Experimental Section[9]

Rearrangement of Quaternary Ion I to Form II and III.—To a stirred suspension of 0.05 mole of sodium amide in 300 ml of liquid ammonia was added 8.85 g (0.025 mole) of benzhydryltrimethylammonium iodide (I).[2a] After 3 hr, the red suspension was neutralized with 1.65 g (0.03 mole) of ammonium chloride, and the ammonia was replaced by an equal volume of ether. The ether was decanted from the solid residue which was washed twice with ether. The ether solutions were combined and dried over magnesium sulfate and the solvent was removed. The residue was distilled to give 4.80 g (85%) of a mixture of 2-benzylbenzyldimethylamine (II) and 2,2-diphenylethyldimethylamine (III), bp 126–128° (1.5 mm), in the ratio of 80–85:15–20,[10] determined by vpc on two different columns (see footnote 9). These amines were identified by the enhancement technique employing authentic samples.[3,4] Slight traces (<1%) of two unidentified amines were indicated, but none of amine IV was detected; an authentic sample of IV[5] showed a peak that was not present in the chromatogram of the product from I. Amine II has previously been isolated as a derivative.[2]

In another experiment, vpc determinations were made on a sample of the crude product, which gave essentially the same results. The precipitate that formed when the crude product was allowed to stand was removed by filtration and recrystallized from ethanol to give approximately 0.1 g (<1%) of 1-[2-(dimethylaminomethyl)phenyl]-1,2,2-triphenylethane (V), mp 175–176° (lit.[11] mp 177.5–179.5°), melting point undepressed upon admixture with an authentic sample prepared from the reaction of quaternary ion I with *n*-butyllithium.[12] The nmr spectrum of V (determined in deuteriochloroform) exhibited a singlet at 138 ± 1, a quartet[13] centered at 193 ± 1, with a coupling constant of 13, and a chemical-shift difference between these AB protons of 43, doublets at 283 and 342 ± 1 with a coupling constant of 12, and a multiplet centered at 433 ± 1 cps attributable to the N-methyl, benzylic, methylene, and aromatic protons, respectively.

---

[9] Melting and boiling points are uncorrected. Vapor phase chromatograms were obtained on F and M Model 500 and 700 gas chromatographs using 6-ft silicone gum rubber and 5-ft Apiezon L columns.

[10] These values are reported as a range because of the small difference in the retention times of amines II and III.

[11] G. Wittig, R. Mangold, and G. Felletschin, *Ann.*, **560**, 116 (1948).

[12] K. P. Klein, D. N. Van Eenam, and C. R. Hauser, unpublished results.

[13] See J. C. Randall, J. J. McLeskey, III, P. Smith, and M. E. Hobbs, *J. Am. Chem. Soc.*, **86**, 3229 (1964).

---

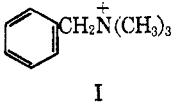
ortho-Substitution Rearrangement of Benzyltrimethylammonium Ion by the Methylsulfinyl Carbanion[1]

KARL P. KLEIN AND CHARLES R. HAUSER

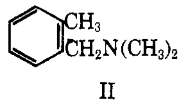
Department of Chemistry, Duke University, Durham, North Carolina

Received June 23, 1966

The *ortho*-substitution rearrangement of the benzyltrimethylammonium ion (I) to form II has previously been effected in high yield only by sodium amide[2] and potassium amide[3] in liquid ammonia at −33°. The yield with sodium amide is 90–95%.[2b]



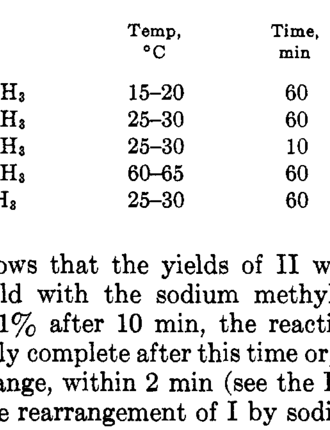
I



II

This rearrangement has now been brought about satisfactorily with the methylsulfinyl carbanion in dimethyl sulfoxide at 15–65°. The reaction presumably involves the intermediate formation of the benzyl and methyl carbanions, I′ and I″, respectively (Scheme I). In the analogous reaction with potassium amide in liquid ammonia, the intermediate benzyl carbanion I′ has been isolated as its benzophenone adduct.[3]

SCHEME I



In Table I are summarized the yields of rearranged amine II obtained from I with the sodium and lithium methylsulfinyl carbanions, which were prepared as described by Corey and Chaykovsky[4] by means of sodium hydride and *n*-butyllithium, respectively. The only other products detected were traces of a higher boiling amine and of a neutral fraction.

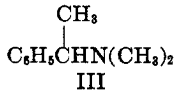
TABLE I

ortho-SUBSTITUTION REARRANGEMENT OF QUATERNARY ION I BY THE METHYLSULFINYL CARBANION IN DIMETHYL SULFOXIDE

Base	Temp, °C	Time, min	Yield of II, %
$NaCH_2SOCH_3$	15–20	60	85
$NaCH_2SOCH_3$	25–30	60	82
$NaCH_2SOCH_3$	25–30	10	81
$NaCH_2SOCH_3$	60–65	60	82
$LiCH_2SOCH_3$	25–30	60	85

Table I shows that the yields of II were 81–85%. Since the yield with the sodium methylsulfinyl carbanion was 81% after 10 min, the reaction appeared to be essentially complete after this time or, as indicated by a color change, within 2 min (see the Experimental Section). The rearrangement of I by sodium amide in liquid ammonia has similarly been observed to be very rapid.[2]

The rearranged amine II, obtained in the yields and under the conditions indicated in Table I, was pure by vpc; it was uncontaminated with the isomeric tertiary amines III and IV, the formations of which were possible through Stevens 1,2 shifts within ylids I′ and I″, respectively.



$$C_6H_5\overset{CH_3}{\overset{|}{C}}HN(CH_3)_2$$

III

---

[1] Supported by the National Science Foundation.

[2] (a) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951); (b) W. R. Brasen and C. R. Hauser, *Org. Syn.*, **34**, 61 (1954).

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

[4] E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1345 (1965).

$C_6H_5CH_2CH_2N(CH_3)_2$
IV

This exclusive *ortho* rearrangement of I to form II at 25–30° or higher seems rather unique since, not only does elevation of temperature generally favor the Stevens 1,2 shift,[5] but I reacts with *n*-butyllithium in ether–hexane at 25–30° to afford III (21–30%) as well as II (35–45%),[6] and with phenyllithium to give largely III.[6,7] Apparently the conversion of ylid I′ to ylid I″ (see Scheme I) is retarded in the aprotic solvents employed with the organolithium reagents so that considerable 1,2 shift of the methyl group within ylid I′ occurs.

Although sodium hydride was employed in the preparation of the sodium methylsulfinyl carbanion which effected the rearrangement of I, no rearrangement was observed when I was refluxed with sodium hydride in tetrahydrofuran at 65–66° for 12 hr, and 96% of I was recovered.

Experimental Section[8]

Rearrangement of Quaternary Ion I to Form II.—In Table I are summarized the yields of II obtained from the rearrangement of quaternary ion I with sodium and lithium methylsulfinyl carbanions. The details are described below.

A. With Sodium Methylsulfinyl Carbanion.—This reagent was prepared under nitrogen from 0.03 mole of sodium hydride and 100 ml of dimethyl sulfoxide as described previously.[4] To the stirred solution of sodium methylsulfinyl carbanion (presumably 0.03 mole) initially brought to the appropriate temperature (see Table I) was added, during 1 min, 6.95 g (0.025 mole) of benzyltrimethylammonium iodide (I)[3] in 50 ml of dimethyl sulfoxide to produce a light red color that changed to yellow within 2 min. After stirring for 1 hr, the reaction mixture was poured into 200 ml of ice-water, and the resulting mixture was extracted three times with methylene chloride. The combined methylene chloride extract was washed with cold water, and then extracted three times with 4 *N* hydrochloric acid. The acid extracts were combined and made basic with excess potassium hydroxide. The resulting mixture was extracted three times with ether, and the etheral solution was dried over magnesium sulfate. The solvent was removed and the residual oil was distilled to give 2,N,N-trimethylbenzylamine (II), bp 80–82° (14 mm) [lit.[3] bp 80–80.2° (14 mm)]. The picrate of II melted at 112–113° (lit.[3] mp 112.5–113°), undepressed on admixture with an authentic sample. The combined methylene chloride extracts were dried over magnesium sulfate and concentrated to yield a neutral fraction of less than 0.1 g of unidentified material.

A vpc of either the crude or distilled product showed it to contain II, identified by enhancement with an authentic sample, and a trace (<1%) of an unidentified higher boiling amine. None of amines III and IV was detected; authentic samples of III and IV showed peaks that were not observed in the vpc of the crude product.

B. With Lithium Methylsulfinyl Carbanion.—This reagent was prepared under nitrogen from 0.03 mole of *n*-butyllithium and 100 ml of dimethyl sulfoxide.[4] To the stirred solution of lithium methylsulfonyl carbanion (presumably 0.03 mole) at room temperature was added, during 1 min, 0.025 mole of quaternary ion I in 50 ml of dimethyl sulfoxide to produce a light red color which changed to yellow within 2 min. After stirring for 1 hr, the reaction mixture was treated as described in A to afford rearranged amine II, bp 82–84° (15 mm) (pure by vpc).

---

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

[6] (a) A. R. Lepley and R. H. Becker, *Tetrahedron*, **21**, 2365 (1965); *J. Org. Chem.*, 30, 3888 (1965); (b) K. P. Klein, D. N. Van Eenam, and C. R. Hauser, unpublished results.

[7] G. Wittig, R. Mangold, and G. Fellestchin, *Ann.*, 560, 116 (1948).

[8] Melting and boiling points are uncorrected. Vapor phase chromatograms were obtained on F and M Model 500 and 700 gas chromatographs using 5-ft Apiezon L and 6-ft silicone gum rubber columns.

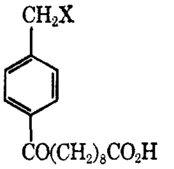
A Monofunctional *ansa* Lactone

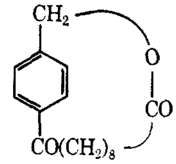
Paul R. Jones, Ronald J. Panicci,[1a]
Ronald M. Stimson,[1b] and Louis Port

*Department of Chemistry, University of New Hampshire,
Durham, New Hampshire 03824*

Received August 2, 1966

We have succeeded in obtaining a 16-membered lactone containing a *p*-phenylene bridge: 9-*p*-hydroxymethylbenzoylnonanoic acid lactone (**4**). In view of the fact that it is the first *ansa* compound with a single lactone functional group, we wish to describe the details of its synthesis through an intramolecular cyclization.


1, X = H
2, X = Br
3, X = OH


4

9-*p*-Toluoylnonanoic acid (**1**) was prepared in 47% yield by the Friedel–Crafts acylation of toluene with ω-carbomethoxynonanoyl chloride. Compound **1** yielded terephthalic acid on oxidation with potassium dichromate and sulfuric acid. Its ultraviolet spectrum in methanol [λ_{max} 251 mμ (ε 17,200)] indicated the *para* isomer.[2] A by-product (14% yield) was 1,8-di-*p*-toluoyloctane, very likely formed from sebacoyl chloride, which arose by disproportionation of ω-carbomethoxynonanoyl chloride in the presence of aluminum chloride.

Compound **1** was brominated with 1 equiv of N-bromosuccinimide (NBS) in CCl_4 to give, after separation by crystallization, 9-(*p*-bromomethylbenzoyl)nonanoic acid (**2**).

Critical evidence for the structure of **2** (rather than isomeric monobromo compounds with the bromine atom in the aliphatic chain) came from its nmr spectrum. The peak due to methyl protons in the spectrum of **1** had disappeared, and a new peak at 4.53 ppm was present.

When **2** was treated at reflux for 4 hr with excess aqueous methanolic KOH, it was converted to 9-(*p*-hydroxymethylbenzoyl)nonanoic acid (**3**). By contrast, the *ansa* compound **4** could be isolated, by a series of preparative thin layer chromatographic separations, as the product of **3** with KOH in tetrahydrofuran under high dilution conditions. Assignment of the structure to **4** is based on its composition and the infrared, ultraviolet, nmr, and mass spectra.

In the nmr spectrum of **4** the shielding effect of the aromatic ring on the methylene protons is evident. While in the nmr spectrum of **1** the methylenes (exclusive of the two adjacent to carbonyl and carboxy) appear at 1–2 ppm, the spectrum of **4** contains two broad peaks at 1.2–1.7 and 0.95 ppm, each corresponding to six protons. This shielding effect, first noted by

---

[1] (a) National Defense Education Act Fellow, 1963–1966; (b) National Science Foundation Cooperative Fellow, 1961.

[2] For spectra of model compounds *o*- and *p*-methylacetophenone, see R. B. Turner and D. M. Voitle, *J. Am. Chem. Soc.*, **73**, 1403 (1951).