

n_D^{25} 1.4566; d_{25}^{25} 1.318; R_D 0.2065, R_D calcd 0.2065. Dreiding and Pratt report n_D^{25} 1.4561 for this compound.⁹

trans-2-Trimethylsilylbutene-2 (3).—*trans*-2-Bromobutene-2 (6.7 g, 0.05 mole) was slowly added to a flask containing lithium wire (0.70 g, 0.10 g-atom) and ether at a temperature of 0°. When the organolithium reagent had been formed, trimethylchlorosilane (5.4 g, 0.05 mole) was added. The resulting solution was filtered, washed, and dried. A sample of **3** was then isolated by distillation and judged to be 96% pure by glpc, n_D^{25} 1.4252.

The infrared spectrum of this material showed the same group bands at 1620, 1375, and 1243 cm^{-1} as **2**. The bands at 610, 460, and 403 cm^{-1} were present at much lower intensity in this sample from which we estimate that this material contains 13% of **2**.

This sample exhibited strong absorptions at 643, 485, and 432 cm^{-1} which we believe to be characteristic of the *trans* isomer **3**.

trans-Butene-2.—*trans*-2-Bromobutene-2 (6.7 g, 0.05 mole) was slowly added to lithium wire (0.70 g, 0.10 g-atom) in ether at 0° with stirring. When the organolithium reagent had formed the solution was treated with acetic acid (3 ml) and the butene which was evolved was collected in a cold trap and distilled to a second cold trap to free it of ether. The infrared spectrum of this material was that reported for *trans*-butene-2¹² except for the presence of about 4% ether.

(12) American Petroleum Institute, Research Project 44, Infrared Spectral Data, Spectra No. 908, 909.

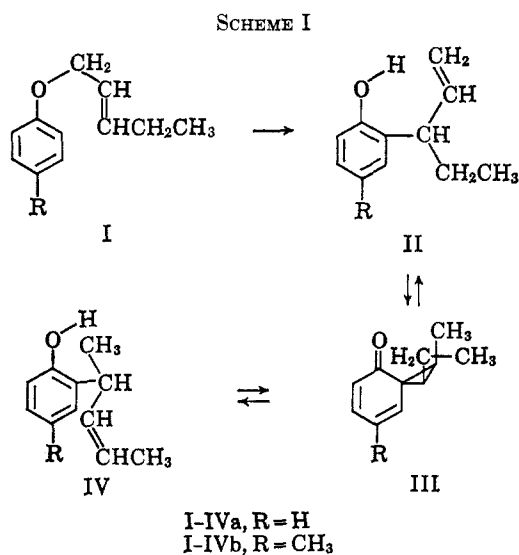
On the Reversibility of the "Abnormal Claisen Rearrangement"^{1a}

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The "abnormal" product IVa (Scheme I) of the Claisen rearrangement of γ -ethylallyl phenyl ether (Ia) has been shown to be formed from the normal product

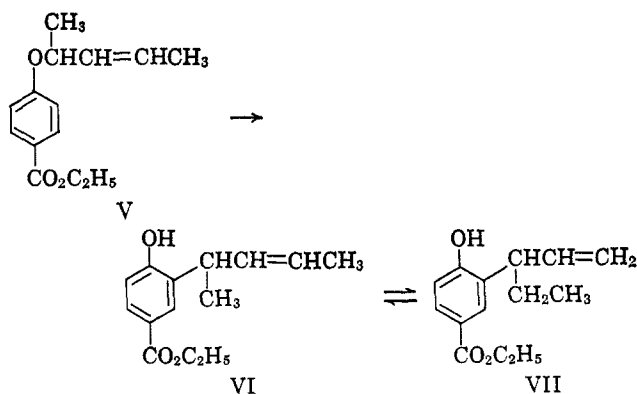


IIa by a secondary thermal rearrangement.² Both normal and "abnormal" products have usually been detected in the cases examined,³ but it was reported that

(1) (a) Financial support by the Robert A. Welch Foundation and the University of Texas Research Institute is gratefully acknowledged; (b) University of Texas Predoctoral Fellow, 1964-1965.

(2) (a) E. N. Marvell, D. R. Anderson, and J. Ong, *J. Org. Chem.*, **27**, 1109 (1962); (b) A. Habich, R. Barner, W. von Philipsborn, and H. Schmid, *Helv. Chim. Acta*, **48**, 1297 (1965).

when IIa was heated for a long time at 200-230°, the conversion to IVa was complete,⁴ as well as could be detected by the infrared analysis used. According to the accepted mechanism,^{2,5} the rearrangement of IIa to IVa *via* the spirodienone intermediate IIIa should be reversible. Although IVa would be expected to be favored in an equilibrium between IIa and IVa, there is one report in the literature which suggests that IIa should be present in a detectable amount. When the ether V was subjected to thermal rearrangement, a mixture of products was obtained which was shown by ozonolysis to contain some VII.^{3a}



We decided to test the reversibility of the rearrangement in this α -ethylallyl II, VII and α,γ -dimethylallyl IV, VI system using the *p*-cresol derivatives IIb and IVb, which were available to us.

Thermolysis of γ -ethylallyl *p*-tolyl ether (Ib) at temperatures of 175-200° gave mixtures of IIb and IVb; higher temperatures and longer heating times gave increased amounts of IVb, as expected, but vpc, nmr, and infrared data revealed evidence of the presence of both isomers in all reaction products.

Authentic samples of IIb and IVb were prepared by independent syntheses.^{6,7} Preliminary experiments in which IVb was heated at 185-200° gave product mixtures that were difficultly resolved by vpc, but definitely contained small amounts of IIb. Better separation of IIb from IVb was accomplished by converting the mixed isomeric phenols to their methyl ethers before applying preparative-scale vapor phase chromatography. In this way, a sample of the methyl ether of IIb was obtained which was pure enough for positive identification by vpc, nmr, and infrared analysis.

In order to demonstrate formation of the same equilibrium mixture of IIb and IVb from either isomer by thermal rearrangement, separate samples of IIb and IVb were heated in *N,N*-diethylaniline at 200° for 9 days. Analysis of the phenolic components of the two reaction mixtures showed them to be identical and to consist of ca. 96% IVb and ca. 4% IIb.

These results support the view that the secondary rearrangement of an α -ethylallylphenol (II) to an α,γ -dimethylallylphenol (IV), which is responsible for "ab-

(3) (a) W. M. Lauer and H. E. Ungnade, *J. Am. Chem. Soc.*, **61**, 3047 (1939); (b) other references given there.

(4) D. R. Anderson, Ph.D. Thesis, Oregon State University, 1962, pp 23, 43 (through University Microfilms, Inc., Ann Arbor, Mich.).

(5) (a) R. M. Roberts and R. G. Landolt, *J. Am. Chem. Soc.*, **87**, 2281 (1965); (b) R. M. Roberts, R. N. Greene, R. G. Landolt, and E. W. Heyer, *ibid.*, **87**, 2282 (1965).

(6) A. Habich, R. Barner, R. M. Roberts, and H. Schmid, *Helv. Chim. Acta*, **45**, 1943 (1962).

(7) N. Kornblum and A. P. Lurie, *J. Am. Chem. Soc.*, **81**, 2705 (1959).

normal Claisen rearrangement" products such as IV, is indeed reversible, but that in the equilibrium between these phenols the latter type of isomer IV is heavily favored.

Experimental Section⁸

γ -Ethylallyl *p*-tolyl ether (Ib) was prepared from 1-chloro-2-pentene⁹ and *p*-cresol by the method of Lauer¹⁰ in 60% yield: bp 80–84° (2 mm), n_D^{25} 1.5118, strong infrared absorption at 970 cm^{-1} .

Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}$: C, 81.89; H, 9.16. Found: C, 81.93; H, 9.04.

Thermolysis of Ib to a Mixture of *o*-(α -Ethylallyl)-*p*-cresol (IIb) and *o*-(α,γ -Dimethylallyl)-*p*-cresol (IVb).—Samples of Ib were sealed in Pyrex tubes, after degassing by freezing and melting repeatedly at ca. 0.1 mm, and the tubes were heated in an oven at temperatures which were maintained constant within $\pm 2^\circ$. The rearrangement was followed by direct vpc and infrared analysis of the reaction mixtures. (Absorption at 915 cm^{-1} was characteristic of the terminal vinyl out-of-plane bending of IIb and, at 978 cm^{-1} , of the *trans* configuration about the internal double bond of IVb.) A sample heated for 23 hr at 160° showed no phenolic product. After 64 hr at 175°, ca. 90% of the starting material was unchanged; the product was almost pure IIb. After 303 hr at 175°, only a trace of starting material remained; the product was a mixture of IIb (major component) and IVb (minor component); the vpc was not well resolved on this sample. A sample heated for 24 hr at 200° was converted to IIb (ca. 40%) and IX (ca. 60%). The product mixture from the 200° thermolysis, which had a very slight brown tint, was analyzed directly.

Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}$: C, 81.89; H, 9.16. Found: C, 81.66; H, 8.98.

Authentic IIb was obtained from Ib by the boron trichloride catalyzed rearrangement procedure which has been shown to give only the normal Claisen product from the ¹⁴C-labeled crotyl homolog of Ib.⁶ The crude product contained no IVb (vpc and infrared analysis), but some *p*-cresol, from cleavage of the phenolic ether (Ib); this was removed by preparative-scale vpc. The pure material showed strong infrared absorption at 915 cm^{-1} and no significant absorption at 978 cm^{-1} .

The methyl ether of IIb was prepared in the usual way,⁶ and purified by preparative-scale vpc. Its nmr spectrum showed the following proton resonance absorptions: multiplet at τ 3.2 (3 H), multiplet at τ 4.1 (1 H), doublet at τ 5.1 (2 H), singlet at τ 6.3 (3 H), multiplet at τ 6.5 (1 H), singlet at τ 7.7 (3 H), quintet at τ 8.3 (2 H), and triplet at τ 9.1 (3 H).

Authentic IVb was synthesized from *p*-cresol and 4-chloro-2-pentene by the C-alkylation technique of Kornblum.⁷ The crude reaction mixture was extracted with Claisen's alkali to separate the C-alkylation products from O-alkylation products. Work-up of the Claisen alkali-soluble fraction gave IVb in 50% yield: bp 82° (0.5 mm), showing only one vpc peak; strong infrared absorption appeared at 978 cm^{-1} and a very small absorption at 915 cm^{-1} .

Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}$: C, 81.89; H, 9.16. Found: C, 81.83; H, 9.07.

The methyl ether of IVb was prepared as was that of IIb. The product (97% pure according to vpc) showed a strong infrared absorption at 975 cm^{-1} and a very weak absorption at 917 cm^{-1} . Its nmr spectrum exhibited the following proton resonance absorptions: multiplet at τ 3.3 (3 H), multiplet at τ 4.5 (2 H), multiplet at τ 6.2 (1 H), singlet at τ 6.3 (3 H), singlet at τ 7.8 (3 H), doublet at τ 8.3 (3 H), and doublet at τ 8.8 (3 H).

Rearrangement of IVb to IIb.—Samples (0.5, 0.5, and 0.1 g) of IVb in *N,N*-diethylaniline (1.0, 1.0, and 2.0 g) were degassed, sealed in Pyrex tubes, and heated at 200° for 24 and 48 hr and at

(8) Beckman IR-5A and Varian A-60 spectrometers were used in infrared and nmr measurements. Beckman GC-2A and Wilkens A-600 (Hi-Fi) and A-700 (Autoprep) instruments were used for vpc analyses and separations. The stationary-phase material most generally used was silicone gum rubber (SE-30); Carbowax (20M) and ethylene glycol succinate were used in some cases. Microanalyses were done by Alfred Bernhardt Microanalytisches Laboratorium, Mülheim, Germany.

(9) W. G. Young, F. F. Caserio, Jr., and D. D. Brandon, Jr., *J. Am. Chem. Soc.*, **82**, 6163 (1960).

(10) W. M. Lauer, G. A. Doldouras, R. E. Hileman, and R. Liepens, *J. Org. Chem.*, **26**, 4785 (1961).

185° for 111 hr, respectively. Vpc analyses of the three reaction mixtures (after removal of the amine solvent as described below) were virtually identical, showing a single peak with a retention time corresponding to the starting material IVb and a small shoulder (estimated at ca. 3–5% of the large peak) at the retention time corresponding to IIb. Further vapor phase chromatography on the preparative scale gave a sample with increased concentration (ca. 50%) and better separation of the shoulder component. This sample showed significant infrared absorption at 915 cm^{-1} , characteristic of IIb.

A larger sample of IVb (6.5 g) was heated in *N,N*-diethylaniline (13 g) at 200° for 24 hr. The amine solvent was removed by aqueous hydrochloric acid extraction from a pentane solution of the crude reaction mixture. After further washing and drying of the pentane solution, the phenols were converted to their methyl ethers as before.⁶

Preparative-scale vpc provided almost complete separation of the methyl ether of IIb from the methyl ether of IVb, the major component. The analytical vapor phase chromatogram of the minor component showed one main peak with the same retention time as that of authentic IIb ether; the nmr and infrared spectra of the minor component were identical with those of authentic IIb ether.

Equilibration of IIb and IVb.—Thermolyses of separate samples (0.15 g) of authentic IIb and IVb in *N,N*-diethylaniline (0.3 g) were carried out at 200° for 9 days. Vpc analysis showed similar proportions of IIb (ca. 4%) and IVb (ca. 96%) in the two reaction mixtures.

The Identity of the Acetone-Urea Condensation Product

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The reaction of acetone with urea in the presence of mineral acid was investigated by Weinschenk,¹ who obtained a complex compound which melted with decomposition at 265–268°. This has been given the name "Triacetonedurea." As a possible structure for this presumed compound, to which he assigned the empirical formula $\text{C}_{11}\text{H}_{20}\text{N}_4\text{O}_2$, he considered the chain structure I, because alkaline or acid hydrolysis gave acetone, ammonia, and carbon dioxide as the products he could identify.

In 1951, another suggested structure, 4,4'-(2,2-dimethyltrimethylene)bis(4-methyl-2-uretidinone), was proposed in a patent reference^{2,3} on the basis of the elementary analysis only.

In the present investigation, the structure of the acetone-urea condensation product has been re-examined. The product was obtained from the reaction of acetone with urea in the presence of sulfuric acid followed by basification of the reaction product. Recrystallization of this free base from water gave a hydrated crystalline solid which could be readily dehydrated by heating, mp 260–262° dec. The elementary analysis and molecular weight determination corresponded to a substance having an empirical formula of $\text{C}_{11}\text{H}_{20}\text{N}_4\text{O}_2$ (II). This showed no absorption

(1) A. Weinschenk, *Ber.*, **34**, 2185 (1901).

(2) M. T. Harvey, U. S. Patent 2,592,565 (1952); *Chem. Abstr.*, **47**, 601a (1953).

(3) It will be noted that the chlorinated acetone-urea condensation product has the formula approximately $\text{C}_{11}\text{H}_{16}\text{N}_4\text{O}_2\text{Cl}_4$; see M. Kokorudz, U. S. Patent 3,158,436 (1964).