[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TENNESSEE A. AND I. STATE UNIVERSITY]

Grignard Reagents and Unsaturated Ethers. II.[1] Reaction of Grignard Reagents with β,γ-Unsaturated Ethers[2]

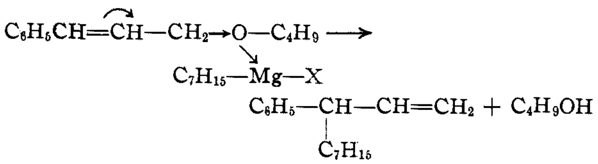
BY CARL M. HILL, LONNIE HAYNES, DORIS E. SIMMONS AND MARY E. HILL

RECEIVED JUNE 12, 1953

The reactivity of several β,γ-unsaturated ethers of the type R—CH=CH—CH$_2$—O—R′, where R is H and phenyl and R′ is alkyl and phenyl groups, with alkyl and aryl Grignard reagents has been investigated. Reaction products obtained were unsaturated hydrocarbons and alcohols and phenol. The composition and structure of these reaction products indicate that the Grignard reagents cleave the ethers by 1,2- and 1,4-addition mechanisms.

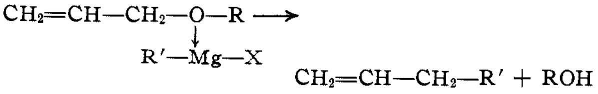
Reaction of aryl Grignard reagents with aryl substituted α,β-unsaturated ethyl ethers has been shown to yield 1,1-diarylethylene compounds and ethanol.[1] Luttringhaus, *et al.*,[3,4] have indicated that certain aryl allyl ethers and thioethers react with phenyl and alkyl Grignard reagents. Recently, Meltzer and King[5] during an investigation of the structure of methyldihydrothebainone studied the mode of addition of phenylmagnesium bromide to *o*-methoxyphenyl crotyl ether. This Laboratory is engaged in a broad investigation of the behavior of both aryl and alkyl Grignard reagents toward several types of unsaturated ethers. This paper describes the reaction of Grignard reagents with one γ-substituted allyl ether and several alkyl allyl ethers.

The results of the present investigation show that when *n*-heptylmagnesium bromide (50% excess) is allowed to react with *n*-butyl γ-phenylallyl ether, 3-phenyl-1-decene (52%) and *n*-butyl alcohol (76%) are formed. Formation of these reaction products can be explained by assuming that the Grignard reagent cleaves the ether by a 1,4-addition mechanism.



$$\begin{array}{l} C_6H_5CH{=}CH{-}CH_2{\rightarrow}O{-}C_4H_9 \longrightarrow \\ \qquad C_7H_{15}{-}Mg{-}X \\ \qquad\qquad C_6H_5{-}\underset{\displaystyle C_7H_{15}}{\underset{|}{CH}}{-}CH{=}CH_2 + C_4H_9OH \end{array}$$

However, the reaction of ethyl-, *n*-heptyl- and phenylmagnesium bromides with *n*-, iso, *s*- and *t*-butyl, *n*-octyl, *n*-cetyl and phenylallyl ethers gave the corresponding olefins (14–73%) and alcohols (15–83%) and phenol (60%) expected from the mechanism



$$\begin{array}{l} CH_2{=}CH{-}CH_2{-}O{-}R \longrightarrow \\ \qquad R'{-}Mg{-}X \\ \qquad\qquad CH_2{=}CH{-}CH_2{-}R' + ROH \end{array}$$

Experimental[6]

Synthesis of Allyl Ethers.—All ethers, except phenylallyl,[7] were synthesized by condensation of the appropriate allyl bromide and sodium alkoxide using xylene as solvent.[8]

Reaction of Allyl Ethers with Grignard Reagents.—All Grignard reagents employed in this investigation were prepared and stored under an atmosphere of dry nitrogen. Inasmuch as all experiments were carried out in essentially the same manner, experimental details are described for *n*-cetyl allyl ether and *n*-heptylmagnesium bromide only. Into a three-neck round-bottomed flask equipped with a mechanical stirrer, water cooled condenser set for reflux, and dropping funnel was placed 0.12 mole of *n*-heptylmagnesium bromide (determined by titration[9]). Twenty-three grams (0.082 mole) of *n*-cetyl allyl ether, b.p. 165 (7 mm.), was dissolved in an equal volume of anhydrous alcohol-free diethyl ether and placed into the dropping funnel. All exits to the apparatus were closed by means of calcium chloride tubes.

The entire apparatus was flushed with dry nitrogen, and the reaction mixture was kept under an atmosphere of nitrogen during the period of the experiment. The ethereal solution of allyl ether was added dropwise over a period of 4 hr. The reaction mixture was then refluxed for 20 hr., cooled and hydrolyzed with a saturated solution of ammonium chloride containing a few ml. of dilute hydrochloric acid. The aqueous layer was first shaken with several small volumes of diethyl ether and then continuously extracted for 24 hr. All ether extracts were combined and dried over anhydrous magnesium sulfate. After removal of the diethyl ether, the reaction products and unreacted allyl ether were separated by fractionation through a Todd precision fractionation column.

In experiments with ethylmagnesium bromide and unsaturated ethers, benzene was used as solvent; and the 1-pentene was collected in a Dry Ice–methanol-bath attached to the head of the condenser.

Physical constants and yields of reaction products are illustrated in Table I.

Identification of Alcohols and Phenol.—Identification of the alcohols and phenol was established by comparison of physical constants and preparation of the *p*-nitro- or 3,5-dinitrobenzoates. The benzoates were prepared according to the procedure of Shriner and Fuson.[10] Physical constants of the alcohols and phenol and their derivatives are shown in Table I.

Identification of Olefins.—The unsaturated hydrocarbons were identified by ozonization and comparison of physical constants. The ozonization procedure was as follows: Two- to five-gram samples of the olefins (1-decene and 3-phenyl-1-decene) were dissolved in 50–150 ml. of petroleum ether, and the solution treated with a stream of ozone until no more was absorbed. This required from 10–24 hr. The solvent was then removed by distillation, and the ozonide treated with an excess of 3% hydrogen peroxide for a period of 24 hr. with intermittent shaking. The hydrogen peroxide solution was made alkaline with 10% sodium hydroxide and extracted with small portions of diethyl ether. During addition of the sodium hydroxide solution, the exit of the apparatus was connected to a trap containing a solution of 3,5-dinitrophenylhydrazine which reacted with the liberated formaldehyde. The diethyl ether extracts of the alkaline solution were dried and the solvent removed. Distillation

---

[1] For the first paper in this series, see C. M. Hill, R. A. Walker and M. E. Hill, THIS JOURNAL, **73**, 1663 (1951).

[2] This research was supported in part by the United States Air Force under Contract AF 18(600)-466 monitored by the Office of Scientific Research, HG. Air Research and Development Command.

[3] A. Luttringhaus, G. v. Saaf and K. Hanschild, *Ber.*, **71**, 1673 (1938).

[4] A. Luttringhaus, G. v. Saaf, E. Sucker and G. Borth, *Ann.*, **557**, 46 (1947).

[5] R. I. Meltzer and J. A. King, THIS JOURNAL, **75**, 1355 (1953).

[6] All melting points are corrected.

[7] Purchased from Aldrich Chemical Co., Inc.

[8] E. A. Talley, A. S. Hunter and E. Yanovsky, THIS JOURNAL, **73**, 3528 (1951).

[9] H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, *ibid.*, **45**, 150 (1932).

[10] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 165.

TABLE I

PRODUCTS FROM REACTION OF GRIGNARD REAGENTS WITH ETHERS OF TYPE: R—CH=CH—CH$_2$—O—R′

Ether		Grignard reagent	Products								
			Olefin				Alcohol or phenol				
R	R′	R″		B.p., °C.	Mm.	Yield, %		B.p., °C.	Mm.	Yield, %	3,5-Dinitrobenzoate M.p., °C.
H	n-C_4H_9[a,8]	n-C_7H_{15}	1-Decene[b]	170–172	746	24	n-Butyl	115–117	746	68	65–66[c,10]
H	n-C_4H_9	C_6H_5	Allylbenzene[d]	160–163	748	40	n-Butyl	113–115	743	64	63–64
H	s-C_4H_9[e]	n-C_7H_{15}	1-Decene	172–174	743	14	s-Butyl	96–99	743	35	72–73[f]
H	i-C_4H_9[g]	n-C_7H_{15}	1-Decene	170–173	748	41	i-Butyl	106–109	756	83	84–85[h]
H	i-C_4H_9	C_2H_5	1-Pentene[i]	30–31	748	29	i-Butyl	101–104	748	44	86–86.5
H	t-C_4H_9[j]	n-C_7H_{15}	1-Decene	170–172	750	62	t-Butyl	95–96	750	58	141–142[k]
H	s-C_4H_9	C_2H_5	1-Pentene	30–32	753	50	s-Butyl	97–100	753	58	74–75
C_6H_5	n-C_4H_9	n-C_7H_{15}	3-Phenyl-1-decene[l]	191–192	748	52	n-Butyl	102–106	748	76	73–75
H	n-C_8H_{17}[m,4]	n-C_7H_{15}	1-Decene	172–175	756	33	n-Octyl	193–195	756	26	59–60[n]
H	n-C_8H_{17}	C_2H_5	1-Pentene	29–31	748	45	n-Octyl	195–198	756	71	59–60
H	n-$C_{16}H_{33}$[o]	n-C_7H_{15}	1-Decene	170–172	758	73	n-Cetyl	39–41 M.p. 47.5–48	12	20	p-Nitro 57–57.6[p]
H	n-$C_{16}H_{13}$	C_6H_5	Allylbenzene	72–75	7	43	n-Cetyl	92–95	7	15	p-Nitro 56–56.5
H	C_6H_5[q]	C_6H_5	Allylbenzene	152–155	743	30	Phenol[r]	174–176	743	60	Tribromophenol 94–95[s,10]

[a] Observed b.p. 107–109° (745 mm.), d^{20}_4 0.8161, n^{20}_D 1.4161; reported[8] b.p. 117.8–118° (763 mm.), d^{20}_4 0.7829 and n^{20}_D 1.4057.[4] [b] Reported b.p. 170–171° (760 mm.), d^{20} 0.7408 and n^{20}_D 1.42146 by "Handbook of Chemistry and Physics," Chemical Rubber Co., Cleveland, Ohio, 1952; observed d^{20}_4 0.7437 and n^{20}_D 1.4250; MR_D (calcd.) 47.91, (found) 48.18. [c] Ref. 10 (p. 226) m.p. 64°; mixed m.p. with an authentic sample of *n*-butyl 3,5-dinitrobenzoate was not lowered. [d] Reported b.p. 157° and n^{20}_D 1.7118, 1.5126, 1.5143 by G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publ. Corp., New York, N. Y., 1946; observed d^{20}_4 0.9237, n^{20}_D 1.5150; MR_D (calcd.) 39.69, (found) 38.52. [e] Observed b.p. 92–93° (748 mm.), d^{20}_4 0.7800, n^{20}_D 1.4010; MR_D (calcd.) 35.70, (found) 35.43; reported b.p. 107.1–107.4° (762 mm.), d^{20}_4 0.7792 and n^{20}_D 1.4023: footnote 8. [f] Literature m.p. 75°: footnote 10; mixed m.p. with an authentic specimen of *s*-butyl 3,5-dinitrobenzoate was not lowered. [g] Observed b.p. 102–104° (748 mm.), d^{20}_4 0.7872, n^{20}_D 1.4089; MR_D (calcd.) 35.70, (found) 35.80; reported b.p. 106.6–107° (749 mm.), d^{20}_4 0.7735 and n^{20}_D 1.4008: footnote 8. [h] Literature m.p. 86°: footnote 10. [i] Reported b.p. 30.5–31°, d^{21} 0.641, n^{21}_D 1.3714 by A. Kirrmann, *Bull. soc. chim.*, **39**, 988 (1926); observed d^{20}_4 0.7028 and n^{20}_D 1.3720. [j] Observed b.p. 100–102° (756 mm.), d^{20}_4 0.7889, n^{20}_D 1.3905; MR_D (calcd.) 35.70, (found) 34.30; reported b.p. 99.2–100° (760 mm.), d^{20}_4 0.7770, n^{20}_D 1.4011: footnote 8. [k] Literature m.p. 142°: footnote 10. [l] B.p. 190–192° (748 mm.), d^{20}_4 0.9849, n^{20}_D 1.5165; MR_D (calcd.) 66.30, (found) 66.09. [m] Observed b.p. 85–88° (12 mm.); reported[4] b.p. 87–88° (12 mm.). [n] Literature m.p. 61°: footnote 10; mixed m.p. of sample with authentic specimen of *n*-octyl 3,5-dinitrobenzoate was 59–60°. [o] Observed b.p. 186–189° (11 mm.), m.p. 25°; reported b.p. 165–176° (7 mm.), m.p. 25° by C. G. Davies, I. M. Heilbron and W. M. Owens, *J. Chem. Soc.*, 2542 (1930). [p] Reported m.p. 58.4° by M. D. Armstrong and J. E. Copenhaver, THIS JOURNAL, **65**, 2253 (1943). [q] Observed b.p. 195–199° (756 mm.); reported b.p. 192° and 85° (19 mm.): footnote *b*. [r] Literature m.p. 42°: footnote 10, p. 271; observed m.p. 42°. [s] Literature m.p. 95°: footnote *r*; mixed m.p. of sample with authentic specimen of tribromophenol was 94–95°.

TABLE II

OZONIZATION PRODUCTS OF OLEFINS

Olefin	Products								3,5-Dinitrophenylhydrazone
	Acid	B.p., °C.	Mm.	Neut. equiv. Calcd.	Neut. equiv. Found	Aldehyde	B.p., °C.	Mm.	M.p., °C.
1-Decene	Pelargonic[a]	100–101	5	158	154	Formaldehyde			165–166[b,10]
Allylbenzene						Phenylacetaldehyde	186	752	123–124[c]
						Formaldehyde			169–170
3-Phenyl-1-decene	n-Heptylphenylacetic	190–192	748	234	230	Formaldehyde			168–169

[a] Acid amide, m.p. 85–86.6°; reported m.p. 99° by S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1947, p. 186. *Anal.* Calcd. for $C_9H_{19}ON$: N, 8.92. Found: N, 9.14. [b] Reported[10] (p. 229) m.p. 166°. [c] Literature m.p. 121°: footnote 10; mixed m.p. of sample with authentic specimen of hydrazone of phenylacetaldehyde was 120–121°.

of the residue separated the aldehydes which were identified by preparation of the 3,5-dinitrophenylhydrazones. The alkaline solution was evaporated to dryness and the residue made acidic with dilute hydrochloric acid. The acidic solution was extracted with small portions of diethyl ether, and the combined extracts dried. Removal of the ether by distillation and distillation of the residue yielded the organic acid component. The organic acids were identified by comparison of the theoretical and observed neutral equivalents.

The ozonide formed from allylbenzene was warmed for 2 hr. with a mixture of zinc dust, water and a trace of silver nitrate. The formaldehyde which formed was converted to the 3,5-dinitrophenylhydrazone. The ozonolysis mixture was extracted with several small portions of diethyl ether and the combined extracts dried. After removal of the solvent, phenylacetaldehyde was isolated from the residue by distillation.

The 1-pentene isolated from several of the experiments was identified by comparison of reported and observed physical constants (Table I) and by conversion to 1,2-dibromopentane, b.p. 182–184° (753 mm.), d^{20} 1.729 and n^{21}_D 1.5085; reported[11] b.p. 184°, d^{18} 1.668 and n^{21}_D 1.5088.

Identification data of the ozonization products are shown in Table II.

NASHVILLE 8, TENNESSEE

---

[11] A. Kirrmann, *Bull. soc. chim.*, **39**, 988 (1926).