[Contribution from the Ohio State University Department of Chemistry]

THE USE OF ALKYL VINYL ETHERS IN OLEFIN SYNTHESES

D. C. ROWLANDS, K. W. GREENLEE, J. M. DERFER, and C. E. BOORD

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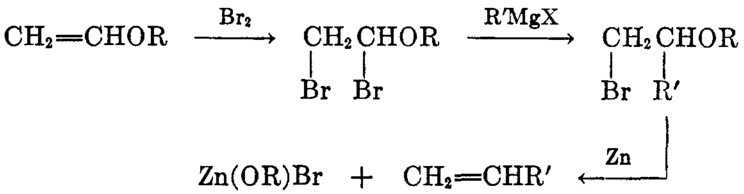
The β-bromoether synthesis of olefins, as developed by Boord and his coworkers, (2, 6–8) gives many types of olefins almost entirely free of isomers, except the geometric forms; however, the synthesis is lengthy and hence the over-all yields are not very high. By the original procedure, α,β-dibromoethers were obtained by brominating α-chloroethers which were prepared by treating aldehyde-alcohol mixtures with hydrogen chloride; reaction of the dibromides with Grignard reagents then gave the desired β-bromoethers. In the past few years simple alkyl vinyl ethers have become available commercially at low cost because of the discovery of Reppe (4) that they can be prepared from alcohols in the presence of alkaline catalysts; prior to this discovery the alkyl vinyl ethers were more difficult to prepare than were the α-chloroethers. The present work was undertaken to investigate the suitability of the commercial alkyl vinyl ethers as starting materials for the β-bromoether synthesis of type I olefins (6), with a view to shortening the synthesis and improving the over-all yields. The following equations illustrate the scheme of preparation:



$$CH_2{=}CHOR \xrightarrow{Br_2} \underset{Br}{CH_2}\,\underset{Br}{CHOR} \xrightarrow{R'MgX} \underset{Br}{CH_2}\,\underset{R'}{CHOR} \xrightarrow{Zn} Zn(OR)Br + CH_2{=}CHR'$$

The commercial alkyl vinyl ethers were studied cryoscopically, were found to be of acceptable purity, as received (see Table I), and were used without further purification.

The dibromides of the alkyl vinyl ethers were prepared at Dry Ice temperature in ether solution and were not isolated for reaction with the Grignard reagents, except in one case. In this instance the dibromide of methyl vinyl ether (b.p. 83–89°/43 mm.) was isolated by rapid distillation in 88% yield; decomposition was noted during distillation and the water-white distillate darkened rapidly on standing, with loss of HBr and formation of tar. Apparently the α-bromine in these dibromides is hydrolyzed by traces of moisture; the α,β-dibromoethers are powerful lachrymators. It is believed that the yields of unisolated dibromides were virtually quantitative.

The dibromide from methyl vinyl ether was condensed with four alkyl Grignard reagents and the resulting β-bromoethers were isolated (see Table II).

Dealkoxybromination of these β-bromoethers with zinc, followed by distillation at low (about 5-plate) efficiency, gave the expected individual olefins in yields of 53 to 84% of theory; the physical properties of these olefins agreed well with reliable literature values (Table IV), indicating that few, if any, by-products were formed along with the desired olefins.

In order to study further the suitability of the various alkyl vinyl ethers, the dibromides from each of six such ethers were prepared and were caused to react separately with a single Grignard reagent, allylmagnesium bromide (see Table III).

TABLE I

ALKYL VINYL ETHERS

ALKYL VINYL ETHER	F.P., °C. (COMMERCIAL PROD.)	ESTIMATED "100% PURE" F.P., °C.[a]	Δt/MOLE-% IMPURITY	PURITY[a]
Methyl[b]	−124.37	−122.8	0.45	96.5
Ethyl[b]	−115.78	−115.4	0.31	98.8
Isopropyl[b]	−127.00	−126.6	0.23	98.2
n-Butyl[b]	−92.16	−91.9	0.23	99.0
Isobutyl[b]	−112.48	−112.1	0.25	98.6
2-Ethylhexyl[c]	Glass	—	—	—

[a] As calculated by the general methods of Glasgow, Streiff, and Rossini, *J. Research Nat'l Bur. Standards*, **35**, 355 (1945).

[b] Obtained from General Aniline and Film Corporation.

[c] Obtained from Carbide and Carbon Chemicals Corporation.

TABLE II

β-BROMOETHERS FROM THE DIBROMIDE OF METHYL VINYL ETHER

R'MgX	PRODUCT	YIELD,[a] %	B.P., °C./MM	n_D^{20}
n-Propyl	1-Bromo-2-methoxypentane	55	88–89/56	1.4487
n-Butyl	1-Bromo-2-methoxyhexane	53	93–94/33	1.4514
n-Amyl	1-Bromo-2-methoxyheptane	62	107–108/28	1.4532
Isoamyl	1-Bromo-2-methoxy-5-methylhexane	69	98–99/23	1.4523

[a] Based on methyl vinyl ether.

Dealkoxybromination of these β-bromoethers gave 1,4-pentadiene in yields of 59 to 67% of theory. Each of the β-bromoethers displayed an induction period before any pentadiene was formed, but, in general, the larger the molecular weight of the alkoxy group, the slower was the reaction. The following sequence was indicated as the order of decreasing reactivity:

Methoxy > Ethoxy > Butoxy > Isobutoxy > 2-Ethylhexoxy.

It appears that the commercially available alkyl vinyl ethers (with the exception of isopropyl vinyl ether) are quite suitable as starting materials for the modified β-bromoether synthesis of type I olefins; their use shortens the synthesis and increases the over-all yields by 10 to 30%. In the usual case, dehydration of the appropriate primary alcohol will produce a type I olefin amenable to satis-

TABLE III

β-Bromoethers Containing the Allyl Residue

ALKYL VINYL ETHER	β-BROMOETHER	YIELD[a], %	B.P., °C.	n_D^{20}	d_4^{20}	ANALYSES					
						Found			Calc'd		
						C	H	Br	C	H	Br
Methyl	1-Bromo-2-methoxypentene-4	65	79.9–81.1 at 35 mm.	1.4665–1.4671	—	40.76 40.58	6.28 6.33	43.95 44.44	40.24	6.19	44.63
Ethyl	1-Bromo-2-ethoxypentene-4	62	81.8–84.0 at 25 mm.	1.4600–1.4602	—	43.33 43.38	6.77 6.79	41.29	43.54	6.74	41.38
Isopropyl	1-Bromo-2-isopropoxypentene-4	very low[b]	83.0–83.2 at 20 mm.	1.4549	—	46.35 46.08	7.32 7.34	38.68	46.38	7.30	38.56
n-Butyl	1-Bromo-2-butoxypentene-4	68	98.5–99.8 at 10 mm.	1.4593–1.4600	1.1435	49.09 49.35	7.70 7.95	32.72	48.88	7.75	36.15
Isobutyl	1-Bromo-2-isobutoxypentene-4	78	91.2–92.0 at 10 mm.	1.4561–1.4563	1.1357	49.62 49.75	7.79 8.18	36.68	48.88	7.75	36.15
2-Ethylhexyl	1-Bromo-2-(2-ethylhexoxy)pentene-4	80	117 at 1 mm.	1.4626–1.4826	1.0684	57.42 57.58	9.38 9.66	27.51	56.31	9.09	28.84

[a] Based on alkyl vinyl ether. [b] Probably because of bromine substitution of the tertiary α-hydrogen in the isopropyl vinyl ether, which seems, therefore, to be unsatisfactory as a starting material.

factory purification and in good yield. When the alcohol is unavailable or difficult to prepare, use of the present method may be indicated. Should *substituted* vinyl ethers become available, application of the modified bromoether synthesis to other olefin types might become practical.

EXPERIMENTAL

Freezing point determinations. All freezing points were measured with a platinum resistance thermometer in connection with a Mueller resistance bridge (Leeds and Northrup, Type G-2). This thermometer was calibrated at the National Bureau of Standards. The apparatus used was essentially that described by Mair, Glasgow, and Rossini (3).

TABLE IV

PHYSICAL PROPERTIES OF OLEFINS AND DIOLEFIN

COMPOUND	THIS WORK			LITERATURE (5)	
	Yield[a], %	B.p., °C. (uncorr.)	n_D^{20}	B.p., °C./760	n_D^{20}
1-Pentene	71	30.0–31.0	1.3718	29.97	1.3714
1-Hexene	53	62.2–62.8	1.3880	63.55	1.3876
1-Heptene	80	92.8–93.8	1.3998	93.3	1.3994
5-Methyl-1-hexene	84	85.4–85.6	1.3973	85.65	1.3970
1,4-Pentadiene	59–67	25.0–26.0	1.3888	26.05	1.388

[a] From β-bromoether.

Dibromides of alkyl vinyl ethers. The same procedure and apparatus were used in each case. In a three-necked flask, suitably equipped, and surrounded by a Dry Ice-acetone bath, were placed 300 to 400 ml. of sodium-dried ethyl ether and one mole of the alkyl vinyl ether. The theoretical amount of bromine was added, with stirring, at a rate of about 1 drop per second. The dibromides were not isolated from the ether solutions, which were used as such in the Grignard reactions.

β-Bromoethers. The Grignard reagents from *n*-propyl, *n*-butyl, *n*-amyl, and isoamyl chlorides (redistilled) were prepared in the manner described by Dreger (1). The condensations were carried out in the conventional way, using a 20% excess of the Grignard reagent. After removal of the ethyl ether solvent by simple distillation, the β-bromoethers were fractionated over solid sodium hydroxide at reduced pressure (column rated at about 10 theoretical plates at atmospheric pressure).

The allyl Grignard reagent was prepared by a special high dilution technique (publication pending), and its concentration was determined by titration. The condensations with the dibromides were carried out in the customary way, the temperature of the reaction mixtures being maintained at 0–10°.

C, H, and Br analyses were obtained for all of the β-bromoethers listed in Table III. The agreement between the theoretical and experimental values in the first three cases is good; the discrepancies in the cases of the three higher molecular weight bromoethers are explained by their tendency toward decomposition during distillation.

Olefins and diolefin. The dealkoxybromination reactions were carried out as previously described (2). The olefins were purified only by washing with water and fractionation over metallic sodium at less than 5-plate efficiency; yet their quality was obviously good.

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COLUMBUS 10, OHIO

LITERATURE CITED

(1) DREGER, *Org. Syntheses*, Coll. Vol. I, 2nd. ed., 306 (1941).
(2) DYKSTRA, LEWIS, AND BOORD, *J. Am. Chem. Soc.*, **52**, 3396 (1930).
(3) MAIR, GLASGOW, AND ROSSINI, *J. Research Natl. Bur. Standards*, **26**, 591 (1941).
(4) REPPE, U. S. Patent 1,959,927 (1934).
(5) ROSSINI, PITZER, TAYLOR, EBERT, KILPATRICK, BECKETT, WILLIAMS, AND WERNER, *Selected Values of Properties of Hydrocarbons*, National Bureau of Standards Circular C-461 (1947).
(6) SCHMITT AND BOORD, *J. Am. Chem. Soc.*, **54**, 751 (1932).
(7) SHOEMAKER AND BOORD, *J. Am. Chem. Soc.*, **53**, 1505 (1931).
(8) SODAY AND BOORD, *J. Am. Chem. Soc.*, **55**, 3293 (1933).