

Improved Preparation of 4-Aminomethyl-2,2-disubstituted-1,3-dioxolanes

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As part of one of our synthetic programs, we have investigated the preparation of 4-aminomethyl-2,2-dimethyl-1,3-dioxolane (I) and the corresponding 2,2-diphenyl compound (II).

These compounds have been prepared previously by treating the corresponding chloride, bromide or tosylate with liquid ammonia in an autoclave (1,2,3). In our hands, attempts to prepare compounds I and II by the above methods were unsatisfactory due to low yields and difficulties encountered in carrying out the reactions on a larger scale than reported in the literature.

We have found that when the tosyl compounds were treated with sodium azide in dimethylsulfoxide, azidomethyldioxolanes could be prepared in good to excellent yields. The azides were readily reduced to the amines I and II in good yields using lithium aluminum hydride.

EXPERIMENTAL (4)

The azidomethyldioxolanes prepared in this work appeared to be stable, but were kept in dilute solution whenever possible. Evaporation of the solutions was carried out behind a safety shield without heating whenever necessary.

2,2-Dimethyl-4-tosyloxymethyl-1,3-dioxolane.

This compound was reported as an oil by Baer and Fischer (5). However, using their method, we obtained a crystalline solid, m.p. 46-48° (from 2-propanol) in 86% yield.

Anal. Calcd. for C₁₃H₁₈O₅S: C, 54.52; H, 6.33; S, 11.19. Found: C, 54.78; H, 6.46; S, 10.98.

2,2-Diphenyl-4-tosyloxymethyl-1,3-dioxolane.

This compound was prepared from 2,2-diphenyl-4-hydroxymethyl-1,3-dioxolane (6) by the general method of Baer and Fischer (5). The product was crystallized from 2-propanol, m.p. 88-90°, yield, 63%.

Anal. Calcd. for C₂₃H₂₂O₅S: C, 67.30; H, 5.40; Found: C, 67.14; H, 5.52.

4-Azidomethyl-2,2-diphenyl-1,3-dioxolane.

A mixture of sodium azide (16.2 g., 0.25 mole), 2,2-diphenyl-4-tosyloxymethyl-1,3-dioxolane (79.8 g., 0.195 mole) and 150 ml. of dimethylsulfoxide was heated on the steam bath for 29 hours with occasional stirring. The solution was allowed to stand over-

night and then poured into 600 ml. of water. The aqueous mixture was extracted three times with ether, the combined ether extracts were washed with water, dried and concentrated *in vacuo* without heating, to an oil which weighed 52.6 g., 96%. The oil showed strong azide absorption bands in the ir (chloroform) at 2119 and 1267 cm⁻¹.

4-Azidomethyl-2,2-dimethyl-1,3-dioxolane.

This compound was prepared similarly to the diphenyl analog as an oil in 58% yield on a 1.42 mole scale.

4-Aminomethyl-2,2-diphenyl-1,3-dioxolane.

A solution of 4-azidomethyl-2,2-diphenyl-1,3-dioxolane (52.6 g., 0.187 mole) in 50 ml. of tetrahydrofuran was added with stirring at a rate causing reflux to a suspension of lithium aluminum hydride (3.55 g., 0.094 mole) in 250 ml. of tetrahydrofuran. A vigorous evolution of nitrogen gas occurred. The mixture was refluxed 1.5 hours, cooled and decomposed by addition of 4 ml. of water followed by 12 ml. of saturated potassium tartrate solution. After stirring for 0.5 hours, the mixture was filtered and the filter cake washed well with tetrahydrofuran. The filtrate and washing were concentrated to an oil *in vacuo*. Distillation yielded 39.2 g. (82.1%) of product, b.p. 151-155° (0.2 mm), n_D³⁰ 1.5762. The hydrochloride had m.p. 195-196° [lit. (7) m.p. 192-193°].

4-Aminomethyl-2,2-dimethyl-1,3-dioxolane.

This compound was prepared similarly to the diphenyl analog, b.p. 70-73° (17 mm), n_D^{29.5} 1.4350, 81.9 g., 64.4% yield. Lit. (2) b.p. 54-55° (8 mm), n_D²⁰ 1.4378.

REFERENCES

- (1) Swiss Patent No. 253,256 (*Chem. Abstr.*, 43, 8180).
- (2) J. C. Sowden and H. O. L. Fischer, *J. Am. Chem. Soc.*, 64, 1291 (1942).
- (3) F. F. Blicke and F. E. Anderson, *ibid.*, 74, 1733 (1952).
- (4) Melting points were taken in capillaries and are corrected.
- (5) E. Baer and H. O. L. Fischer, *J. Am. Chem. Soc.*, 70, 610 (1948).
- (6) J. S. Brimacombe, A. B. Foster and A. H. Haines, *J. Chem. Soc.*, 2582 (1960).
- (7) F. F. Blicke and E. L. Schumann, *J. Am. Chem. Soc.*, 74, 2613 (1952).

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