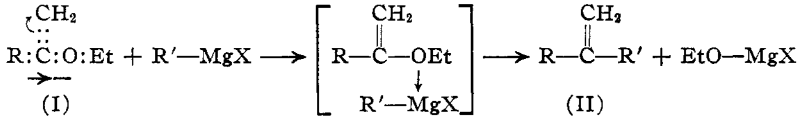
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TENNESSEE AGRICULTURAL AND INDUSTRIAL STATE COLLEGE]

The Reaction of Grignard Reagents with α,β-Unsaturated Ethers

BY CARL M. HILL, ROBERT A. WALKER AND MARY E. HILL

Theoretical considerations of the electron displacement tendencies in α,β-unsaturated ethers indicate a possibility of reaction with Grignard reagents, as indicated in I. The formation of a Grignard complex with the ether oxygen would render the electron deficiency on the alpha carbon more acute, thus favoring an alpha-gamma migration of the aryl group of the Grignard with its electron pair as shown in the scheme



Woods and Tucker[1,2] have reported that phenylmagnesium bromide reacts with the ethyl enol ethers of dimedone and dihydroresorcinol to yield 5,5-dimethyl-3-phenyl-Δ²-cyclohexenone and 3-phenyl-Δ²-cyclohexenone, respectively.

Ethers of the type of α-ethoxystyrene together with aryl Grignard reagents were selected as reactants. Results of this investigation have clearly shown that the reaction predicted by the above mechanism does occur. In addition to the anticipated product (II), a second product (III), R–R¹, was isolated from the reaction mixture.

When 1-phenyl-1-ethoxyethylene was allowed to react with phenylmagnesium bromide, the principal products isolated were biphenyl (21%), unreacted α,β-unsaturated ether (50%), and 1,1-diphenylethylene (88%). Similar results were observed from the reaction of 1-phenyl-1-ethoxy-1-butene, 1-phenyl-1-ethoxy-1-heptene and 2-methyl-1-phenyl-1-ethoxypropene with phenylmagnesium bromide. The ethylenic derivatives were those predicted by the above mechanism and designated as (II). Although coupling of Grignard reagent with phenyl bromide would be the obvious source of biphenyl, treatment of 1-phenyl-1-ethoxyethylene with *p*-anisylmagnesium bromide gave *p*-methoxybiphenyl (50%), along with 1-*p*-anisyl-1-phenylethylene (22%). This must mean that the phenyl group of the unsaturated ether and the *p*-anisyl group of the Grignard interacted. The amount of biphenyl obtained from the Grignard reagent was small as compared to the quantity isolated after the same number of moles of Grignard reacted with the unsaturated ether. Furthermore, when 1-*p*-tolyl-1-ethoxyethylene reacted with *p*-anisylmagnesium bromide, only unchanged α,β-unsaturated ether (6%) and 1-*p*-anisyl-1-*p*-tolylethylene (63%) were isolated.

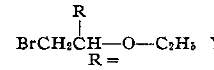
Experimental

Synthesis of α,β-Unsaturated Ethers.—The α,β-unsaturated ethers employed in this investigation were synthesized by the procedure reported by Lauer and Spielman.[3] The intermediate bromo ethers are new compounds. Their properties are given in Table I.

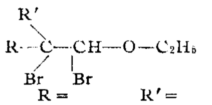
The unsaturated ethers used in this study have not been previously described in the literature. Table II shows the properties and analytical data for these ethers.

TABLE I

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR BROMO ETHERS


$BrCH_2CH(R)—O—C_2H_5$

R =		Yield, %	B.p., °C.	Mm.	Formula	Br,[a] % Calcd.	Br,[a] % Found	d^{20}_4	n^{20}_D	MRD Calcd.	MRD Found
p-$CH_3C_6H_4$		60	125–127	10	$C_{11}H_{15}OBr$	32.88	33.12	1.2490	1.5298	58.81	60.08
m-$CH_3C_6H_4$		63	131–132	15	$C_{11}H_{15}OBr$	32.88	32.56	1.2561	1.5332	58.81	60.65

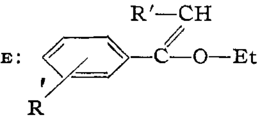

$RR'CBr—CHBr—O—C_2H_5$

R =	R′ =	Yield, %	B.p., °C.	Mm.	Formula	Br,[a] % Calcd.	Br,[a] % Found	d^{20}_4	n^{20}_D	MRD Calcd.	MRD Found
C_2H_5	H	68	79–81	12	$C_6H_{12}OBr_2$	61.47	61.47	1.5429	1.4700	47.06	47.02
CH_3	CH_3	67	73–75	8	$C_6H_{12}OBr_2$	61.47	61.52	1.5480	1.4730	47.08	47.53
n-C_5H_{11}	H	59	114–116	18	$C_9H_{18}OBr_2$	52.91	52.73	1.4060	1.4790	60.94	60.93

[a] Analyzed by modified Stepanow method: THIS JOURNAL, **31**, 49 (1939).

TABLE II

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR α,β-UNSATURATED ETHERS OF TYPE:



R =	R′ =	Yield, %	B.p., °C.	Mm.	d^{20}_4	n^{20}_D	MRD Calcd.	MRD Found	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
p-CH_3	H	62	115–117	19	0.9643	1.5250	50.57	51.45	81.43	81.08	8.64	8.37
m-CH_3	H	65	102–103	10	.9672	1.5269	50.57	51.00	81.43	80.97	8.64	8.78
H	C_2H_5	70	104–105	11	.9881	1.5255	55.19	54.65	81.79	81.17	9.09	9.13
H	*n*-C_5H_{11}	96	115–116	12	.9832	1.5242	69.06	68.01	82.30	82.86	9.80	9.75

---

(1) G. F. Woods, THIS JOURNAL, **69**, 2549 (1947).

(2) G. F. Woods and I. W. Tucker, *ibid.*, **70**, 2174 (1948).

(3) W. M. Lauer and M. A. Spielman, THIS JOURNAL, **53**, 1533 (1931).

Reaction of α,β-Unsaturated Ethers with Grignard Reagents.—The same procedure was followed in studying the reactivity of all unsaturated ethers with the Grignard reagents. This procedure is described in detail for 1-phenyl-1-ethoxyethylene and phenylmagnesium bromide: Into a three-necked flask equipped with a mechanical stirrer, water-cooled condenser and dropping funnel was placed 0.48 mole of phenylmagnesium bromide (determined by titration).[4] The head of the condenser was connected to a gas washing bottle containing an absorbent for volatile olefins. Thirty grams (0.20 mole) of 1-phenyl-1-ethoxyethylene dissolved in twice its volume of purified diethyl ether was added dropwise over a period of two hours. The reaction mixture was then refluxed for forty-eight hours, cooled, and hydrolyzed with dilute hydrochloric acid. The ether layer was combined with extracts of the aqueous layer and dried. The diethyl ether and ethanol were separated by distillation through an efficient fractionation column. The colored residue was then distilled under diminished pressure from a modified Claisen flask. Products from each experiment are described in Table III.

TABLE III

REACTION OF UNSATURATED ETHERS WITH PHENYLMAGNESIUM BROMIDE[a]

Ether $CHR=C(C_6H_5)OEt$ R	Ethylenic compound[b] $CHR=C(C_6H_5)_2$ R	B.p. °C.	Mm.	Yield, %	Yield of biphenyl,[c,6] %	Yield of ethanol,[d,5] %
H	H[e,5]	115–117	7	88	21	64
C_2H_5	C_2H_5[f]	129–131	5	60	18	51
C_5H_{11}	C_5H_{11}[g,5]	153–155	1	83	22	..
CH_3[h]	CH_3[i]	186–188	2	52	17	59

REACTION OF UNSATURATED ETHERS WITH *p*-ANISYLMAGNESIUM BROMIDE[a]

	—$CHR=C(C_6H_5)(C_6H_4OCH_3)$—				Yield of 4-methoxybiphenyl[j]	
H	H[k,5]	115–117	6	22	50	80
H[l]	H[m]	145–146	2[n]	63	..	94

[a] Number moles of Grignard reagent used in each experiment was twice that of unsaturated ether. [b] Yields of products are based on unsaturated ether not recovered. Grams of ethers (in order shown in Table III) recovered were as follows: 15, 8, 3.1, 8.8, 14 and 1. [c] Identified by mixed m.p., 68°; reported[5] m.p. 70°. All observed melting points are corrected. [d] Converted to 3,5-dinitrobenzoate, m.p. 91–92°; reported[5] m.p. 93°. [e] Ozonization gave benzophenone, m.p. 45–46°, mixed m.p. 46–47°, reported[5] m.p. 48°; oxime m.p. 138–139°, reported[5] m.p. 141°. [f] Density$^{20}_4$ 0.9994, n^{20}D 1.5800, *MR*D 68.90 (calcd.), 69.37 (found). Identified by ozonization to benzophenone and propiophenone, m.p. 19–20°; 2,4-dinitrophenylhydrazone of propiophenone melted at 186.5–187.5°; reported m.p. for propiophenone and its hydrazone are 18° and 191°, respectively: S. M. McElvain, "Characterization of Organic Compounds," The Macmillan Company, New York, N. Y., 1945, p. 241. [g] Density$^{20}_4$ 0.9583, n^{20}D 1.5400, *MR*D 82.27 (calcd.), 81.99 (found). Ozonization gave benzophenone and *n*-hexanal, b.p. 90–91° (30 mm.); *n*-hexanal semicarbazone m.p. 105–106°; reported[5] m.p. 106°. [h] In this case 2,2-dimethyl-1-phenyl-1-ethoxyethylene was used. [i] This product was 2,2-dimethyl-1,1-diphenylethylene; d^{20}_4 0.9973, n^{20}D 1.5700, *MR*D 68.99 (calcd.), 68.53 (found). Ozonization gave some as *e*, 5. [j] M.p. 87°; mixed m.p. with authentic specimen was not depressed. [k] Identified by ozonization to *p*-methoxybenzophenone, m.p. 60°, mixed m.p. 60–61°, reported[5] m.p. 62°. [l] In this case 1-*p*-tolyl-1-ethoxyethylene was used. [m] This product was 1-*p*-tolyl-1-*p*-anisylethylene. Ozonization gave *p*-tolyl *p*-anisyl ketone, m.p. 87–88°, reported m.p. 89° by Oryekhopp and Brouty, *Bull. Soc. Chim.*, [4] **47**, 621 (1930). [n] M.p. 72–73°.

All experiments were performed under an atmosphere of nitrogen.

The solvent ether (maximum ethanol, 0.01%) employed in this investigation was distilled three times from sodium through an efficient column, and finally stored over sodium.

Identification of 1,1-Diarylethylenic Compounds.—The identity of all ethylenic derivatives was established by ozonization in the manner described for 1,1-diphenylethylene: Into a solution of 4 g. of 1,1-diphenylethylene dissolved in 50 ml. of petroleum ether was passed a stream of ozone until no more was taken up. After removal of the solvent, the ozonide was hydrolyzed with a hot solution of 200 ml. of water, 5 g. of zinc dust, 0.5 g. of silver nitrate and a trace of hydroquinone. The mixture was then extracted with diethyl ether. Recrystallization of the residue from the ether extracts gave 0.2 g. (54%) of benzophenone, m.p. 45–46°; mixed m.p. with an authentic specimen, 46–47°; reported[5] m.p. 48°. The aqueous layer from hydrolysis of the ozonide gave a positive test with Schiff reagent. For description of ozonization products and their derivatives see footnotes to Table III.

Biphenyl from Coupling of Grignard Reagent.—Samples of phenylmagnesium bromide of approximately the same number of moles as used in this study were carefully prepared from purified bromobenzene and dry magnesium turnings. The amount of biphenyl obtained was as follows: 0.49 mole phenylmagnesium bromide yielded 0.25 g.; 0.29 mole gave 0.15 g.; and 0.12 mole yielded 0.09 g.

NASHVILLE, TENN. RECEIVED JUNE 1, 1950

---

[4] H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, THIS JOURNAL, **45**, 150 (1923).

[5] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1948, pp. 226, 229, 259 and 264.