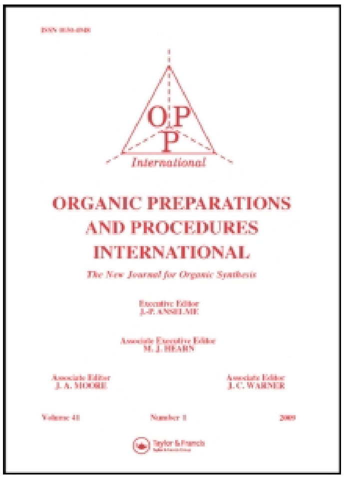

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NEW MIXED KETENE DIALKYL ACETALS

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NEW MIXED KETENE DIALKYL ACETALS

Submitted by (8/9/74)

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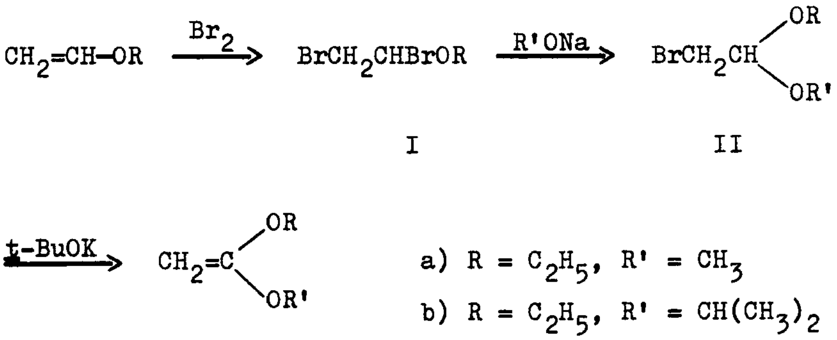
New "mixed" ketene acetals (III, where R and R' are different alkyl groups) have been prepared[1,2] by the dehydrobromination of the corresponding α-bromoacetals (II).[3]



$$CH_2{=}CH{-}OR \xrightarrow{Br_2} BrCH_2CHBrOR \xrightarrow{R'ONa} BrCH_2CH(OR)(OR') \xrightarrow{t\text{-}BuOK} CH_2{=}C(OR)(OR')$$

I II III

a) $R = C_2H_5$, $R' = CH_3$

b) $R = C_2H_5$, $R' = CH(CH_3)_2$

EXPERIMENTAL

Bromoacetaldehyde ethyl methyl acetal (IIa). - A solution of ethyl vinyl ether (564 g, 7.84 moles) in 2 l. of dry diethyl ether in a 5 l. 3-necked flask, was cooled to -30° in a Dry Ice-acetone bath. To this solution, 404 ml (7.84 moles) of bromine was added, with stirring, at such a rate that the temperature remained below -25°; this required $2\frac{1}{2}$ hrs. The addition of bromine was stopped when a faint permanent yellow colour became apparent. The colour was eliminated by back-titrating with ethyl vinyl ether.

To the resulting solution of ethyl 1,2-dibromoethyl ether maintained at -30°, was added, with stirring, a solution of one equivalent of sodium methoxide in 2 l. of methanol. The rate of addition was regulated to keep the temperature below -30°. When the addition was complete the reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was poured into 1 l. of 20% w/v aqueous potassium carbonate solution. The organic layer was separated, the aqueous layer was extracted once with 400 ml of diethyl ether and the combined organic layers were dried over anhydrous potassium carbonate. Substantially pure IIa was then obtained by distilling and discarding all material boiling below 80°. The pale yellow residue, liquid IIa, was formed in 84% yield.

NMR (CCl_4): 5.4τ (1H,t,-C$\underline{H}$) 6.35τ (2H,q of d,-O$C\underline{H_2}CH_3$) 6.6τ (3H,s,-O$C\underline{H_3}$) 6.65τ (2H,d,-$C\underline{H_2}Br$) 8.8τ (3H,t,-O$CH_2C\underline{H_3}$)

<u>Bromoacetaldehyde ethyl isopropyl acetal (IIb)</u> was prepared by the procedure described above with the substitution of a slurry of sodium isopropoxide in isopropanol for the sodium methoxide. The product was isolated by distilling the diethyl ether and isopropanol on a steam bath and then distilling the residual liquid at atmospheric pressure. The product was collected at 160-165° (39% yield).

Ketene ethyl methyl acetal (IIIa). - To dry potassium *t*-butoxide (0.577 mole) under a nitrogen atmosphere was added 400 ml of dry xylene. The mixture was stirred rapidly for 30 min. to break up the lumps of *t*-butoxide. Bromoacetaldehyde ethyl methyl acetal (105 g, 0.577 mole)[4] was added and the mixture was distilled at atmospheric pressure. At about 80°, the dehydrobromination reaction took place and the associated rapid boiling was controlled by removing the heat source momentarily.[5] A fraction consisting largely of *t*-butanol (58%) was collected at 105-115°/740 torr. Xylene also acts as a "chaser" solvent in the distillation.

The dehydrobromination of IIb to ketene ethyl isopropyl acetal was carried out by the McElvain and Kundinger[3] procedure. The product was collected at 74-79°/125 torr.

NMR spectra of new ketene acetals (CCl_4)

Ketene ethyl methyl acetal: 6.25τ (2H,q,$-O\underline{CH_2}CH_3$) 6.45τ (3H,s,$-O\underline{CH_3}$) 7.00τ (2H,s,$\underline{CH_2}=$) 8.75τ (3H,t,$-OCH_2\underline{CH_3}$)

Ketene ethyl isopropyl acetal: 5.5-6.0τ (1H,m,$-O\underline{CH}(CH_3)_2$) 6.25τ (2H,q,$-O\underline{CH_2}CH_3$) 6.95, 7.05τ (1H,1H,s,s,$\underline{CH_2}=$) 8.6-8.9τ (9H,m,$-OCH_2\underline{CH_3}$,$-OCH(\underline{CH_3})_2$)

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REFERENCES

1. D. J. Dunn and P. H. Plesch, Makromol. Chem., 175, 2821 (1974).
2. D. J. Dunn, Ph.D. Thesis, University of Keele, 1973.
3. S. M. McElvain and D. Kundinger, Org. Syn., Coll. Vol.III, 506 (1955).
4. As with other ketene acetals[3] it is advisable to wash all glassware with aqueous alkali prior to rinsing with water and drying. This treatment prevents the oligomerization of the ketene acetal caused by the acidic surface of the glass.
5. When this procedure was repeated on a larger scale (using *t*-butoxide from 200 g of potassium and 940 g of the bromoacetaldehyde acetal), the heat from the exothermic dehydrobromination reaction was not dissipated rapidly enough to avoid the loss of about one third of the contents of the flask during the subsequent violent boiling. When the boiling subsided, the distillation was continued normally to give 160 g of the ketene acetal.

4H-BENZPYRANO[3,4-d]OXAZOL-4-ONES AND 3-[N,N-BIS(CARBOXYMETHYL)AMINO]-4-HYDROXYCOUMARIN DERIVATIVES

Submitted by (8/12/74)
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Some derivatives of 3-amino-4,7-dihydroxy-8-methyl coumarin (AHC),[1-3] a structural component of the antibiotic *novobiocin* as well as AHC itself have been reported as bactericidal and fungicidal agents.[4] In an effort to enhance the