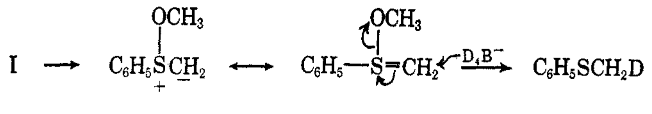
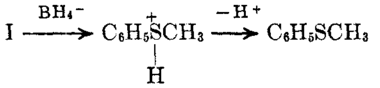
SCHEME IV



$$\mathrm{I} \longrightarrow \mathrm{C_6H_5}\overset{\mathrm{OCH_3}}{\overset{+}{\mathrm{S}}}\overset{-}{\mathrm{C}}\mathrm{H_2} \longleftrightarrow \mathrm{C_6H_5{-}}\overset{\mathrm{OCH_3}}{\mathrm{S}}\mathrm{{=}CH_2} \xrightarrow{\mathrm{D_4B^-}} \mathrm{C_6H_5SCH_2D}$$

SCHEME V



$$\mathrm{I} \xrightarrow{\mathrm{BH_4^-}} \mathrm{C_6H_5}\underset{\mathrm{H}}{\overset{+}{\mathrm{S}}}\mathrm{CH_3} \xrightarrow{-\mathrm{H^+}} \mathrm{C_6H_5SCH_3}$$

observation that sulfoxides are not reduced by sodium borohydride under the reaction conditions. In Schemes II, III, and IV, the borohydride first takes the role of a base, abstracting a proton from the salt to form an ylide intermediate. However, appropriate deuterium-labeling experiments indicate that none of these ylide pathways are operative.

Earlier work has shown that such ylides are readily formed and often undergo rapid collapse through the cyclic pathway shown to sulfide and a carbonyl compound.[1b] The carbonyl compound would subsequently be reduced by the borohydride (Scheme II). If such a mechanism were responsible for the production of sulfide in these reactions, methylphenyltrideuteriomethoxysulfonium fluoroborate would yield monodeuteriomethyl phenyl sulfide, provided the reaction were conducted in a nonexchanging solvent such as THF. The mass spectrum of the methyl phenyl sulfide obtained from such an experiment revealed the incorporation of only trace amounts of deuterium.

The operation of either Schemes III or IV would result in the incorporation of a deuterium in the product if sodium borodeuteride were employed. However, when I was reduced with sodium borodeuteride in methanol, the methyl phenyl sulfide produced was unlabeled. Reactions pathways analogous to Scheme III have been proposed in the reaction of certain alkoxysulfonium salts with alkoxides,[1b] in the Pummerer reaction,[5] and in methylthiomethylation reactions involving dimethyl sulfoxide and cyclohexylcarbodiimide[6] or acetic anhydride.[7] Scheme IV is adopted from the mechanism proposed for the Pummerer reaction by Oae and co-workers.[8]

The evidence forces the conclusion, although by an elimination process, that the methoxide is displaced from the sulfur by the borohydride anion. The protonated sulfide which is formed then loses a proton to form the product. This pathway is illustrated in Scheme V.

Experimental Section

General.—The alkoxysulfonium salts were prepared as previously reported.[1b] The mass spectra were determined with an Atlas CH4 mass spectrometer[9] at an ionizing potential of 70 ev and an ionizing current of 10 or 18 μa.

General Procedure for Reduction of Alkoxysulfonium Salts.—To 1 equiv of alkoxysulfonium salt in methanol, ethanol, or THF was added 4 equiv of sodium borohydride. After stirring for 30 min to 1 hr, the solvent was removed on the rotary evaporator. Ether was added to the residue and the inorganic salts which precipitated were filtered off. Removal of the ether gave the crude sulfide which was purified by distillation or recrystallization. The sulfides were identified by comparison of the melting points, mixture melting points, infrared spectra, etc., with those of authentic samples.

Deuterium-Labeling Experiments.—Methylphenylmethoxysulfonium fluoroborate was reduced with sodium borodeuteride in methanol. The mass spectrum of the methyl phenyl sulfide thus obtained exhibited a molecular ion (M) at 124 with M + 1 and M + 2 peaks of 8.66 and 5.09%, respectively, of the molecular ion intensity (calcd for C_7H_8S: M at 124 with M + 1 of intensity 8.63% and M + 2 of intensity 4.90%). Reduction of methylphenyltrideuteriomethoxysulfonium fluoroborate with sodium borohydride in THF gave methyl phenyl sulfide of mass spectrum 124, 100%; 125, 10.10%; and 126, 4.04%. Reduction of the same compound employing methanol as solvent gave sulfide of mass spectrum 124, 100%; 125, 8.65%; and 126, 4.91%.

Treatment of Methyl Phenyl Sulfoxide with Sodium Borohydride.—Methyl phenyl sulfoxide was recovered unchanged (70% recovery) when it was treated with sodium borohydride in methanol in the manner described above for alkoxysulfonium salts. The infrared spectra for the starting material and recovered product were identical.

Registry No.—Methylphenyl sulfoxide, 1193-82-4.

---

[5] W. E. Parham and S. H. Groen, *J. Org. Chem.*, **30**, 728 (1965).

[6] K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **87**, 5670 (1965).

[7] Sayed M. Ifzal and D. A. Wilson, *Tetrahedron Letters*, 1577 (1967); J. B. Jones and D. C. Wigfield, *ibid.*, 4103 (1965).

[8] S. Oae and M. Kise, *ibid.*, 1409 (1965), and references cited therein.

[9] The mass spectrometer was purchased from funds provided by a National Science Foundation Research Equipment Grant. We are grateful to Miss R. Van Fossen for the mass spectra.

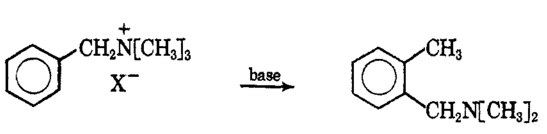
Quaternary Benzylammonium Rearrangements with Organolithium Compounds. IV. Benzyltrimethylammonium *p*-(*t*-Butyl)phenoxide with *n*-Butyllithium[1]

ARTHUR R. LEPLEY AND TERRY A. BRODOF

Department of Chemistry, Marshall University, Huntington, West Virginia 25701

Received March 14, 1967

The conversion of benzyltrimethylammonium ion (I) to *o*,N,N-trimethylbenzylamine (II) (eq I) in 81–85% yield by the attack of the methylsulfinyl carbanion has recently been reported.[2] The simplicity of the dimethylsulfoxide system and the room-temperature conditions offer definite advantages for reaction mechanism studies over sodium amide[3] or potassium amide[4] in liquid ammonia even though the yields are slightly less than the 90–95% achieved in the latter systems. Of particular note in the methylsulfinyl case was the absence of side products which were observed when other organometallics were used in the rearrangement.[5] Therefore we wish to report on the change from high conversion to competing reactions observed with



(1)

I II

---

[1] (a) Supported by U. S. Public Heath Service Grant GM 13987 from the National Institute of General Medical Sciences; (b) taken in part from the M.S. thesis of T. A. B., 1967; (c) part III, A. R. Lepley and A. G. Giumanini, *J. Org. Chem.*, **32**, 1706 (1967).

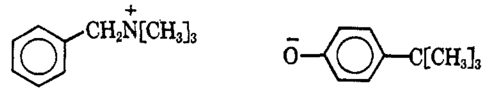
[2] K. P. Klein and C. R. Hauser, *J. Org. Chem.*, **31**, 4276 (1966).

[3] S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951); W. R. Brasen and C. R. Hauser, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 585.

[4] W. H. Puterbaugh and C. R. Hauser, *J. Am. Chem. Soc.*, **86**, 1105 (1964).

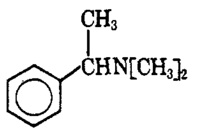
[5] A. R. Lepley and R. H. Becker, *Tetrahedron*, **21**, 2365 (1965); *J. Org. Chem.*, **30**, 3888 (1965).

temperature variation in the system benzyltrimethylammonium p-(t-butyl)phenoxide (I′) and n-butyllithium in ethers.

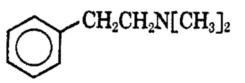


I′

n-Butyllithium reacts rapidly with I′ in anhydrous ethyl ether at 0–15° to give a high yield of II.[6] At higher temperatures in ethyl ether or tetrahydrofuran, α-phenethyldimethylamine (III) begins to appear as a competing product (Table I). The phenoxide salt



III



IV

can be recrystallized from ethyl ether or tetrahydrofuran (THF) while the iodide used in earlier studies[2-5] is insoluble in these solvents. This enhanced solubility is particularly apparent in an increased reaction rate; the iodide requires 4 hr for reaction completion with n-butyllithium in ethyl ether[5] while the phenoxide reactions were complete after 0.5–1.0 hr under similar conditions.

TABLE I

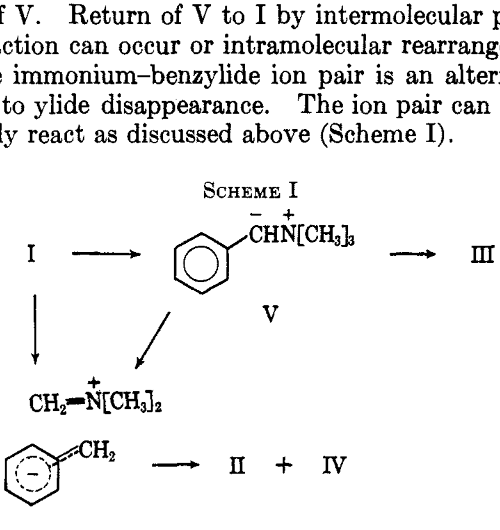
o,N,N-TRIMETHYLBENZYLAMINE (II) AND α-PHENETHYLDIMETHYLAMINE (III) FROM THE REARRANGEMENT OF BENZYLTRIMETHYLAMMONIUM p-(t-BUTYL)PHENOXIDE (I′) WITH n-BUTYLLITHIUM

Temp, °C	Solvent	Yield, % II	Yield, % III
0–15	Ether	88–92	*a*
30–35	Ether	72–75	*b*
30–35	THF	56–60	2–3
60–65	THF	67–80	14–17

[a] If present, below level of detection. [b] Less than 1%.

The *ortho* rearrangement product is accompanied by β-phenethyldimethylamine (IV)[6] even in the absence of III. Using an ion pair analogous to that suggested by that suggested by Bumgardner,[7] II would be formed by attack on the CH_2 of the immonium cation by the *ortho* site of the benzyl anion while IV requires attack by the methylene of the benzyl anion at the same location on the immonium member of the ion pair. However, the variation of yields with temperature strongly supports the previous evidence[5] that the α and *ortho* shift products are not formed from a common intermediate since parallel rate changes would occur if a common intermediate precedes the two rate-controlling transition states. The α rearrangement begins to occur at higher temperatures than that required for the *ortho* process. Since the benzyl ylide (V), which has been identified by reaction with benzophenone as the moss stable intramolecular ion pair,[4] probably gives rise to the α product III, a high activation energy for α rearrangement is reasonable. Thus under low-temperature conditions, alternative routes account for the fate of V. Return of V to I by intermolecular proton abstraction can occur or intramolecular rearrangement to the immonium–benzylide ion pair is an alternative route to ylide disappearance. The ion pair can subsequently react as discussed above (Scheme I).

SCHEME I



The ion pair mechanism for *ortho* rearrangement involves greater charge separation than in the ylide. Although intimate rather than solvent separated ion pairs are evident from the absence of intermolecular reaction,[3] increased solvent polarity should enhance charge separation and promote ion pair formation. Thus in dimethyl sulfoxide only *ortho* rearrangement was reported[2] while in the ethers of this study both *ortho* and α rearrangements were obtained. Although base and solvent changes both occur in the reactions compared, the influence of anion in the initial salt is not apparent. The enhanced solubility of I′ may play an important role if a homogeneous reaction favors II. But a much more complicated situation involving an association between the attacking base and the salt anion[8] may be a key to anion participation. However there is no direct data available on this last hypothesis.

Slow addition of n-butyllithium or variations in the initial n-butyllithium concentration influenced the time required for reaction completion but caused no noticeable change in the distribution of products.[1b]

Experimental Section

Benzyltrimethylamminium p-(t-Butyl)phenoxide.—Benzyltrimethylammonium iodide[3] (10 g, 36 mmoles) and 5.4 g (36 mmoles) of p-t-butylphenol were dissolved in 200 ml of commercial methanol. The solution was swirled rapidly for 1 min with 20 g (144 mmoles) of 40 mesh silver oxide and the mixture was quickly suction filtered.[9] The methanol was vacuum evaporated on a warm water bath (less than 60°). The brown viscous liquid which remained was extracted first with low-boiling petroleum ether (bp 35–60°) and then three times with anhydrous ether to give a crystalline product. Recrystallization from 30% t-butyl alcohol and 70% THF gave 7.9 g (22 mmoles, 62% yield) of the white crystalline product: mp 121–122°; thermal gravimetric analysis (80°, 2–3 mm) weight loss, 14.2% (calcdf or $C_{20}H_{29}NO \cdot 3H_2O$, 15.2%). The infrared spectrum (KBr disk) had bands at 3700–3300 s*, 2975 w, 1715 w, 1590 m, 1110 w, 995 w, 835 m, 780 m, 775 m, and 750 m cm^{-1}. The proton magnetic resonance spectrum of a saturated solution in hexamethylphosphoramide with a tetramethylsilane standard had chemical shifts (δ ppm, splitting s = singlet (peak integral ratio)): 1.13 s (9) CH_3 of t-butyl, 3.19 s (9) CH_3 on N, 4.05 s (6) H_2O, 4.80 s (2) CH_2 of benzyl, and two complex aromatic multiplets centered at 6.57 (4) phenoxide and 7.41 (5) benzyl.

---

(6) A product (<1%) with gas chromatographic characteristics of β-phenethyldimethylamine or n-pentylbenzene was observed but was not collected in adequate quantity or purity for positive identification. The assignment of the β-phenethyl compound, on the basis of peak enhancement, has been suggested by K. P. Klein, D. N. VanEenan, and C. R. Hauser, *J. Org. Chem.*, **32**, 1155 (1967).

(7) C. L. Baumgardner, *J. Am. Chem. Soc.*, **85**, 73 (1963).

(8) Association between base and salts has been shown for some lithium reagents, *cf.*, W. Glaze and R. West, *ibid.*, **82**, 4437 (1960).

(9) Prolonged contact with silver oxide gave low yields and considerable coloration of the product.

Anal. Calcd for $C_{20}H_{35}NO_4$: C, 68.00; H, 9.92; N, 3.96. Found: C, 67.76; H, 9.57; N, 3.94.

Rearrangement of Benzyltrimethylammonium *p*-(*t*-Butyl)-phenoxide.—The product yields are summarized in Table I. The details of a characteristic reaction and product identification procedures are described here. The quaternary salt (3.0 g, 8.6 mmoles) was placed in 100 ml of anhydrous ethyl ether and cooled to 10°.[10] *n*-Butyllithium in hexane (1.5 *N*;[11] 50 ml, 75 mmoles) was mixed with 50 ml of anhydrous ethyl ether and cooled to the same temperature as the previous mixture. The *n*-butyllithium solution was then quickly added to the salt without cooling. The temperature rapidly rose to 30–35°; the new temperature was maintained by a water bath during the remainder of the reaction.

The progress of the reaction was monitored by removing 1-ml samples at intervals, quenching with ice, adding a standard (N,N-dimethyl-*o*-toluidine), and gas chromatographic (gc) analysis of 100 μl of the organic phase. Gc analyses were made with an F & M Model 700 using a 0.25 in. × 16 ft column of 27% Apiezon L and 6% KOH on 40–60 mesh Chromosorb P. Separation characteristics and calculations for quantitative yields were comparable to those previously described.[5]

Product identification was definitive for *o*,N,N-trimethylbenzylamine; all other assignments were compatible by peak enhancement only. Compound II was confirmed by collecting the material separated by gc directly in an NMR Specialites 25-μl spherical cavity microtube, diluting with 1% TMS in CCl_4, and immediate measurement of the pmr spectrum. The spectrum was identical with that of II under similar conditions and showed no evidence of trace impurities.

Registry No.—I′, 13427-01-5; II, 4525-48-8; III, 2449-49-2; *n*-butyllthium, 109-72-8.

[10] Reactions were not performed under nitrogen but care was taken to exclude moisture and reactive amines or alcohols from reagents and equipment.

[11] The concentration of active carbanion was determined by the double titration method: H. Gilman and A. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944); H. Gilman and F. H. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1965).

Ozonide Stability during Gas Phase Chromatography

HARRY RUBINSTEIN[1]

Department of Chemistry, Lowell Technological Institute, Lowell, Massachusetts 01854

Received March 20, 1967

There is renewed interest in olefin ozonolysis[2–10] concerned with evaluating the "zwitterion" mechanism proposed by Criegee.[11,12] The experiments carried out for this purpose rely mostly upon product analysis wherein the amount of ozonides formed from the *cis* and *trans* olefins is determined using gas chromatography (gc).[2–7,9,10] Ozonides have been gas chromatographed by several workers on various substrates at temperatures between 40 and 100°.[2–4] More recent articles on this subject do not list column temperatures.[5–7,9] Since ozonides are unstable, existing data suggest that ozonide stabilities during gas chromatography should be investigated.

Results

Tables I and II summarize the gc analysis of *cis*- and *trans*-3-hexene ozonides. Separation of the *cis* and *trans* isomers was achieved on column A, but not on column B.

TABLE I

DECOMPOSITION STUDY OF 3-HEXENE OZONIDES (COLUMN A)

Run	Sample size, μl	Column temp, °C	Detector temp, °C	Injector temp, °C	Decomposition ratio $\times 10^2$
1	1	65	100	90	No decomposition observed
2	1	81	98	88	8.0
3	4	81	97	91	1.25
4	1	85	118	108	3.7
5	4	90	101	98	4.2
6	4	90	125	100	4.1
7	4	95	125	105	8.2
8	5	100	125	110	5.5
9	5	105	126	113	7.3
10	4	110	126	118	13.5
11	4	115	147	123	41.6
12	4	120	146	125	71.5
13	4	125	147	125	No ozonide peak observed

TABLE II

DECOMPOSITION STUDY OF 3-HEXENE OZONIDES (COLUMN B)

Run	Sample size, μl	Column temp, °C	Detector temp, °C	Injector temp, °C	Decomposition ratio $\times 10^2$
14	1	65	98	90	No decomposition observed
15	1	85	118	108	0.535
16	5	88	101	99	No decomposition observed
17	4	90	125	101	No decomposition observed
18	4	110	125	120	2.27
19	4	110	145	125	2.32
20	4	124	147	128	9.66

The last column in Tables I and II gives the relative amount of decomposition undergone by the samples. The origin and significance of these numbers may be seen by reference to Figures 1 and 2. Figure 1 shows a typical gc analysis of hexene 3-ozonides carried out at low temperatures on column A. The region between the aldehyde and ozonide peaks shows no appreciable recorder deflection. Figure 2 shows the same sample analyzed on column A at an elevated temperature. In the higher temperature run a considerable recorder deflection can be seen in the region between the aldehyde peak and the ozonide peaks. This deflection is caused by decomposition of the ozonides to propionaldehyde during the gc analysis. The decomposition ratio was calculated by comparing the average peak height of the propionaldehyde between point 1 and point 2 (see Figure 2) with that of the first ozonide peak. While this comparison is not usually so valid as a comparison of the relative peak areas, comparison of peak heights or peak areas gave the same relative de-

[1] This work was carried out under the support of Academic Year Extension Grant GY-414 from the National Science Foundation.

[2] G. Schröder, *Chem. Ber.*, **95**, 733 (1962).

[3] O. Lorenz and C. R. Parks, *J. Org. Chem.*, **30**, 1976 (1965).

[4] L. D. Loan, R. W. Murray, and P. R. Story, *J. Am. Chem. Soc.*, **87**, 737 (1965).

[5] R. W. Murray, P. R. Story, and L. D. Loan, *ibid.*, **87**, 3025 (1965).

[6] F. L. Greenwood and B. J. Haske, *Tetrahedron Letters*, 631 (1965).

[7] R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Am. Chem. Soc.*, **88**, 3143 (1966).

[8] P. R. Story, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **88**, 3144 (1966).

[9] F. L. Greenwood, *ibid.*, **88**, 3146 (1966).

[10] R. W. Murray and R. D. Youssefhyeh, *ibid.*, **88**, 3655 (1966).

[11] R. Criegee and G. Schroeder, *Chem. Ber.*, **93**, 689 (1960).

[12] P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).