

REPLACEMENT OF HYDROXYL BY METHYL,
VIA THE SODIUM SALT OF DIMETHYL SULPHOXIDE*

By T. J. BROXTON,† Y. C. MAC,† A. J. PARKER,† and M. RUANE†

Corey and Chaykovsky¹ have described useful reactions of "dimsyl sodium", i.e. the sodium salt of dimethyl sulphoxide in dimethyl sulphoxide (DMSO). We have investigated reactions of this base with carbon compounds because of our interest in reaction sequence (1), which it was hoped might give replacement of OH by CH₃ with inversion.



Tridecylmethyl sulphoxide and pentadecylmethyl sulphoxide were prepared in 83% yield from a 4 : 1 mixture of dodecyl and tetradecyl tosylates and in 91% yield from a 4 : 1 mixture of dodecyl and tetradecyl bromides, with dimsyl sodium in DMSO at 50°. Reduction of the sulphoxides with Raney nickel in refluxing ethanol gave a 75% yield of a 4 : 1 mixture of tridecane and pentadecane.‡

When R was aryl, reaction sequence (1) was not successful; although phenyl methyl sulphoxide is formed from chlorobenzene and dimsyl sodium,¹ phenyl tosylate with dimsyl sodium gives 82% sodium phenoxide and 23% *p*-tolylsulphonylmethylenesulphinylmethane. β -Naphthyl tosylate gave 65% sodium β -naphthoxide and 33% *p*-tolylsulphonylmethylenesulphinylmethane with dimsyl sodium. Nucleophilic attack on sulphur, rather than on aryl carbon, cleaves the S-O bond of the tosylate.

With R as cyclohexyl, elimination rather than substitution took place with dimsyl sodium. Cyclohexene in 72% yield was obtained from cyclohexyl tosylate with a twofold excess of dimsyl sodium. No cyclohexylmethylenesulphinylmethane was detected.

Clearly dimsyl sodium behaves as a carbon nucleophile, a sulphur nucleophile, or a hydrogen nucleophile towards ROTs, according to the nature of R. It would seem that *S_N2* reactions of dimsyl sodium, followed by Raney nickel desulphurization of the sulphoxide product, introduce methyl groups only at primary carbon atoms, which are readily susceptible to *S_N2* attack, or at aryl carbon if the leaving group is weakly electrophilic, e.g. chlorine.

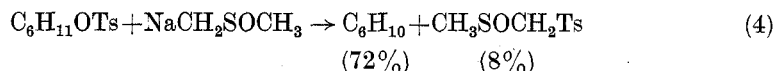
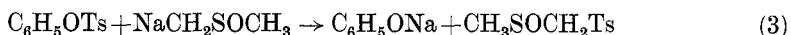
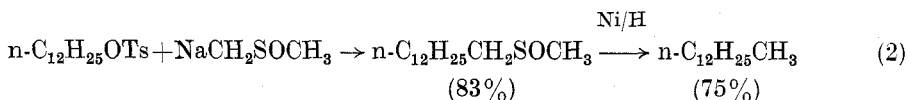
* Manuscript received August 12, 1965.

† Department of Organic Chemistry, University of Western Australia, Nedlands, W.A.

‡ We had intended to use dodecanol as starting material. However, the "dodecanol" supplied by B.D.H. was shown by mass spectrometry, at the conclusion of this work, to be a 4 : 1 mixture of dodecanol and tetradecanol. This finding does not alter our conclusions as to reaction sequence (1) for saturated primary alcohols.

¹ Corey, E. J., and Chaykovsky, M., *J. Am. Chem. Soc.*, 1965, **87**, 1345.

Equations (2)–(4) summarize reaction types and yield in this work.



Experimental

Dimethyl sodium was prepared in a two-necked flask from sodium hydride and DMSO as described by Corey and Chaykovsky.¹ It was kept at 50° under dry nitrogen (CO₂ and O₂ free) for 1 hr until gas evolution ceased. The solution was filtered through a glass wool plug in one of the necks of the reaction vessel, without exposing it to the atmosphere. When a trace of triphenylmethane was added, it gave the red colour of sodium triphenylmethide. A sample was poured into water and analysed for base.

Tosylates were prepared from alcohols or phenols by a standard procedure.^{2,3} Dodecyl bromide was prepared from "dodecanol" (see Footnote above), bromine, and red phosphorus.³ DMSO was dried with Molecular Sieves 5A and distilled at 5–10 mm. It was redistilled at 5–10 mm from calcium hydride just before use.

Dodecyl Tosylate with Dimethyl Sodium

Dodecyl tosylate, m.p. 15–18° (7.4 g, 0.02 mole), in 10 ml of DMSO under nitrogen was added over 5 min to 0.03 mole dimethyl sodium in 20 ml DMSO at 50° until the red colour of the triphenylmethide disappeared. After 15 min, the reaction mixture was poured into 200 ml saturated brine and extracted with ether. The ether extract was dried over anhydrous sodium sulphate and run through a column of activated charcoal. Removal of solvent gave a waxy solid, which recrystallized from light petroleum, m.p. 54–55°. The yield of tridecylsulphinylmethane was 83%. ν_{max} (CCl₄) 2950, 2925, 1460 (C–H); 1060 cm⁻¹ (S=O).

The compound analysed for C₁₃H₂₇SOCH₃ (Found: C, 68.4; H, 12.2; S, 13.0. Calc.: C, 68.2; H, 12.2; S, 13.0%). The crude sulphoxide (4 g) was desulphurized with a tenfold excess of Raney nickel in refluxing ethanol over 8 hr. The reaction mixture was poured into water, extracted with light petroleum (b.p. < 45°), and chromatographed on alumina. The colourless liquid distilled at 112°/9 mm to give a 75% yield calculated as tridecane. It analysed for C₁₃H₂₈ (Found: C, 84.7; H, 15.15. Calc.: C, 84.7; H, 15.3%). Infrared spectrum (CCl₄ solution) ν_{max} : 2900, 1450, 1370 cm⁻¹ (C–H); n.m.r. spectrum: τ 8.72, 9.12. A tetranitromethane test for unsaturation was negative. The mass spectrum showed a mass peak at 184 and a smaller peak at 212 mass units. The peak at 212 was attributed to pentadecane. The starting material, "dodecanol", had mass peaks at 168 and 196 mass units, with no peak in between. The peaks correspond to dehydrated dodecanol and tetradecanol respectively. Relative peak heights for the dehydrated alcohols and the tridecane–pentadecane product of reaction (1) were 4 : 1 in each case. Clearly the B.D.H. "dodecanol" contained up to 25% tetradecanol and this ratio of dodecyl to tetradecyl is maintained throughout the reaction sequence (1). The analysis figures would not clearly distinguish between C₁₃ and C₁₅ derivatives (e.g. C₁₅H₃₂ requires C, 84.8; H, 15.2%).

Dodecyl bromide, prepared from the same "dodecanol", reacted with dimethyl sodium, as described for dodecyl tosylate, to give 90% of tridecylsulphinylmethane, m.p. 55°.

² Drahowzal, F., and Klamann, D., *Mh. Chem.*, 1951, **82**, 460.

³ Vogel, A. I., "A Textbook of Practical Organic Chemistry." (Longmans: London 1951.)

β -Naphthyl Tosylate and Phenyl Tosylate with Dimsyl Sodium

β -Naphthyl tosylate, m.p. 125°, was treated with a twofold excess of dimsyl sodium as described above, except that the reaction temperature was raised to 70° for 2 hr. The reaction mixture was poured into saturated brine and extracted with chloroform. The extract, after crystallization from carbon tetrachloride, gave a colourless solid, m.p. 111°, in 33% yield, calculated as C₉H₁₀O₃S₂. The *p*-tolylsulphonylmethylenesulphinylmethane analysed as C₉H₁₀O₃S₂ (Found: C, 46.4; H, 5.2; S, 27.6. Calc.: C, 46.5; H, 5.2; S, 27.6%). The n.m.r. spectrum τ 7.50 (3H); 7.05 (3H); 5.58 (2H); and symmetrical quartet centred at 460 c/s, integrating for 4H, confirmed the structure. Acidification of the brine solution gave 65% β -naphthol.

Phenyl tosylate gave, with dimsyl sodium under the same conditions, 82% phenol and 23% *p*-tolylsulphonylmethylenesulphinylmethane.

Cyclohexyl Tosylate with Dimsyl Sodium

Cyclohexyl tosylate, m.p. 45°, 0.02 mole in 10 ml DMSO, was added to 0.04 mole dimsyl sodium in 20 ml DMSO at 50°. The reaction vessel was sealed and kept at 50° for 2 hr. It was cooled to room temperature. When the reaction vessel was opened, a positive pressure had developed and the odour of cyclohexene was detected.

The cold solution was extracted several times with carbon tetrachloride and the olefin content was estimated by treatment with bromine at 0° in the dark. Unchanged bromine was estimated iodometrically.⁴ Blank experiments with DMSO and cyclohexyl tosylate showed no reaction with bromine under these conditions. The extract had an i.r. spectrum identical with cyclohexene in carbon tetrachloride.

In a separate experiment, the reaction mixture was poured into 200 ml of water. Extraction with chloroform, following the procedure for β -naphthyl tosylate with dimsyl sodium, gave 8% *p*-tolylsulphonylmethylenesulphinylmethane, m.p. 111°.

Acknowledgment

We thank Mr J. L. Occolowitz, Defence Standards Laboratories, for measuring and interpreting the mass spectra.

⁴ Polgár, A., and Jungnickel, J. L., "Organic Analysis." Vol. 3. (Interscience: New York 1956.)