

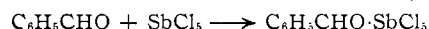
uring acid strength such as titration curves,<sup>15</sup> polarization measurements,<sup>16</sup> and bond energy calculations of benzaldehyde-metallic halide complexes.<sup>17</sup> The bond energies of Dilke and Eley were calcu-

(15) W. S. Peterson, C. J. Heimerzheim and G. B. L. Smith, *THIS JOURNAL*, **65**, 2403 (1943).

(16) F. Fairbrother, *J. Chem. Soc.*, 503 (1945).

(17) M. H. Dilke and D. D. Eley, *ibid.*, 2601 (1949).

lated from the measured heats of reactions; e.g.,



The comparison of the relative acid strengths from the benzazide decomposition rates (kinetic method) and the bond energy calculations (thermodynamic method), as shown in Table IV is striking.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TENNESSEE AGRICULTURAL AND INDUSTRIAL STATE UNIVERSITY]

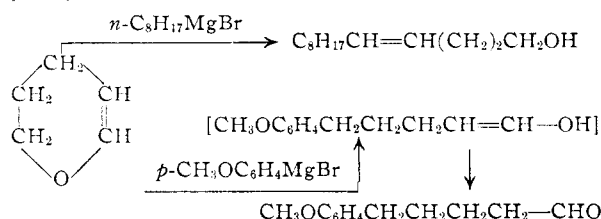
## Grignard Reagents and Unsaturated Ethers. III.<sup>1</sup> Reaction of Grignard Reagents with Cyclic Unsaturated Ethers<sup>2</sup>

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RECEIVED FEBRUARY 12, 1954

The reactivity of cyclic unsaturated ethers with Grignard reagents has been investigated. Results of this study indicate that alkyl and aryl Grignard reagents cleave 2,3-dihydropyran and 4-methyl-3,4-dihydro-2H-pyran at the ether linkage to form unsaturated alcohols and saturated aldehydes. *n*-Hexylmagnesium bromide reacts with 2-methyl- and 2,5-dimethylfuran to yield  $\beta,\gamma$ -unsaturated methyl ketones.

Previous papers<sup>1,3</sup> in this series have illustrated that both aryl and alkyl Grignard reagents cleave aryl substituted vinyl ethyl and allyl alkyl ethers with the formation of aryl and alkyl substituted olefins and alcohols. In the present paper, we have extended these studies to two  $\alpha,\beta$ -unsaturated cyclic ether systems, namely, the furan and dihydropyran. It was postulated that by structural comparison with the open chain vinyl analogs  $\alpha,\beta$ -unsaturated cyclic ethers should be susceptible to reaction with Grignard reagents. The results of the present investigation have fulfilled this prediction. For example, reaction of 2,3-dihydropyran with *n*-octylmagnesium bromide (25% excess) gave as reaction product 4-tridecen-1-ol (36%); while reaction of 2,3-dihydropyran with *p*-anisylmagnesium bromide (25% excess) yielded 5-(*p*-methoxyphenyl)-pentanal (30%).



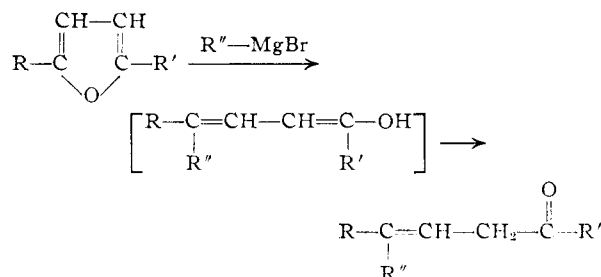
However, when 4-methyl-3,4-dihydro-2H-pyran is allowed to react with *n*-hexyl- and *p*-anisylmagnesium bromides (25% excess), 3-methyl-4-hendecen-1-ol (31%) and 3-methyl-5-(*p*-anisyl)-4-penten-1-ol (40%) are formed, respectively.

Our studies were extended to furans by an investigation of the reaction of 2-methyl- and 2,5-dimethylfuran with *n*-hexylmagnesium bromide which yielded 4-hendecen-2-one (36%) and 5-methyl-4-hendecen-2-one (30%), respectively

(1) The second paper in this series was published by C. M. Hill, L. Haynes, D. E. Simmons and M. E. Hill, *THIS JOURNAL*, **75**, 5408 (1953).

(2) This research was supported in part by the United States Air Force under Contract AF 16(600)-466 monitored by the Office of Scientific Research, H. G. Air Research and Development Command.

(3) C. M. Hill, R. A. Walker and M. E. Hill, *THIS JOURNAL*, **75**, 1663 (1951).



where R = H or CH<sub>3</sub>, R' = CH<sub>3</sub> and R'' = *n*-C<sub>6</sub>H<sub>13</sub>. Recent investigations of Fuson and Wallingford<sup>4</sup> have shown that mesitylmagnesium bromide cleaves 2-mesitylfuran to yield 1-mesityl-4-mesityl-1-hydroxy-1,3-butadiene.

Reaction products were identified through their benzoates or hydrazones and by characterization of their ozonization products. In addition, 4-tridecen-1-ol and 5-methyl-4-hendecen-2-one were converted to the corresponding saturated alcohols.

**Acknowledgment.**—The authors express thanks to George Canty, who gave valuable assistance in the development of this investigation.

### Experimental<sup>5</sup>

**Cyclic Unsaturated Ethers.**—The 2,3-dihydropyran used in this investigation was purchased from Matheson, Coleman and Bell, Inc., and 2-methyl- and 2,5-dimethylfuran from Eastman Kodak. The 4-methyl-3,4-dihydro-2H-pyran was synthesized according to the procedure reported by Parham and Holmquist.<sup>6</sup>

**Reaction of 2,3-Dihydropyran with *n*-Octylmagnesium Bromide.**—*n*-Octylmagnesium bromide (1 mole) was prepared under dry nitrogen in the usual manner, and treated with 69 g. (0.8 mole) of freshly distilled 2,3-dihydropyran in an equal volume of absolute ether added during 5 hours. The reaction mixture was refluxed 40 hours and then hydrolyzed with saturated ammonium chloride. The ether layer was separated and the aqueous layer extracted continuously with ether for 36 hours. The ether extracts were combined, dried and concentrated to give a dark residue which was distilled through a Podbielniak column. Fifty-

(4) R. C. Fuson and H. P. Wallingford, *ibid.*, **75**, 5950 (1953).

(5) All melting points are corrected.

(6) W. E. Parham and H. E. Holmquist, *THIS JOURNAL*, **73**, 913 (1951).

TABLE I  
 REACTION PRODUCTS FROM GRIGNARD REAGENTS AND CYCLIC ETHERS

Cyclic ether	Grignard reagent, R	Product	B.p.				Yield, %	Derivative, m.p., °C.
			°C.	Mm.	$d_{20}^4$	$n_D^{20}$		
2,3-Dihydropyran	$n\text{-C}_8\text{H}_{17}$	4-Tridecen-1-ol <sup>a</sup>	127–128	9	0.8710	1.4480	48	3,5-Dinitrobenzoate, <sup>b</sup> 50–51
	$p\text{-CH}_3\text{OC}_6\text{H}_4$	5- <i>p</i> -Anisylpentanal <sup>c</sup>	108–111	750	.9932	1.4610	30	2,4-Dinitrophenylhydrazone, <sup>d</sup> 107–107.2
4-Methyl-3,4-dihydro-2H-pyran	$n\text{-C}_8\text{H}_{17}$	3-Methyl-4-hendecen-1-ol <sup>a</sup>	92–95	10	.7939	1.4250	31	3,5-Dinitrobenzoate, <sup>f</sup> 58–59
	$p\text{-CH}_3\text{OC}_6\text{H}_4$	3-Methyl-5-( <i>p</i> -anisyl)-4-penten-1-ol <sup>g</sup>	89–92	13	1.4069	1.5550	40	3,5-Dinitrobenzoate, <sup>h</sup> 233–234
2-Methylfuran	$n\text{-C}_6\text{H}_{13}$	4-Hendecen-2-one <sup>i</sup>	62–63	649	0.7748	1.4018	36	2,4-Dinitrophenylhydrazone, <sup>j</sup> 95
2,5-Dimethylfuran	$n\text{-C}_6\text{H}_{13}$	5-Methyl-4-hendecen-2-one <sup>k</sup>	200–203	750	0.8050	1.4298	30	2,4-Dinitrophenylhydrazone, <sup>l</sup> 80–81

<sup>a</sup> Anal. Calcd. for  $\text{C}_{13}\text{H}_{26}\text{O}$ : C, 78.78; H, 13.13. Found: C, 78.56; H, 13.65. <sup>b</sup> Anal. Calcd. for  $\text{C}_{20}\text{H}_{30}\text{O}_6\text{N}_2$ : N, 7.12. Found: N, 7.43. <sup>c</sup> Anal. Calcd. for  $\text{C}_{12}\text{H}_{18}\text{O}_2$ : C, 75.00; H, 8.33. Found: C, 74.56; H, 8.76. <sup>d</sup> Anal. Calcd. for  $\text{C}_{18}\text{H}_{26}\text{O}_5\text{N}$ : N, 15.10. Found: N, 15.36. <sup>e</sup> Observed  $M_R$  59.23, (calcd.) 58.67. <sup>f</sup> Anal. Calcd. for  $\text{C}_{12}\text{H}_{24}\text{O}$ : C, 78.26; H, 13.05. Found: C, 78.56; H, 13.22. <sup>g</sup> Anal. Calcd. for  $\text{C}_{19}\text{H}_{28}\text{O}_6\text{N}_2$ : N, 7.41. Found: N, 7.69. <sup>h</sup> Anal. Calcd. for  $\text{C}_{13}\text{H}_{18}\text{O}_2$ : C, 75.73; H, 8.74. Found: C, 75.90; H, 9.01. <sup>i</sup> Anal. Calcd. for  $\text{C}_{20}\text{H}_{32}\text{O}_5\text{N}$ : N, 3.94. Found: N, 3.95. <sup>j</sup> This ketone gave a positive iodoform test.  $M_R$  (calcd.) 52.54, (found) 52.77. <sup>k</sup> Anal. Calcd. for  $\text{C}_{11}\text{H}_{20}\text{O}$ : C, 78.57; H, 11.90. Found: C, 78.18; H, 11.46. <sup>l</sup> Anal. Calcd. for  $\text{C}_{17}\text{H}_{24}\text{O}_4\text{N}_4$ : N, 16.10. Found: N, 16.34. <sup>m</sup> Observed  $M_R$  58.36, (calcd.) 57.16. <sup>n</sup> Anal. Calcd. for  $\text{C}_{12}\text{H}_{22}\text{O}$ : C, 79.12; H, 12.08. Found: C, 79.11; H, 12.13. This compound was converted to 5-methyl-2-hendecanol by catalytic hydrogenation; b.p. 205–208° (750 mm.). M.p. of 3,5-dinitrobenzoate was 75–76°. <sup>o</sup> Anal. Calcd. for  $\text{C}_{19}\text{H}_{28}\text{O}_6\text{N}_2$ : N, 7.37. Found: N, 7.47. <sup>p</sup> Anal. Calcd. for  $\text{C}_{13}\text{H}_{26}\text{O}_4\text{N}_4$ : N, 15.47. Found: N, 15.30.

 TABLE II  
 OZONIZATION OF REACTION PRODUCTS

Reaction product	Ozonization product	B.p.		2,4-Dinitrophenylhydrazone		
		°C.	Mm.	M.p., °C.	Nitrogen, % Calcd.	Found
4-Tridecen-1-ol	Pelargonic acid <sup>a</sup>	250–253	752			
3-Methyl-4-hendecen-1-ol	<i>n</i> -Heptaldehyde	103–104	600	107–108 <sup>b</sup>	19.03	18.70
3-Methyl-5-( <i>p</i> -anisyl)-4-penten-1-ol	Anisaldehyde	110–112	50	210–211	17.72	17.30
	4-Hydroxy-2-methylbutyraldehyde			143–144	19.85	19.86
4-Hendecen-2-one	<i>n</i> -Heptaldehyde	151–153	750	107–108 <sup>c</sup>		
5-Methyl-4-hendecen-2-one	2-Octanone <sup>d</sup>	158–160	700	87–88 <sup>e</sup>		

<sup>a</sup> Neutral equivalent (calcd.) for  $\text{C}_9\text{H}_{18}\text{O}_2$ , 158; (found) 155. Neutral equivalent was determined by non-aqueous titration, using benzene-methanol and sodium methoxide: J. S. Fritz and N. M. Lisicki, *Anal. Chem.*, **23**, 589 (1951). <sup>b</sup> Reported m.p. is 108° by S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1953, p. 207. <sup>c</sup> Mixed m.p. with 2,4-dinitrophenylhydrazone prepared from authentic *n*-heptaldehyde was 107–108°; footnote b. <sup>d</sup> Observed  $d_{20}^4$  0.805 and  $n_D^{20}$  1.4154;  $M_R$  (calcd.) 39.16, (found) 39.40; reported  $d_{20}^4$  0.818,  $n_D^{20}$  1.41613 and b.p. 173.5° (760 mm.) by "Handbook of Chemistry and Physics," Chemical Rubber Co., Cleveland, Ohio, 1952. <sup>e</sup> Mixed m.p. with 2,4-dinitrophenylhydrazone prepared from authentic sample of 2-octanone was not depressed.

seven and one-tenth grams (36%) of 4-tridecen-1-ol, b.p. 127–128° (9 mm.),  $d_{20}^4$  0.8710,  $n_D^{20}$  1.4480, was obtained.

The procedure followed in experiments with the other cyclic ethers and Grignard reagents was similar to that described for 2,3-dihydropyran and *n*-octylmagnesium bromide. In the reaction of 2,5-dimethylfuran with *n*-hexylmagnesium bromide di-*n*-butyl ether was used as solvent.

Physical constants and solid derivatives of the reaction products from cyclic unsaturated ethers and Grignard reagents are shown in Table I.

**Catalytic Hydrogenation of 4-Tridecen-1-ol and 5-Methyl-4-hendecen-2-one.**—A mixture of 5 g. of 4-tridecen-1-ol, 50 ml. of 95% ethanol and 5 g. of 5% palladium-on-charcoal was shaken with hydrogen at 106 atmospheres and 225° for 6 hours. After removal of the solvent, the residue was distilled, yielding 3.2 g. (63%) of 1-tridecanol, b.p. 201–204° (750 mm.).

To a 2.1-g. sample of 5-methyl-4-hendecen-2-one was added 40 ml. of 95% ethanol and 6 g. of Raney nickel cata-

lyst. The mixture was shaken for 4 hours with hydrogen at 150 atmospheres at 150°. Isolation of the reaction product gave 1 g. (47%) of 5-methyl-2-hendecanol, b.p. 205–208° (750 mm.),  $d_{20}^4$  0.800,  $n_D^{20}$  1.4260.

**Ozonization of Unsaturated Alcohols and Ketones.**—Four to seven-gram samples of 3-methyl-4-hendecen-1-ol, 3-methyl-5-(*p*-anisyl)-4-penten-1-ol, 4-hendecen-2-one, 5-methyl-4-hendecen-2-one and 4-tridecen-1-ol were dissolved in 50–125 ml. of petroleum ether or chloroform. Each solution was treated at 0° with a 5% ozone stream 12 to 24 hours. Ozonides of the first four compounds were decomposed by a mixture of water, zinc and traces of silver nitrate and hydroquinone; the ozonide of 4-tridecen-1-ol was treated with 6% hydrogen peroxide. Each ozonolysis mixture was extracted with ether. The ozonization products were isolated by distillation.

Physical constants and solid derivatives of the ozonization products are described in Table II.

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