$$\underset{\text{IV}}{C_6H_5CH_2CH_2N(CH_3)_2}$$

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).

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(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

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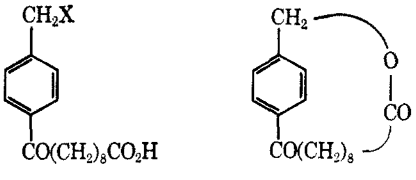
We have succeeded in obtaining a 16-membered lactone containing a *p*-phenylene bridge: 9-*p*-hydroxymethylbenzoylnonanoic acid lactone (**4**). In view of the fact that it is the first *ansa* compound with a single lactone functional group, we wish to describe the details of its synthesis through an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

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(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).

Waugh and Fessenden,[3] indicates that the aliphatic chain is part of a ring, which is situated over the aromatic nucleus.

This new class of *ansa* compounds is of extraordinary interest for several reasons. The physical and chemical properties may serve as criteria for estimating interatomic distances, electronic effects, ring strain, and other steric effects. Compounds of the type **4** are useful models for macrocyclic ring tautomers[4] and for macrolide antibiotics.[5] We are currently investigating other properties of **4** and the synthesis of lower and higher homologs.

Experimental Section[6]

ω-(*p*-Toluoyl)nonanoic Acid.—To a mixture of 15 g (0.065 mole) of methyl hydrogen sebacate and 125 ml of dry ligroin, heated to 70°, was added 31 g (0.26 mole) of thionyl chloride in several portions. Then the mixture was heated at 70–75° for 7 hr, and excess thionyl chloride and ligroin were removed by distillation at atmospheric pressure. The residual viscous, dark brown liquid was distilled: bp 124–127° (0.6 mm), yield 15.2 g (47%). In several experiments the yield of ω-carbomethoxynonanoyl chloride varied from 59 to 83%.

To a solution of 130 g (0.55 mole) of ω-carbomethoxynonanoyl chloride and 500 ml of dry, freshly distilled toluene, cooled to 3°, was added, with stirring, 150 g (1.13 moles) of anhydrous aluminum chloride so as to maintain the temperature at 5–10°. The mixture was stirred in the cold for 1 hr, then heated on the steam bath for 8 hr. After decomposition with ice–dilute hydrochloric acid, the organic layer was removed and combined with two ether washings of the water layer. The organic phase was steam distilled until no more toluene could be collected. Then the residue was extracted with ether. The ether solution was washed four times with saturated sodium bicarbonate and twice with water, dried over anhydrous sodium sulfate, and concentrated to yield 148 g of crude product. This was distilled up to 340° (21 mm). The distillate (123 g) was heated under reflux with aqueous, methanolic KOH for 3.5 hr. The solution was cooled and the 1,8-di-*p*-toluoyloctane was removed by filtration and recrystallized from ligroin: mp 100–101°, yield 27.5 g (14%), $\bar{\nu}_{CO}$ 1680 cm^{-1}, λ_{max} 251 mμ (log ϵ 4.50).

Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 82.12; H, 8.39.

The **semicarbazone** had mp 223–224°.

Anal. Calcd for $C_{26}H_{36}N_6O_2$: C, 67.21; H, 7.81; N, 18.09. Found: C, 67.29; H, 7.82; N, 18.32.

The filtrate from above was acidified to yield ω-(*p*-toluoyl)nonanic acid (**1**), which was recrystallized from ligroin: mp 92–93°, yield 71.8 g (47%), $\bar{\nu}_{CO}$ 1720 and 1695 cm^{-1}.

Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 74.06; H, 8.79.

Ultraviolet showed λ_{max} 251 mμ (log ϵ 4.16); nmr peaks (CCl_4) at 1–2 (broad multiplet), 2.28 (triplet), 2.38 (singlet), 2.88 (triplet), and 7.44 ppm (quartet).

The **semicarbazone** of **1** had mp 155–156° (ethanol–water).

Anal. Calcd for $C_{18}H_{27}N_3O_3$: C, 64.84; H, 8.16; N, 12.60. Found: C, 65.19; H, 8.44; N, 12.68.

Oxidation of 1.—A mixture of 1 g of acid **1**, 7 g of potassium dichromate, 10 ml of concentrated sulfuric acid, and 40 ml of water was heated under reflux for 2 hr. It was poured into 50 ml of water and the solid was collected. The solid was purified by trituration in warm 5% sulfuric acid, dissolution in 10% potassium hydroxide, acidification of the alkaline filtrate, and recrystallization of the resulting solid from ethanol–water, mp 295–300° dec. The infrared spectrum was identical with one of terephthalic acid.

ω-(*p*-Bromoethylbenzoyl)nonanoic Acid (2).—A mixture of 5 g (0.018 mole) of acid **1**, 3.23 g (0.018 mole) of N-bromosuccinimide, a few crystals of "Vazo" (azobisisobutyronitrile, E. I. du Pont de Nemours and Co.), and 100 ml of carbon tetrachloride was heated at reflux for 2 hr. It was filtered while still hot, and the filtrate was allowed to cool. The solid was recrystallized several times from benzene–pentane, mp 103–104°, and finally once from acetone–water, mp 105–106°. Its nmr spectrum exhibited a singlet at 4.53 ($ArCH_2Br$) and none at 2.38 ppm ($ArCH_3$).

Anal. Calcd for $C_{17}H_{23}BrO_3$: C, 57.50; H, 6.54; Br, 22.46. Found: C, 57.65; H, 6.45; Br, 22.29.

In several experiments the yield of **2** ranged from 30 to 70%.

ω-(*p*-Hydroxymethylbenzoyl)nonanoic Acid (3).—A mixture of 1 g of bromo acid **2**, 2 g of potassium hydroxide, and 100 ml of 50% aqueous methanol was heated at reflux for 3 hr. After acidification, concentration, ether extraction, and removal of the ether, there remained a dark yellow semisolid. Repeated recrystallization from ether–pentane raised the melting point to 90–91°: $\bar{\nu}_{OH}$ 3500–3700 cm^{-1}, a singlet in the nmr (chloroform) at 5.50 ppm, λ_{max} 251 mμ (log ϵ 4.31).

Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.64; H, 8.29.

ω-(*p*-Hydroxymethylbenzoyl)nonanoic Acid Lactone (4).—A 5-l., round-bottomed flask, containing 2 l. of tetrahydrofuran, was fitted with two reflux condensers, each topped with a dropping funnel. One contained a solution of 0.5 g of ω-(*p*-bromomethylbenzoyl)nonanoic acid (**2**) in 250 ml of tetrahydrofuran; the other, a solution of 0.08 g of potassium hydroxide, 25 ml water, and 100 ml of tetrahydrofuran. The solutions were added dropwise and simultaneously to the refluxing solvent over a period of 6 hr, while magnetic stirring was maintained. The supernatant solution was removed from a white solid by decantation and concentrated to an oily solid. The crude product, dissolved in chloroform, was separated into two fractions by thick layer chromatography (1:1 benzene–chloroform eluent) in several batches. The faster moving component was recovered as a white solid: mp 78–79.5°; $\bar{\nu}_{CO}$ (deuteriochloroform) 1685 and 1720 cm^{-1}; nmr peaks at 7.68 (doublet), 5.19 (singlet), 2.88 (triplet), 2.15 (triplet), 1.2–1.7 (broad multiplet), and 0.95 ppm (broad); λ_{max} 246 mμ (log ϵ 4.14). The mass spectrum[7] contains peaks at 274 (molecular ion), 256, 228, 216, 189, 134, 118, 90, with metastable peaks at about 239, 204, and 191.

Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.25; H, 8.11.

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[3] J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).

[4] P. R. Jones, *Chem. Rev.*, **63**, 461 (1963).

[5] M. Berry, *Quart. Rev.* (London), **17**, 343 (1963); H. Griesbach and W. Hofheinz, *J. Roy. Inst. Chem.*, **88**, 332 (1964).

[6] Infrared spectra were determined as halocarbon and Nujol mulls (unless otherwise stated) with a Perkin-Elmer 337 grating spectrophotometer; ultraviolet spectra were measured in methanol either with a Perkin-Elmer Model 4000 Spectracord or a Cary 14 spectrophotometer. Nmr spectra were determined in deuteriochloroform (unless otherwise stated) with a Varian A-60 instrument and are reported in parts per million (ppm) relative to tetramethylsilane. Combustion analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points and boiling points are uncorrected.

[7] We are grateful to Dr. Kenneth L. Rinehart, Jr., and associates, University of Illinois, Urbana, Ill., for determination of the mass spectrum.

Reactions of Hypochlorous Acid with Hindered Olefins[1]

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The reaction of *unsym*-dineopentylethylene oxide with anhydrous hydrogen chloride in ether or with other acids leads to the formation of dineopentylacetal-

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[1] (a) Taken in part from the M.S. thesis submitted by J. G. M.; (b) presented at the Western Regional Meeting of the American Chemical Society, Los Angeles, Calif., Nov. 18, 1965.

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