

Short Communication

Preparation of a Cyclic Ketene Acetal with Phase-Transfer Catalysis in a Water-Containing System

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Recently Diez-Barra *et al.*¹ and Bailey and Zhou² have described a new method for the synthesis of cyclic ketene acetals from cyclic acetals of bromoacetaldehyde. In both cases this was accomplished by elimination of the elements of hydrogen bromide using phase-transfer catalysis under more-or-less anhydrous conditions. The Spanish group¹ sonicated a mixture of the bromoacetal, a phase-transfer catalyst, and powdered potassium hydroxide (i.e., solvent-free conditions) at 75°C while Bailey and Zhou² used Aliquat® 336 and potassium *tert*-butoxide in tetrahydrofuran (THF) at low temperature. One of the examples given by the latter authors was the preparation of 3-methylene-1,5-dihydro-2,4-benzodioxepine **2**. This prompts me to report my finding that **2** may be prepared in a yield consistently better than 90% under standard phase-transfer catalysis conditions, *viz.* 50% aqueous NaOH and benzene with tetrabutylammonium ion as the catalyst.

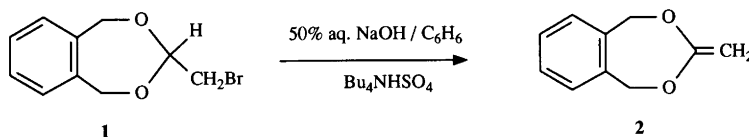
The ketene acetal **2** was first synthesized by Grewe and Struve³ and reported to be exceptionally stable. It is a versatile starting material for a variety of cyclopropanone derivatives obtainable via the addition of carbenoid entities over its electron-rich exocyclic double bond.^{3,4a,b} Owing to the benzylic character of the *o*-xylyl moiety of the molecule catalytic hydrogenolysis gives access to cyclopropanone hydrates and derivatives thereof.

Experimental

In a typical run 50% aq. NaOH (20 ml) was added to a vigorously stirred mixture of **1**³ (4.0 g, 16.5 mmol), TBAH (tetrabutylammonium hydrogensulfate, 5.8 g, 17.1 mmol)

and benzene (40 ml) in a 100 ml Erlenmeyer flask. The flask was stoppered and stirring continued at ambient temperature for an additional 75 min. The organic phase was then diluted with about 50 ml of diethyl ether and the resulting solution washed twice with cold water made slightly alkaline by dissolution of 1–2 pellets of potassium hydroxide. Work-up continued with filtration through a pad of anhydrous potassium carbonate followed by drying over potassium hydroxide pellets and vacuum evaporation (rotary evaporator, bath temperature ≤45°C) afforded 2.61 g (98% yield) of a colourless oil which crystallized spontaneously on cooling. The melting point was 42.5–44°C (lit.³ 44°C). NMR spectral data for **2**: ¹H (CDCl₃, Me₄Si): δ 3.71 (s, 2 H), 5.01 (s, 4 H) and ca. 6.93–7.28 (m, 4 H); ¹³C (CDCl₃, Me₄Si): δ 69.5, 71.9, 126.1, 127.4, 135.8 and 164.3.

Occasionally the product was accompanied by a slight amount of tributylamine (barely discernible signals in the ¹H NMR spectrum) formed via Hofmann elimination from some of the quaternary ammonium salt. No other phase-transfer catalysts besides TBAH have, as yet, been tried. Washing the ethereal solution quickly with cold 1% aqueous citric acid followed by an alkaline wash removes the tertiary amine but instead gives rise to some very weak ¹H NMR signals tentatively ascribed to the expected monoacetate of benzene-1,2-dimethanol. As judged from NMR data this substance is also one of the main products from the treatment of an ethereal solution of **2** with silica gel (Merck Kieselgel 60 for column chromatography). As might be expected from this **2** is destroyed (at least partially) on attempted TLC on silica gel or GC on packed columns.



Scheme 1.

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References

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3. Grewe, R. and Struve, A. *Chem. Ber.* 96 (1963) 2819.
4. (a) Dowd, P., Kaufman, C., Kaufman, P. and Paik, Y. H. *Tetrahedron Lett.* 26 (1985) 2279; (b) Dowd, P., Kaufman, C. and Paik, Y. H. *Tetrahedron Lett.* 26 (1985) 2283.

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