 6 was added to a stirred suspension of x grams of lithium aluminum hydride in diethyl ether, tetrahydrofuran, di-n-butyl ether or diglyme. The mixture was heated at the temperature of the refluxing solvent (except in the case of diglyme) for periods of time varying between 6 and 192 hours. To the cooled mixture were added successively x ml. of water, x ml. of 15% sodium hydroxide solution and 3x ml. of water. The mixture was stirred for 30 min., filtered and the filter cake was washed several times with ether. The combined filtrate and washings were concentrated to a small volume and the basic products extracted with hydrochloric acid. Mild conditions (diethyl ether or tetrahydrofuran) gave only recovered amide

and no basic products. Refluxing di-n-butyl ether or diglyme at 115° gave mixtures of 4 or 5 basic components, as determined by gas chromatography (silicone grease, 150°). One of these, the desired tertiary amine 7 was collected and analyzed for deuterium: deuterium,[18] 0.745 atom per molecule.

Di-t-butylacetamide-2-d_1 (8).—Ammonia-d_3,[19] *ca.* 5 l., was allowed to pass into a previously degassed and evacuated mixture of 15.9 g. of di-t-butylketene in 20 ml. of benzene and 0.5 ml. of 0.0882 N deuterium chloride in benzene in a glass-lined pressure vessel cooled by liquid nitrogen. The vessel was then heated under 2000 p.s.i. of nitrogen at 80° for 24 hr., then at 120° for 48 hr., and finally at 200° for 72 hr. The mixture was then evaporated to dryness under reduced pressure and the residue was dissolved in ether and stirred overnight with sodium bicarbonate solution. The ether solution was dried (magnesium sulfate) and evaporated and the residue was recrystallized from benzene and sublimed at 70–80° (0.3 mm.), giving 11.7 g. (66%) of di-t-butylacetamide-2-d_1, m.p. 110°.

Anal. Calcd. for $C_{10}H_{20}DNO$: C, 69.71; H + D, 12.29; N, 8.13. Found: C, 69.92; H + D, 12.04; N, 8.34; deuterium, 1.01 atoms per molecule[18]; 2.4% d_0, 97.6% d_1, 0.0% d_2.[20]

2-t-Butyl-3,3-dimethylbutylamine-2-d_1 (9).—In a typical experiment equal weights of the amide 8 and lithium aluminum hydride were heated for 144–168 hours in refluxing tetrahydrofuran, after which the mixture was treated in the manner described for the tertiary amine 7. The aqueous hydrochloric acid solution was evaporated to dryness under reduced pressure and below 60°. The crystalline residue was dissolved in water and the solution was made alkaline with 30% sodium hydroxide solution and extracted with ether. The residue after removal of ether from the dried (potassium hydroxide) extracts was distilled through a semimicro column. The amine 9 had b.p. 105–106° (31 mm.) and was obtained in 48% yield.

Anal. Calcd. for $C_{10}H_{22}ND$: C, 75.88; H + D, 14.64; N, 8.85. Found: C, 75.66; H + D, 14.54; N, 8.92; deuterium.[18] 0.904 atom of per molecule.

The picrate after 3 recrystallizations from ethanol had m.p. 244–245°.

Anal. Calcd. for $C_{16}H_{25}DN_4O_7$: C, 49.73; H + D, 6.78; N, 14.50. Found: C, 49.94; H + D, 6.86; N, 14.43.

N,N,N-Trimethyl-2-t-butyl-3,3-dimethylbutylammonium Iodide-2-d_1 (10).—A mixture of 3.0 g. of the primary amine 9, 8.0 g. of methyl iodide, 5.0 g. of sodium bicarbonate and 30 ml. of methanol was heated under gentle reflux for 96 hr. After 24 and 48 hr., additional 8.0-g. portions of methyl iodide were added. The mixture was evaporated to dryness under reduced pressure and the residual solid was extracted with four 30-ml. portions of boiling chloroform. The combined extracts were cooled, filtered and evaporated to dryness. The residue was recrystallized from acetone, giving 4.89 g. (79%) of the methiodide 10.[10]

Preparation and Pyrolysis of N,N,N-Trimethyl-2-t-butyl-3,3-dimethylbutylammonium Hydroxide-2-d_1.—A mixture of 0.37 g. of silver oxide, 0.505 g. of 10 and 15 ml. of water was stirred for 12 hr. At the end of this time a drop of solution gave a negative test for iodide ion. The mixture was filtered and the solid was washed with water until the washings were neutral. The combined solutions were evaporated at 0.1–1.0 mm. and at a temperature below 35° and the grayish solid residue was used immediately for pyrolysis.

The pyrolysis procedure and the apparatus used to collect the volatile products have been described previously.[5] Pyrolysis was carried out until most, but not all, of the hydroxide had decomposed, and the pot was then immersed in a cold bath to prevent further decomposition or exchange. The low-boiling components were separated from the less volatile ones by distillation at −40° (0.15 mm.) of each of the pyrolysis cuts into a trap cooled by liquid nitrogen. The resulting mixtures of gases were analyzed by gas chromatography[21] and samples of trimethylamine were collected from each fraction for analysis by mass spectrometry. Quantitative estimation of the trimethylamine in each fraction was made by comparison of peak areas with those of samples of known concentration. Small amounts of dimethyl ether (not greater than 5% of the trimethylamine) were found in each of the fractions.

After distillation of the gaseous products at −40° the less volatile materials were extracted with pentane and analyzed by gas chromatography (silicone oil, 150°). A sample of 1,1-di-t-butylethylene was collected from the last fraction of the Hofmann decomposition for mass spectrometric analysis.

The results of a typical decomposition are summarized in Table II.

(16) As a check on the accuracy of this method, known standard mixtures of the hydrochlorides of trimethylamine-d_1 (95%) and undeuterated trimethylamine were prepared and the amine freed from these was analyzed. For mixtures where the percentage of d_1-species was known to be 60.8%, 78.6% and 88.1%, the values calculated from the mass spectra were 61.5%, 78.9% and 87.2%, respectively.

(17) Melting points are corrected and boiling points are uncorrected. Microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory, Copenhagen, Denmark. Deuterium analyses by combustion were performed by Mr. Josef Nemeth, Urbana, Ill. Mass spectra were determined with a C.E.C. 21–130 mass spectrometer equipped with a heated inlet system (150°). Ionizing potential was 70 e.v.

(18) By combustion.

(19) From Merck and Co., Canada.

(20) By mass spectrometry.

(21) A 3.5-m. column packed with 30% of silicone oil on 80–100 mesh firebrick was used. Elutions were made at 34° with a helium pressure of 10 p.s.i.

Compound	Millimoles
Quaternary iodide used	1.94
Quaternary iodide recovd.	0.35
Trimethylamine formed, total	.875
1,1-Di-*t*-butylethylene formed, total	.686
Dimethyl ether formed,[a] total	.039
Tertiary amine 7 formed,[b] total	.235

[a] Presumably arising by displacement of a methyl group from the quaternary nitrogen by methoxide (in equilibrium with methanol formed by a prior displacement).   [b] By displacement.

To the unchanged hydroxide (pot residue) were added 3 ml. of water and 3 ml. of ether, and the aqueous layer was acidified by dropwise addition of hydriodic acid. The solution was evaporated to dryness under reduced pressure and the residue was washed with cold acetone, leaving the methiodide as a white crystalline solid.

N,N-Dimethyl-2,2-di-*t*-butylethylamine-2-d_1 (7) from the **Methiodide 10.**—Samples of the starting methiodide and of the above methiodide from the quaternary hydroxide were separately reduced with lithium aluminum hydride in refluxing tetrahydrofuran for 96–144 hr.[22] Water and 30% aqueous sodium hydroxide were added, the solutions were filtered and the precipitates were washed several times with ether. The solvents were distilled and samples of the amine were collected by gas chromatography for analysis by mass spectrometry. The mass spectra of the two samples showed the deuterium distribution

	d_0, %	d_1, %	d_2, %
Amine 7, before Hofmann	6.5	93.4	0.1
Amine 7, after Hofmann	5.7	92.2	2.0

The difference in analyses indicates the amount of exchange occurring during the Hofmann elimination; deuterium analysis[18] of **7**, before Hofmann: 0.923 atom of deuterium per molecule.

Methyl-d_1 *p*-Toluenesulfonate (11).—Formaldehyde, obtained by heating paraformaldehyde at 130–150°, was passed under nitrogen through an electrically heated tube into a stirred solution of a slight excess of lithium aluminum deuteride in ether. The excess deuteride was decomposed with the requisite amount of water, and one equivalent of *p*-toluenesulfonyl chloride (based

(22) The procedure is described by A. C. Cope, E. Ciganek, L. J. Fleckenstein and M. A. P. Meisinger, *J. Am. Chem. Soc.*, **82**, 4651 (1960).

on formaldehyde) was added, followed by one equivalent of 30% sodium hydroxide solution with vigorous stirring over a 2-hr. period. The temperature was kept below 28° during the addition. The mixture was acidified with 5% hydrochloric acid and extracted with ether, and the combined extracts were washed with saturated sodium bicarbonate solution and water, and dried over magnesium sulfate. The ether was removed under reduced pressure and the residue was chromatographed on silica gel. Unchanged tosyl chloride was eluted with benzene and the desired methyl-d_1 *p*-toluenesulfonate with ether. The tosylate was distilled, b.p. 154° (7 mm.);   the maximum yield obtained was about 25%; deuterium analysis[20]: d_0, 4.94%; d_1, 94.8%; d_2, 0.22%. When a large excess of formaldehyde was used the deuterium content was: d_0, 9.8%; d_1, 90.2%; d_2, 0%.

Trimethylamine-d_1.—A mixture of 3.03 g. of methyl-d_1 *p*-toluenesulfonate, 9 ml. of anhydrous dimethylamine and 17 ml. of dry benzene was heated at 100° in a sealed tube for 12 hr. The tube was cooled to −70°, 15 ml. of concentrated hydrochloric acid was added and the mixture was warmed to room temperature and then evaporated to dryness. To the cooled residue (13.5 g.) dissolved in 50 ml. of water was added a cold solution of sodium hydroxide (17.2 g.) in water (50 ml.) followed by 20 ml. of benzenesulfonyl chloride. The mixture was shaken at room temperature for 4 hr., cooled and acidified with concentrated hydrochloric acid. N,N-Dimethylbenzenesulfonamide and excess benzenesulfonyl chloride were extracted from the mixture with ether. The aqueous layer was evaporated to dryness and the trimethylamine-d_1 hydrochloride was extracted from the residue with chloroform using a Soxhlet extractor. After removal of the chloroform the residual semisolid was treated with 50% sodium hydroxide solution and the liberated trimethylamine-d_1 gas was dissolved in concentrated hydrochloric acid. The basic solution was heated to drive out all of the dissolved trimethylamine. The aqueous acidic so'ution was evaporated to dryness and the residue was recrystallized from absolute ethanol; m.p. 281.8–282.2° dec.

Trimethylamine-d_1, obtained by the addition of aqueous base to the pure hydrochloride, was collected by distillation at 3 mm. in a trap cooled by liquid nitrogen.

Trimethylamine-d_1 picrate (90% yield, m.p. 218°) was prepared and had m.p. 223° after 3 recrystallizations from absolute ethanol.

Anal. Calcd. for $C_9H_{11}DN_4O_7$: C, 37.38; H + D, 4.18; N, 19.37. Found: C, 37.28; H + D, 4.31; N, 19.06; deuterium analysis[18]: 0.954 atom per molecule.

Polycondensation of Ferrocenylcarbinols and Substitution Orientation Effects[1]

By Eberhard W. Neuse and Daniel S. Trifan

Based on previous studies on the reaction of ferrocene with representative α-arylcarbinols, self-condensation reactions of three ferrocenylcarbinols, hydroxymethylferrocene, (1-hydroxyethyl)-ferrocene and α-hydroxybenzylferrocene, resulting in the formation of –CH(R)– linked ferrocenylene polymers are described. The acid-catalyzed reactions are conducted in the melt phase and lead to crude reaction products in the M_n range 1000–6000. The polymers are soluble in a number of organic solvents, and the lower members show a defined melting range. Quantitative infrared spectroscopic analysis has been applied to elucidate structural correlations and the effect of variables on the ring substitution orientations occurring under these conditions of polymer formation compared to the general behavior of the ferrocene nucleus under usual non-polymeric conditions.

Introduction

As part of a comprehensive study of carbinol condensations with the ferrocene nucleus, a previous investigation[2] has dealt with the condensation of ferrocene with representative α-arylcarbinols in the melt phase, rapid, almost quantitative reaction being exhibited by the limiting case of triphenylcarbinol, decreasing to slow, very slight conversions with primary α-aryl-substituted alcohols. In the present work, we have investigated the characteristics of the self-condensation reactions of some ferrocenylcarbinols, utilizing both

the highly nucleophilic character of the ferrocene ring as well as the high rate of ionization of metallocenyl α-carbinyl derivatives,[3] whose origin has been established as a general metal–electron backside participation with resulting metallocarbonium cation structures of the type I.[4] Under conditions as earlier applied,[2] a rapid self-condensation of ferrocenylcarbinols was thus anticipated, in its final stage leading to polymeric compounds consisting of ferrocenylene and methylene or methine groups alternating along the

(1) This research was supported by the Army, Navy and Air Force under Signal Corps Contract DA-039sc-78105.

(2) E. W. Neuse and D. S. Trifan, *J. Am. Chem. Soc.*, **84**, 1850 (1962).

(3) (a) N. Weliky and E. S. Gould, *ibid.*, **79**, 2742 (1957); (b) J. H. Richards and E. Hill, *ibid.*, **81**, 3484 (1959).

(4) (a) D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, No. **13**, 1 (1960); (b) E. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 4216 (1961).