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DESULPHURIZATION WITH RANEY NICKEL

III. BENZYL N-ALKYL-N-BENZENESULPHONYLCARBAMATES[1,2]

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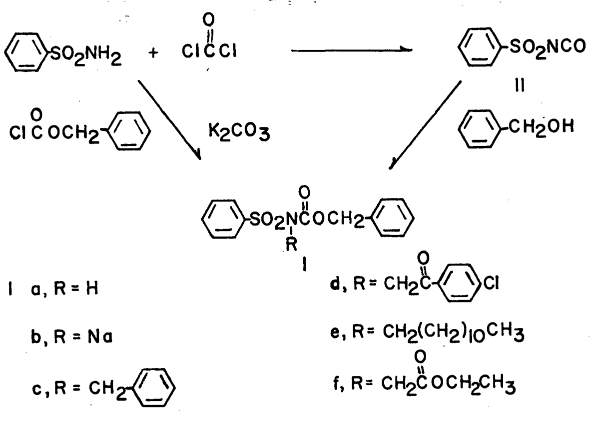
Alkylation of sodium saccharin followed by Raney nickel desulphurization has been found useful for converting certain alkyl halides to N-alkylbenzamides or N-alkylcyclohexylcarboxamides. In addition, Raney nickel desulphurization of N-alkylated dibenzenesulphonamides has been briefly considered for converting alkyl halides to amines. However, alkylation of sodium dibenzenesulphonamide generally proved inefficient, and this route was not further investigated.[1]

The present study was undertaken to evaluate benzyl N-alkyl-N-benzenesulphonylcarbamates (I) as amine precursors. The anion derived from benzyl N-benzenesulphonylcarbamate (I*a*) was predicted[3] to be a stronger nucleophilic agent than its dibenzenesulphonamide counterpart. Alkylation of sodium salt I*b* by normally reactive alkyl



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[1] *Part II, G. R. Pettit and R. E. Kadunce, J. Org. Chem. 27, 4566 (1962).*
[2] *Abstracted in part from the Master of Science thesis submitted by R. E. Kadunce to the Graduate School, University of Maine, June, 1961.*
[3] *Compare Part II, footnote 7.*

halides was, therefore, expected to proceed satisfactorily. Subsequent cleavage of the N-alkyl derivative with hydrogen bromide (1) or by concomitant desulphurization and hydrogenolysis using Raney nickel might then yield the corresponding amine.

Synthesis of carbamate I*a* was accomplished by condensing (e.g., ref. 2) benzenesulphonamide with carbobenzoxy chloride or, more conveniently and in good yield (91%), by treating benzenesulphonyl isocyanate (II) with benzyl alcohol. The isocyanate was prepared (cf. ref. 3) from benzenesulphonamide and phosgene. Generally, the carbobenzoxy chloride procedure led to carbamate I*a* (72%) accompanied by benzyl N-benzenesulphonyl-N-benzylcarbamate (I*c*). The N-benzyl derivative apparently arises from N-alkylation of initially formed carbamate (I*a*) by benzyl chloride, already present, or generated (4) during partial decomposition of carbobenzoxy chloride. Comparison of the N-benzyl derivative (I*c*) with a specimen prepared from benzyl chloride and the sodium salt of benzyl N-benzenesulphonylcarbamate (I*b*)[4] confirmed the structural assignment.

In contrast to our prior experience with dibenzenesulphonamide, the sodium salt of carbamate I*a*, in dimethylformamide, was easily N-alkylated by *p*-chlorophenacyl bromide, *n*-dodecyl bromide, and ethyl bromoacetate. Interestingly, the principal products (I*d-f*, 68 to 87% yield) were usually accompanied by small quantities of another N-alkyl derivative: subsequently identified as benzyl N-benzenesulphonyl-N-benzylcarbamate (I*c*). Formation of N-benzyl derivative I*c* apparently proceeds by competitive intermolecular condensation of carbamate I*b*.

Both the N-dodecyl (I*e*) and N-α-acetate (I*f*) carbamates were selected for cleavage studies. Treating the N-dodecyl (I*e*) derivative with Raney nickel (W-4) under mild conditions (70° in dioxane) afforded only the product of hydrogenolysis, N-dodecylbenzenesulphonamide. A variety of more vigorous desulphurization techniques (5) also proved unsatisfactory. These experiments led to mixtures of nitrogen-containing products bonded to the nickel residues. Isolation required continuous extraction with benzene and/or dissolution of the nickel components in hydrochloric acid. Raney nickel desulphurization of N-α-acetate I*f* was similarly unrewarding. However, carbamates I*e* and I*f* were readily converted by hydrogen bromide in acetic acid to, respectively, *n*-dodecylamine and glycine ethyl ester hydrobromides.

Although hydrogen bromide cleavage of N-alkyl-N-benzenesulphonylcarbamates appears to offer a practical route to amines, concurrent N-benzylation of carbamate I*b* during the alkylation step limits the overall usefulness of this approach.[5]

EXPERIMENTAL

Before evaporation, all solvent extracts were dried over magnesium or sodium sulphate. Melting points are uncorrected and were observed employing a silicone oil bath and open Kimble glass capillaries. Reaction products were shown to be identical with known specimens by mixture melting point determination and infrared spectral comparison (in potassium bromide). Dr. R. A. Hill of this laboratory recorded the infrared spectra and Dr. A. Bernhardt, Max-Planck Institute, Mülheim, Germany, provided the microanalyses.

Benzenesulphonyl Isocyanate (II)

Phosgene (38 ml) was condensed in a dry-ice trap and then slowly distilled into a refluxing solution of benzenesulphonamide (41 g) in 1,2,4-trichlorobenzene (85 ml). Heating and stirring (in a nitrogen atmosphere) was continued 2 hours. The reaction mixture was next swept with dry nitrogen and distilled through an 8-in. Vigreux column. The fraction boiling at 69–75° (0.5 mm) weighed 31 g and was sufficiently pure for subsequent work. Billeter (6) reported a b.p. of 129.6° at 9 mm.

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[4] *Benzenesulphonyl isocyanate may occasionally be a useful reagent for separating alcohols from neutral substances, since reaction between the isocyanate and alcohols may yield carbamates soluble in aqueous base.*

[5] *For example, selection of t-butyl N-benzenesulphonylcarbamate for alkylation might improve this alkyl halide → amine sequence.*

Benzyl N-Benzenesulphonylcarbamate (Ia)

A. From Benzenesulphonyl Isocyanate

In a typical experiment, benzenesulphonyl isocyanate (3.3 g) was added to benzyl alcohol (2 g) and the mixture was allowed to remain 2 hours at room temperature, in a flask protected from moisture. The viscous oil was triturated with petroleum ether and the colorless needles (m.p. 90–96)° which separated were collected; yield, 4.8 g (91%). Purification was achieved by reprecipitation (at pH 6 using dil. hydrochloric acid) of the amide from 15% sodium hydroxide solution and then recrystallization from chloroform – petroleum ether. A pure colorless crystalline sample of carbamate I*a* melted at 104.5–105.5°; ν_{max} 3290, 1750, 1720, 1350, and 1165 cm^{-1}. Anal. Calc. for $C_{14}H_{13}NO_4S$: C, 57.72; H, 4.47; N, 4.81; S, 11.01. Found: C, 57.78; H, 4.52; N, 4.78; S, 10.72.

B. From Benzenesulphonamide

Carbobenzoxy chloride (14 g, 0.08 mole) was added to a mixture of benzenesulphonamide (10 g, 0.06 mole) and anhydrous potassium carbonate (25 g) in dry acetone (100 ml). Following an overnight period of stirring and heating at reflux the mixture was cooled and filtered. Solid material was treated with 10% hydrochloric acid (200 ml) and extracted with benzene (2×100 ml). Concentration of the benzene extract to ca. 25 ml and dilution with petroleum ether gave 12.5 g (72%) of colorless crystals, m.p. 102.5–105°. Recrystallization from benzene – petroleum ether raised the melting point to 104.5–106°. The carbamate (I*a*) prepared by this method was identical with the substance descibed in procedure A.

Diluting the filtrate (acetone solution), from the original reaction mixture, with water gave 3.4 g, m.p. 106–109°, of benzyl N-benzenesulphonyl-N-benzylcarbamate (I*c*). Six recrystallizations from chloroform – petroleum ether yielded a pure specimen as colorless prisms, m.p. 111.5–112.5°; ν_{max} 1725, 1365, and 1170 cm^{-1}. Anal. Calc. for $C_{21}H_{19}NO_4S$: C, 66.13; H, 5.02; N, 3.67; S, 8.41. Found: C, 65.94; H, 5.01; N, 3.93; S, 8.49.

The benzyl derivative (I*c*) was identical with an authentic specimen obtained by the following method:

Benzyl N-Benzenesulphonyl-N-benzylcarbamate (Ic)

A solution of sodium methoxide in ethanol was added to an equivalent quantity of benzyl N-benzenesulphonylcarbamate in a minimum quantity of absolute ethanol. The sodium derivative (I*b*) which separated was collected and washed with benzene; 95% yield, colorless crystals, d.p. 298–300°. One recrystallization from dimethylformamide – ethyl ether gave microcrystals decomposing at 299–300°.

A mixture of the sodium salt of benzyl N-benzenesulphonylcarbamate (I*b*, 3.14 g, 0.01 mole), benzyl chloride (1.25 g, 0.01 mole), and dimethylformamide (25 ml) was heated (steam bath) 45 minutes. Solvent was removed *in vacuo* and the residue washed with chloroform and filtered. The filtrate was evaporated to a yellow solid (1.6 g, 42%) melting at 110–112°. Recrystallization from acetone – petroleum ether gave large colorless prisms, m.p. 110.5–113°. The product (I*c*) was characterized as noted above (cf. I*a*, procedure B).

Benzyl N-Benzenesulphonyl-N-(p-chlorophenacyl)carbamate (Id)

The preceding experiment was repeated using *p*-chlorophenacyl bromide (1.23 g, 0.05 mole), excess carbamate (I*b*, 2.5 g, 0.08 mole) and a 1.5-hour reaction period. The product recrystallized from benzene – petroleum ether as colorless needles; yield 2.0 g, m.p. 136–140°. Several recrystallizations from the same solvent raised the melting point to 141.5–143°; $\nu_{max}^{CHCl_3}$ 1730, 1705, 1355, 1220, and 1170 cm^{-1}. Anal. Calc. for $C_{22}H_{18}ClNO_5S$: C, 59.51; H, 4.09; S, 7.22. Found: C, 59.12; H, 4.00; S, 7.34.

Benzyl N-Benzenesulphonyl-N-dodecylcarbamate (Ie)

The experimental procedure described for synthesis of N-benzylcarbamate I*c* was repeated using dodecyl bromide (2.49 g, 0.01 mole) in place of benzyl chloride. In this case, a 2-hour reaction period was employed. A petroleum ether solution of the crude oily product slowly (24 hour) deposited benzyl N-benzensulphonyl-N-benzylcarbamate (I*c*, 0.15 g), m.p. 108–110.5°, which was identified by comparison with an authentic specimen. Concentrating and cooling the filtrate led to a waxy solid (2.8–3.4 g, 50–68%) melting at 40–46°. Five recrystallizations from ethyl ether provided an analytical sample of benzyl N-benzenesulphonyl-N-dodecylcarbamate as colorless needles, m.p. 47.5–49.5°; $\nu_{max}^{CHCl_3}$ 1712, 1355, and 1175 cm^{-1}. Anal. Calc. for $C_{26}H_{37}NO_4S$: C, 67.94; H, 8.12; N, 3.05; S, 6.98. Found: C, 67.44; H, 7.89; N, 3.30; S, 6.95.

Cleavage of Benzyl N-Benzenesulphonyl-N-dodecylcarbamate (Ie)

A. By Raney Nickel

A mixture of carbamate I*e* (0.50 g), Raney nickel (4 ml, W-4, 2 weeks old, ref. 7), and dioxane (25 ml) was stirred for 50 minutes at 70±2°. After collecting residual nickel the filtrate was concentrated (*in vacuo*) to 0.15 g of colorless solid, m.p. 45–53°. Recrystallization from methanol–water yielded a pure specimen of N-dodecylbenzenesulphonamide melting at 57–58.5° (ref. 8, m.p. 59°). The product was identical with an authentic specimen prepared from dodecylamine and benzenesulphonyl chloride.

A variety of more vigorous experimental conditions using dioxane as solvent and variously aged samples of W-2 and W-4 Raney nickels gave unsatisfactory results. The mixtures (evidenced by thin-layer chromatograms) obtained were not considered of further interest.

B. By Hydrogen Bromide (8)

A solution composed of carbamate I*e* (1.4 g), 35% hydrogen bromide in acetic acid (12 ml), and phenol (0.7 g) was allowed to remain at room temperature 48 hours. Dilution with ethyl ether precipitated 0.31 g (74%) of *n*-dodecylamine hydrobromide, d.p. 190° (sintering from 140°). Both the hydrobromide and *p*-toluenesulphonamide (m.p. 74–75°, ref. 9) derivatives were identical with authentic specimens.

Ethyl α-Aminoacetate Hydrobromide

The sodium salt of benzyl N-benzenesulphonylcarbamate (5.5 g) in dimethylformamide (20 ml) was alkylated with ethyl α-bromoacetate (2.9 g) as described using benzyl chloride (cf. I*c*). In this example, a 1-hour reaction period was employed and the crude reaction residue was extracted with benzene. Following removal of benzene, *in vacuo*, a petroleum ether solution of the resulting oily product (6.3 g) was maintained at room temperature 2 days. The benzyl N-benzenesulphonyl-N-benzylcarbamate (0.2 g, m.p. 103–109°) which separated was recrystallized (to m.p. 111–112°) from acetone–water and shown to be identical with an authentic sample (I*c*). Concentrating the petroleum ether filtrate afforded an impure specimen of N-benzenesulphonyl-N-carbobenzoxyglycine ethyl ester. A portion (0.70 g) of the crude oily mixture was treated with 35% hydrogen bromide in acetic acid (7 ml, containing 0.5 g of phenol) as reported using *n*-dodecylcarbamate I*e*. The crude semisolid hydrobromide of glycine ethyl ester weighed 0.22 g. Four recrystallizations from ethanol – ethyl ether led to colorless needles decomposing at 177–178°. Comparison with an authentic specimen of ethyl α-aminoacetate hydrobromide (d.p. 175–176°, ref. 10) confirmed the structural assignment.

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NUCLEAR SPIN–SPIN COUPLING CONSTANTS INVOLVING THE GROUP IV ELEMENTS

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Consideration of correlations involving coupling constants between different nuclei has been mostly confined to those involving C^{13} and hydrogen (1–4). The interest has centered around the following topics: dependence of $J_{C^{13}-H}$ on *s* character (1–4), the variation of $J_{C^{13}-H}$ in molecules of the type CHXYZ (5–8), and the use of $J_{C^{13}-H}$ in conjunction with chemical shift data to indicate diamagnetic anisotropy (9). $J_{Si^{29}-H}$ coupling constants have been measured (16) but these are influenced by polar effects besides being dependent on hybridization (6). Long range $J_{C^{13}-C-H}$ and $J_{C^{13}-C-C-H}$ coupling constants have been

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