in 50 ml. of anhydrous ether. The mixture was stirred for 3 hr. and worked up in the usual manner. See Table II.

2,3,4,4-Tetramethyl-5-methylene-2-oxazolinium Chloride (III).—Dry hydrogen chloride was bubbled into a solution of N-methyl-N-acetyl-3-methyl-1-butyne-3-amine in ether. The solid which formed was filtered and recrystallized from a mixture of dry ethyl acetate and dry isopropyl alcohol, m.p. 191–193°.

Anal. Calcd. for $C_8H_{14}ClNO$: C, 54.70; H, 8.03. Found: C, 54.76; H, 8.10.

3,4-Diethyl-2,4-dimethyl-5-methylene-2-oxazolinium Bromide.—This compound had m.p. 196–198°.

Anal. Calcd. for $C_{10}H_{18}BrNO$: C, 48.39; H, 7.31. Found: C, 48.33; H, 7.29.

Due to the rapid reaction with water these compounds were difficult to purify; hence only a few were obtained in an analytically pure state.

Preparation of the Enol Esters (IV).—The amide hydrochlorides were suspended in acetone, and a small amount of water was added until the salt went into solution. The mixture was concentrated at reduced pressure, and the residue was recrystallized from a mixture of acetone and ethyl acetate. See Table III.

Preparation of the Keto Amides (V).—The oxazolinium salt was dissolved in water, and the solution was made basic with sodium hydroxide. The mixture was extracted with ether, and the ether solution was dried and concentrated. The residue was recrystallized from methylcyclohexane or a mixture of ether–petroleum ether or was distilled at reduced pressure. See Table IV.

N-Formyl-N-methyl-1,1-dimethylpropargylamine.—To 29.1 g. (0.3 mole) of the amine there was added slowly, with stirring, a mixture of 25 g. (0.6 mole) of formic acid and 51 g. (0.5 mole) of acetic anhydride. The temperature of the solution was kept below 65° by cooling with ice. After all of the anhydride solution had been added, the reaction mixture was poured onto ice, and the resulting solution was made basic with sodium hydroxide. The mixture was extracted with ether and the ether solution was dried over magnesium sulfate and concentrated. The residue was distilled at reduced pressure. See Table II.

N-Ethyl-3-acetamido-3-methyl-2-pentanone Hydrochloride.—To a solution of N-ethyl-3-acetamido-3-methyl-2-pentanone in ether dry hydrogen chloride was added. The solid was filtered and recrystallized from methylethyl ketone, m.p. 93–95°.

Anal. Calcd. for $C_{10}H_{20}ClNO$: Cl, 15.99. Found: Cl, 15.89.

N-Isopropyl-3-acetamido-3-methyl-2-pentanone hydrochloride was prepared in the same manner, m.p. 170–172°.

Anal. Calcd. for $C_{11}H_{22}ClNO_2$: Cl, 15.04. Found: Cl, 14.69.

3-Methylamino-3-methyl-2-butanone.—A solution of 20 g. of N-acetyl-N-1,1-trimethylpropargylamine, 100 ml. of water, and 25 ml. of concentrated hydrochloric acid was refluxed for 3 hr. The solution was cooled, made basic with a 50% solution of sodium hydroxide, and saturated with potassium carbonate. The layers were separated and the water layer extracted twice with 50-ml. portions of ether. The organic layers were combined, dried over magnesium sulfate, and distilled. The yield was 14.6 g. (89%), b.p. 84–85° (82 mm.).

Anal. Calcd. for $C_6H_{13}NO$: C, 62.57; H, 11.38. Found: C, 62.42; H, 11.26.

Acknowledgment.—The microanalyses were performed by Messrs. William Brown, Howard Hunter, George Maciak, and Alfred Brown. Many of the starting materials were prepared by Dr. Dwight Morrison and Mr. Lawrence White. The infrared spectra were obtained by Mrs. Doris Stephens and Miss Martha Hoffmann. The authors wish to thank especially Messrs. Paul Landis and Donald Woolf, Jr., for their invaluable services in interpreting and compiling the infrared and n.m.r. data. The authors also express their sincere appreciation to Dr. George Hennion for his many helpful suggestions and much appreciated encouragement.

Solvent Effects on the Claisen Rearrangement of β-Methylallyl Phenyl Ether

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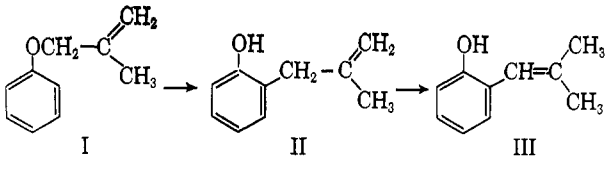
Received March 11, 1963

The need for highly purified samples of variously substituted *o*-allyl- and *o*-propenylphenols, in connection with a study of intramolecular hydrogen bonding, has led to the employment of gas–liquid chromatography both for the isolation as well as for the verification of homogeneity of various synthetic samples. A previously studied compound,[1] *o*-(β-methylallyl)phenol (II), was found, by analysis upon an ethylene glycol succinate chromatographic column, to contain a sizeable per cent of a faster moving component; this was readily identified as the isomeric *o*-isobutenylphenol (III).



I II III

TABLE I

PRODUCT DISTRIBUTION IN THE CLAISEN REARRANGEMENT OF β-METHYLALLYL PHENYL ETHER (I)

No.	Solvent	Solvent b.p., °C.	Reaction temp. °C.	At 5% of unchanged starting material: Elapsed time, Hr.	% II	% III	% IV
1	None	...	205–216	3.3	53	12	26
2	Nitrobenzene	211	200–206	4.2	73	11	10
3	2,6-Xylenol	212	198–199	3.5	6	10	73
4	2,6-Xylidine	217	212–215	3.7	8	44	32
5	N,N-Dimethyl-*m*-toluidine	211	208–216	3.5	81	4	1
6	Tributylamine	214	205–215	7.8	85	3	2
7	*p*-Tolunitrile	217	208–218	3.0	80	9	6
8	Dodecane	215	203–210	5.5	76	9	10

TABLE II

EFFECTS OF VARIOUS TERTIARY AROMATIC AMINES AS SOLVENTS IN THE CLAISEN REARRANGEMENT OF β-METHYLALLYL PHENYL ETHER

Solvent	Solvent b.p., °C.	Reaction temp., °C.	At 5% of unchanged starting material: Elapsed time, hr.	% II	% III	% IV
N,N-Dimethyl-*o*-toluidine	184	188–200	10	81	3	1
N,N-Dimethylaniline	193	199–205	4.8	90	2	1
N,N-Dimethyl-*m*-toluidine	212	208–216	3.5	81	4	1
N,N-Diethylaniline	216	207–218	2.8	86	4	2
N,N-Diethyl-*p*-toluidine	229	214–225	1.9	87	3	2

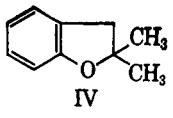
(1) A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **81**, 4524 (1959).

TABLE III

	o-(β-Methylallyl)-phenol (II)	o-Isobutenyl-phenol (III)	2,2-Dimethyl-2,3-dihydrobenzo-furan (IV)
G.l.c. retention time[a]	13.0 min.	9.4 min.	2.8 min.
M.p.—N-phenyl carbamate	M.p. 73.0–73.5° (from cyclo-hexane)	M.p. 97.0–97.5° (from cyclo-hexane)	...
Principal infrared bands, cm.$^{-1}$ (carbon disulfide)	754 (s)	750 (s)	749 (s)
	890 (s)	826 (mw)	781 (w)
	902 (s)	1031 (m)	886 (s)
	1091 (m)	1170 (m)	1018 (w)
	1174 (m)	1220 (s)	1087 (w)
	1216 (s)	1338 (m)	1140 (m)
	1260 (m)		1262 (s)
Proton assignments n.m.r. (solvent, carbon tetrachloride; internal standard, tetramethylsilane) in p.p.m.	CH_3 1.69	CH_3 1.67	CH_3 1.38
	$ArCH_2$ 3.28	1.93	CH_2 2.88
	$=CH_2$ 4.79	OH 4.81	ArH 6.43–7.18
	OH 5.20	CH 6.04	
	ArH 6.50–7.15	ArH 6.62–7.16	

[a] Partitioning fluid, 15% ethylene glycol succinate, 5-ft. column, 15-p.s.i. helium, flow 150 ml./min., temp., 155°.

Reported synthetic procedures employ either diethylaniline[2] as a solvent, or no solvent whatsoever.[3] The yield was higher when diethylaniline was employed. Repetition of the procedure without solvent yielded a mixture of products as shown in the first entry of Table I. After removal of a neutral component, identified as 2,2-dimethyl-2,3-dihydrobenzofuran (IV) and distillation of the base-soluble phenolic fraction,



IV

an "o-(β-methylallyl)phenol" was obtained which was invariably contaminated with perhaps 20% of the conjugated isomer III.

A variety of solvents was investigated in the Claisen rearrangement of I to establish the conditions which would enhance the yield of o-(β-methylallyl)phenol. The solvents were chosen with boiling points lying near the temperature (205–216°) of the refluxing reaction mixture when no solvent was employed. At the time when only 5% unreacted ether remained, the product distribution was determined. The results are recorded in Table I.

Neutral solvents afford the expected allylic compound (II) as the principal product, contaminated with both the isobutenyl and cyclic isomers, III and IV. An acidic solvent, 2,6-xylenol [but surprisingly, not o-(β-methylallyl)phenol] led to the nearly exclusive formation of the dihydrobenzofuran (IV). o-(β-Methylallyl)phenol was an intermediate in the formation of IV as shown by its presence to the extent of some 6% within the first few minutes of the reaction, this level being consistently maintained until the last of the starting ether had been consumed. This is supported by the complete conversion of pure II to IV in less than an hour of reflux employing 2,6-xylenol as solvent.

(2) O. Schales, *Ber.*, **70**, 116 (1937).

(3) Q. R. Bartz, R. F. Miller, and R. Adams, *J. Am. Chem. Soc.*, **57**, 371 (1935); C. D. Hurd and W. A. Hoffman, *J. Org. Chem.*, **5**, 212 (1940).

Basic solvents can successfully preclude the previous side reactions. Employing 2,6-xylidine, it was found that, at the end of the first half-hour of reflux, the sole product was the expected phenol, II. At the conclusion of the reaction, however, III and IV were observed as principal products. This catalytic effect of xylidine was verified by the complete conversion of pure o-(β-methylallyl)phenol in four hours reflux to a 53:47 mixture of the isomers III and IV.

Accepting N,N-dimethyl-*m*-toluidine as the best compromise within this group, a series of N,N-dialkylanilines of various boiling points was investigated (Table II). It is apparent that as the boiling point of the solvent (and thus also the reaction temperature) increases, the time required to consume 95% of the starting ether decreases. Maximum yield and purity appear to be realized with N,N-dimethylaniline.

Although disubstituted anilines (usually N,N-diethyl) frequently have been employed as solvents in the Claisen rearrangement, their virtues have been claimed to be easy removal and prevention of polymerization due to excessive heating. In the case of β-methylallyl phenyl ether, the anilines appear also to participate in directing the course of reaction.

Experimental

The starting ether (I) was prepared from methylallyl chloride, phenol, and potassium carbonate as described.[3] Equal weights of ether and solvent were employed in all rearrangements. Refluxing was maintained with a heating mantle until only 5% starting ether remained, as shown by gas–liquid chromatographic analysis. Product distributions were calculated from peak areas. In several instances unidentified peaks occurred, accounting for the frequently incomplete analyses shown in Tables I and II.

Chromatographic analyses were effected on a 5 ft. long, 0.375-in. diameter, preparative column containing 15% ethylene glycol succinate on 60–80-mesh Chromosorb. The column and the instrument (A-700 Autoprep) were from the Wilkens Instrument Co. in Walnut Creek, Calif. In every case, except for that of N,N-dimethylaniline, the five major components (*i.e.*, I, II, III, IV, and solvent) were resolved into separate peaks, allowing immediate analysis at any desired reaction time. With N,N-dimethylaniline, acid extraction was required prior to analysis.

The properties of the chromatographically pure phenols, II and III, as well as those of the dihydrobenzofuran, are recorded in Table III.