run was again washed with two 1-l. portions of water, dried and redistilled affording an additional 29 g. of product. Refractionation of the forerun, b.p. 100–118°, gave 28 g. of product, b.p. 118–120°. The total yield of 1,1-dichloro-2,2-dimethylcyclopropane was 90 g. (65%), b.p. 118–120°, n^{20}_D 1.4461, d^{22}_4 1.0854.

Anal. Calcd. for $C_5H_8Cl_2$: C, 43.2; H, 5.8; Cl, 51.0. Found: C, 43.4; H, 6.0; Cl, 51.3.

Reaction of Chloroform with Potassium *t*-Butoxide.—Chloroform (75 g., 0.63 mole) was added with shaking to a solution of 20 g. (0.51 g. atom) of potassium in 500 ml. of *t*-butyl alcohol. The reaction mixture, after the chloroform had been added, was poured into water and the mixture was extracted with pentane. Distillation gave 5 g. of material, b.p. 119.5–120°, n^{26}_D 1.4454, having an infrared spectrum identical with that of 1,1-dichloro-2,2-dimethylcyclopropane.

Reaction of Chloroform with 4-Vinylcyclohexene.—A solution of chloroform (200 ml., 2.5 moles) in an equal volume of 4-vinylcyclohexene was added slowly to a stirred, ice-cooled solution of 89 g. (2.2 g. atoms) of potassium metal in 1200 ml. of *t*-butyl alcohol containing 600 ml. of 4-vinylcyclohexene. Following the addition of the chloroform, the reaction mixture was stirred for 1 hr., after which it was poured into water. The olefin layer was separated, dried and concentrated by distillation to a residue which was fractionally distilled *in vacuo*, to yield the following fractions: a, 3 g., b.p. 68–81° at 8 mm.; b, 8 g., b.p. 81–90° at 8 mm.; c, 10 g., b.p. 90–95° at 8 mm.; d, 19 g., b.p. 95–96° at 8 mm.; e, 17 g., b.p. 96° at 8 mm.; f, 25 g., 96–96.5° at 8 mm.

Fraction e was ozonized by the procedure of Wilms,[24] forming an oil which was converted to its S-benzylisothiouranium salt, m.p. 135.5–136°.

Anal. Calcd. for $C_{16}H_{20}O_2N_2Cl_2S$: C, 51.2; H, 5.4; Cl, 18.9. Found: C, 50.9; H, 5.2; Cl, 18.2.

Reaction of Chloroform with β-Pinene.—Analcoholic potassium *t*-butoxide stirred with 350 ml. of pentane and 500 g. of β-pinene was allowed to react with 120 ml. (1.5 moles) of chloroform with ice-cooling. After the chloroform had been added, the reaction mixture was stirred for 5 min. and poured into 2 l. of water. The pentane extract of the water layer was combined with the pinene layer and dried over magnesium sulfate. The pentane and pinene was removed by distillation *in vacuo*. The residue was fractionally distilled *in vacuo* yielding 164 g. (50%) of product having a b.p. of 70–71° at 0.5 mm., n^{25}_D 1.5070, d^{26}_4 1.1402.

Anal. Calcd. for $C_{11}H_{16}Cl_2$: C, 60.3; H, 7.4; Cl, 32.4. Found: C, 60.6; H, 7.2; Cl, 32.1.

Reaction of Chloroform with α-Pinene.—Chloroform (158 ml., 2 moles) was added dropwise to an iced solution of 70 g. of potassium in 1.2 l. of *t*-butyl alcohol containing 1 l. of α-pinene (b.p. 155–156°). After completion of the addition of chloroform, the ice-bath was removed and stirring was continued for 0.5 hr. The reaction mixture diluted with 500 ml. of pentane was poured into 4 l. of water and thoroughly washed with additional portions of water. Distillation of the pentane and α-pinene *in vacuo* yielded a residue which was fractionally distilled. Four fractions were obtained: a, 3 g., b.p. 68–77° at 2 mm.; b, 13 g., b.p. 77–79° at 2 mm.; c, 26 g., b.p. 79–82° at 2 mm.; d, 13 g., b.p. 82–84° at 2 mm. Each of these fractions showed unsaturation to bromine in carbon tetrachloride solution and darkened and became viscous on standing.

1,1-Dichloro-2,2,3-trimethylcyclopropane.—Analcoholic potassium *t*-butoxide prepared from 60 g. (1.5 g. atoms) of potassium and 1.2 l. of *t*-butyl alcohol was stirred with 450 g. of 2-methylbutene-2 in an ice-bath. Chloroform (180 g., 1.5 mole) was added dropwise with stirring. After the addition of chloroform was completed, the reaction mixture was stirred for 5 min. and poured into 1 l. of water. The butene layer was separated, and the water layer was washed with two 50-ml. portions of pentane. The pentane and butene layers were combined and dried over sodium sulfate. The pentane and olefin was removed by distillation and the residue fractionally distilled *in vacuo*. Two fractions were collected; a, 14.6 g., b.p. 68° at 55 mm.; and b, 152 g. (66%), b.p. 69–70° at 55 mm., n^{25}_D 1.4555, d^{26}_4 1.0927. At 760 mm. the b.p. is 144° with some decomposition and evolution of a small amount of hydrogen chloride.

Anal. Calcd. for $C_6H_{10}Cl_2$: C, 47.1; H, 6.6; Cl, 46.3. Found: C, 47.3; H, 7.0; Cl, 46.6.

1-Butyl-2,2-dichlorocyclopropane.—Sodium *t*-amylate was prepared from 46 g. (2 g. atoms) of sodium dissolved in 1.8 l. of refluxing *t*-amyl alcohol with stirring. Removal of the *t*-amyl alcohol by distillation followed by heating at 160–170° at 1 mm. for 2 hr. afforded analcoholic sodium *t*-amylate. The sodium amylate was stirred with 450 g. of hexene-1 in an ice-bath, while 240 g. (2 mole) of chloroform was added dropwise. The reaction was considerably more vigorous than the reactions of potassium *t*-butoxide, olefin and chloroform. After half the chloroform had been added, the reaction mixture was diluted with 200 ml. of pentane. After the addition of chloroform was completed, the reaction mixture was washed well with three 1-l. portions of water, dried and fractionally distilled to give 54 g. (16%) of product having a b.p. of 75–76° at 25 mm., n^{25}_D 1.4501, d^{26}_4 1.0522.

Anal. Calcd. for $C_7H_{12}Cl_2$: C, 50.3; H, 7.2; Cl, 42.4. Found: C, 50.5; H, 7.1; Cl, 42.1.

NEW HAVEN, CONN.

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(24) H. Wilms, *Ann.*, **567**, 96 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Ortho–Para Migration in the *Para*-Claisen Rearrangement[1]

BY ELLIOT N. MARVELL AND ROY TERANISHI

RECEIVED APRIL 7, 1954

The Hurd–Pollack mechanism for the *para*-Claisen rearrangement postulates a dienone intermediate. If the two groups *ortho* to the keto function are both of allylic nature either could migrate further to the *para* position. Rearrangement of γ-phenylallyl 2,6-diallylphenyl ether gives a product in which 2,6-diallyl-4-(γ-phenylallyl)-phenol was identified. However, identical treatment of allyl 2-allyl-6-(α-phenylallyl)-phenyl ether gives at least two products, both 2,4-diallyl-6-(α-phenylallyl)-phenol and 2,6-diallyl-4-(γ-phenylallyl)-phenol being identified. This evidence supports the Hurd–Pollack mechanism for it indicates the equivalence of the ether and the *ortho*-allyl groups during the migration process, and it shows that migration from the *ortho* to the *para* position proceeds with inversion.

Recent studies on the *para*-Claisen rearrangement[2] have revived interest in the Hurd–Pollack[3] mechanism for the rearrangement. One requirement of that mechanism is that a dienone intermediate I should be formed. It is reasonable to conclude that if both A and B in I are of allylic nature either may migrate further to the *para* position. To test this conclusion two new ethers, γ-phenylallyl 2,6-diallylphenyl ether and allyl 2-allyl-6-(α-phenylallyl)-phenyl ether, have been prepared and rearranged. While this material was being prepared for publication results of similar studies

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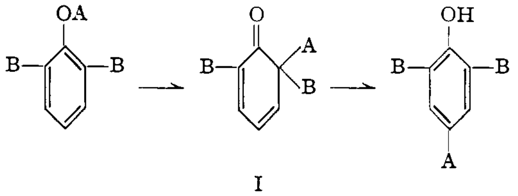
(1) Published with the approval of the Monographs Publications Committee, Oregon State College, as Research Paper No. 225, School of Science, Department of Chemistry.

(2) (a) H. Conroy and R. Firestone, THIS JOURNAL, **75**, 2530 (1953); (b) S. J. Rhoads, R. Raulins and R. Reynolds, *ibid.*, **75**, 2531 (1953); (c) E. N. Marvell and R. Ledeen, *ibid.*, **76**, 1922 (1954); (d) K. Schmid, W. Haegele and H. Schmid, *Experientia*, **9**, 414 (1953); (e) D. Y. Curtin and H. W. Johnson, Jr., Abstracts of Papers, American Chemical Society Meeting, Kansas City, April, 1954, p. 23N.

(3) C. D. Hurd and H. Pollack, *J. Org. Chem.*, **3**, 550 (1939).



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were published.[2d,e] Though our studies reach the same conclusions the method is different and the use of alpha and gamma substituted allyl groups is new.

Preparation of γ-phenylallyl 2,6-diallylphenyl ether was accomplished by a Williamson synthesis using the known 2,6-diallylphenol[4] and cinnamyl bromide. The ether was separated from any phenolic material, including starting materials, C-alkylation and rearrangement products, by exhaustive extraction with Claisen alkali. Purification of this ether by distillation proved impossible because it rearranged below its boiling point. The ether was rearranged to give a phenolic product which was obtained in 31% over-all yield from the 2,6-diallylphenol. The rearrangement product gave only a single identifiable phenylurethan, m.p. 136–137°, which was isolated in 29% yield. This phenol absorbed three moles of hydrogen when treated with hydrogen and palladium-on-charcoal. The phenylurethan of the phenol so obtained melted sharply at 108–109°.

In order to ascertain the structure of the phenol obtained by rearrangement of γ-phenylallyl 2,6-diallylphenyl ether, the γ-phenylallyl ether of the known 2,6-dipropylphenol[4] was prepared and rearranged. It is known[5] that propyl ethers unlike allyl ethers are stable to heat and there is no record in the literature of displacement of saturated alkyl groups from an *ortho* or *para* position during a Claisen rearrangement. Therefore, it was assumed that the propyl groups would stay put during this rearrangement and that the migrating γ-phenylallyl group would go exclusively to the *para* position. The rearrangement product was hydrogenated, absorbing one mole of hydrogen, to give a phenol whose phenylurethan melts at 108–109°. The melting point of a mixture of this phenylurethan and that of the hydrogenated phenol from the rearrangement of γ-phenylallyl 2,6-diallylphenol was also 108–109°. Therefore, no migration of the *o*-allyl group to the *para* position was detectable by this method. Since migration of an allylic group to an *ortho* position is inevitably associated with inversion,[6] it may be assumed that an α-phenylallyl group migrates more readily than an unsubstituted allyl group. This is in accord with earlier observations[2b] concerning the ease of migration of substituted allyl groups.

If this preferential migration of the α-phenylallyl group is inevitable then allyl 2,6-di-(α-phenylallyl)-phenyl ether should give exclusively 2-(α-phenylallyl)-4-(γ-phenylallyl)-6-allylphenol. An attempt to prepare allyl 2,6-di-(α-phenylallyl)-phenyl ether failed. Thus the less desirable case using allyl 2-allyl-6-(α-phenylallyl)-phenyl ether was carried out. This ether was made, as is shown in the equations, from the previously known[4] 2-allylphenol and also from the known 2-(α-phenylallyl)-phenol.[7,8] Due to the extreme ease of rearrangement it proved impossible to purify this ether by distillation but all phenolic material was removed by exhaustive extraction with Claisen alkali. Rearrangement of the crude ether gave a phenolic material of the expected composition. Only a single phenylurethan was isolated (14%) from this rearrangement product. Melting point (136–137°) and mixed melting point data showed that this was the phenylurethan of 2,6-diallyl-4-(γ-phenylallyl)-phenol, indicating that at least a partial migration of the *ortho* substituent had occurred. The product of the rearrangement absorbed three moles of hydrogen and this hydrogenated material gave a phenylurethan which was separated by fractional crystallization into two components, m.p. 136–137° (21% yield) and m.p. 108–109° (7% yield). The lower melting fraction did not depress the melting point of an authentic sample of phenylurethan of 2,6-dipropyl-4-(γ-phenylpropyl)-phenol.

That the higher melting product was indeed the phenylurethan of 2,4-dipropyl-6-(α-phenylpropyl)-phenol was shown by synthesis of that material. That synthesis was accomplished by hydrogenation of 2-allyl-6-(α-phenylallyl)-phenol to give 2-propyl-6-(α-phenylpropyl)-phenol, formation and rearrangement of the allyl ether of that product, and hydrogenation to the desired 2,4-dipropyl-6-(α-phenylpropyl)-phenol. The phenylurethan of this sample melted at 136–137° and a mixture of this phenylurethan and the higher melting fraction obtained earlier also melted at 136–137°.

Two conclusions may be drawn from this data. The allylic group migrating from the ether must be bonded to an *ortho* carbon in such a manner as to become equivalent to an allylic group originally in that position. This requirement is satisfied by the dienone intermediate of the Hurd–Pollack mechanism. However, as Curtin[2e] has pointed out the results also are explainable if the dienone is formed by a reversible side reaction rather than as an intermediate in the rearrangement. Migration to the *para* position without inversion would be accomplished then by the Dewar[9] mechanism. However, the data of both Curtin and Johnson,[2e] and Schmid, Haegele and Schmid[2d] show that the dienone is a true intermediate in the *para*-Claisen rearrangement.

The data also show that the group migrating from the *ortho* position undergoes inversion during passage to the *para* position. The compound designated as 2,6-diallyl-4-(γ-phenylallyl)-phenol was assigned that structure for three reasons. First, it was obtained by rearrangement of the γ-phenylallyl ether of the known 2,6-diallylphenol, and migration to the *para* position does not invert.[2b,c,d,10] Second, the same product was

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(4) L. Claisen, O. Eisleb and F. Kremers, *Ann.*, **418**, 69 (1919).

(5) *Cf.* D. S. Tarbell in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 4.

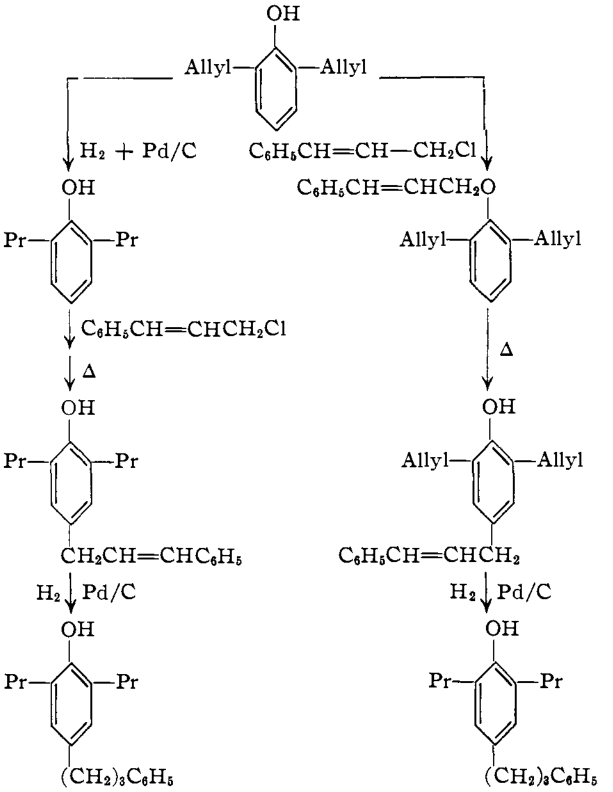
(6) *Cf.* reference 5, p. 9.

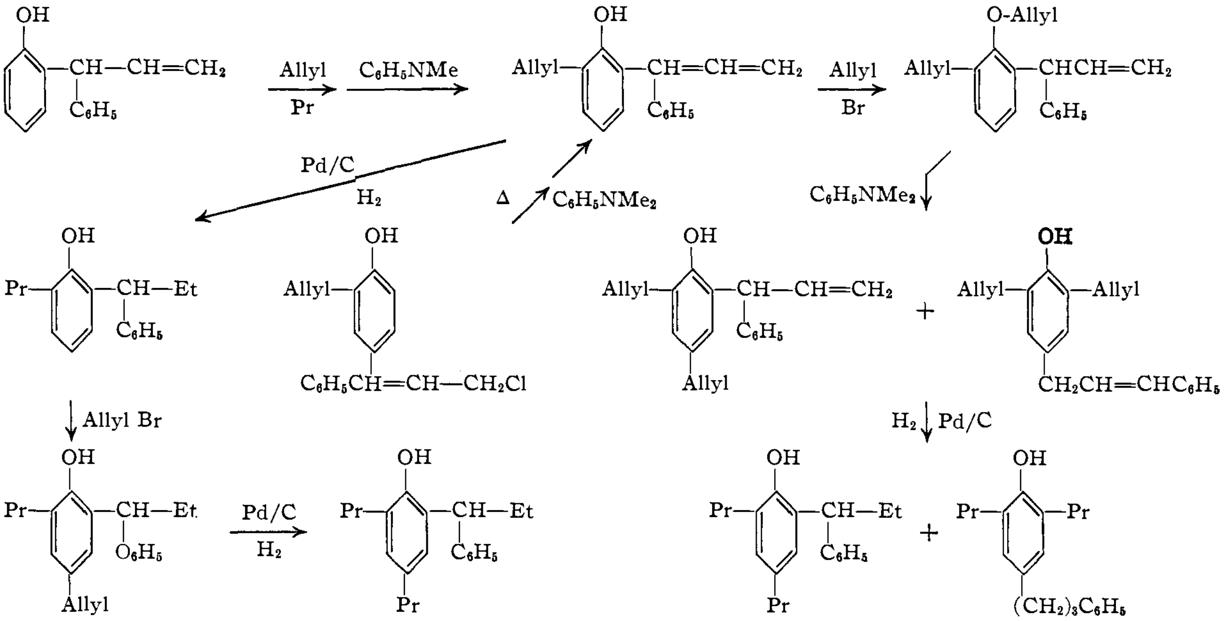
(7) L. Claisen, F. Kremers, F. Roth and E. Tietze, *Ann.*, **401**, 21 (1913).

(8) C. D. Hurd and L. Schmerling, THIS JOURNAL, **59**, 107 (1937).

(9) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford Press, London, England, 1949, p. 229.

(10) (a) O. Mumm and F. Moller, *Ber.*, **70**, 2214 (1937); (b) O. Mumm, F. Hornhardt and J. Diederickson, *ibid.*, **72**, 100 (1939); (c) O. Mumm and J. Diederickson, *ibid.*, **72**, 1523 (1939).





obtained by C-alkylation of 2,6-diallylphenol with cinnamyl bromide and C-alkylation is known to occur without inversion.[7a,b] Finally, the product can be reduced to give 2,6-dipropyl-4-(γ-phenylpropyl)-phenol, identical with that formed by rearrangement of γ-phenylallyl 2,6-dipropylphenyl ether followed by hydrogenation. It seems reasonable to conclude that the phenyl group is in the gamma position. Since 2,6-diallyl-4-(γ-phenylallyl)-phenol is obtained on rearrangement of allyl 2-allyl-6-(α-phenylallyl)-phenyl ether inversion occurred during migration from the *ortho* to the *para* position. Preparation of the required ether from *o*-(α-phenylallyl)-phenol[7b] provides evidence for assigning the phenyl group to the alpha position.

It must be acknowledged that the method of identification of products employed here is not capable of showing up small amounts of material. However, it cannot be supposed that the substances identified in the products were originally present in the crude ethers since those ethers were shown to be free of phenols to the limit of the infrared method of analysis. Since all products were found to be present to at least 14%, there is no doubt that they were the result of a reaction of the ether. Although this method does not eliminate the possibility of other products being present, that does not appear to alter the conclusions reached above.

Acknowledgment.—It is indeed a pleasure to note that this research was made possible by generous financial support from the Research Corporation.

Experimental

2,6-Diallyl-4-(γ-phenylallyl)-phenol.—A solution of sodium 2,6-diallylphenoxide in absolute methanol was prepared by mixing 44.0 g. (0.25 mole) of 2,6-diallylphenol[4] with 200 ml. of methanol containing 6 g. (0.25 mole) of sodium. After the addition of 49.0 g. (0.25 mole) of γ-phenylallyl bromide the reaction mixture was heated under reflux for three hours, and stirred at room temperature for 24 additional hours. This solution was diluted then with 300 ml. of water and extracted four times with 50-ml. portions of petroleum ether. The combined petroleum ether solution was washed with four 25-ml. portions of Claisen alkali, in which 2,6-diallylphenol is readily soluble. Further treatment with Claisen alkali followed by acidification of the alkali and extraction with petroleum ether showed that no alkali-soluble material remained. The petroleum ether solution of the alkali insoluble material was washed once with 50 ml. of water and dried over anhydrous magnesium sulfate. The desiccant was removed by filtration and the petroleum ether by evaporation under reduced pressure at room temperature.

The residual material was distilled *in vacuo*, b.p. 200–205° (1–2 mm.). The distillate was an oil, $n^{20}\text{D}$ 1.5920, which was soluble in Claisen alkali. The yield was 22.3 g. or 31%.

Anal. Calcd. for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.74; H, 7.50.

The phenylurethan of the above phenol was prepared according to the directions of Shriner and Fuson.[11] Starting with 0.5 g. of the phenol only 0.2 g. of the phenylurethan, m.p. 136–137°, was obtained.

Anal. Calcd. for $C_{28}H_{27}NO_2$: C, 82.12; H, 6.65. Found: C, 81.87; H, 6.59.

The Claisen alkali extracts from above were acidified carefully in the cold with dilute hydrochloric acid, and the acid solution extracted three times with 50-ml. portions of petroleum ether. The petroleum ether extracts were combined, washed with water, and dried over anhydrous magnesium sulfate. The residue after filtration and evaporation boiled at 200–205° (1–2 mm.), n^{20}D 1.5919, weight 18 g. (25%). The phenylurethan prepared from this material melted at 136–137° and did not depress the melting point of the phenylurethan prepared from the phenol obtained from the alkali-insoluble substance.

2,6-Dipropyl-4-(γ-phenylpropyl)-phenol.—A solution of 8.32 g. (0.29 mole) of 2,6-diallyl-4-(γ-phenylallyl)-phenol (from the rearrangement) was dissolved in 100 ml. of 95% ethanol and hydrogenated at 30–40 p.s.i. using 0.50 g. of palladium-on-charcoal catalyst. Hydrogen uptake ceased after absorption of three moles per mole of phenol. The hydrogenated product boiled at 170–180° (0.5–1 mm.), n^{20}D 1.5448, weight 8.10 g. (95%).

Anal. Calcd. for $C_{21}H_{28}O$: C, 85.09; H, 9.52. Found: C, 85.09; H, 9.52.

A phenylurethan of this product was prepared in the usual manner,[11] m.p. 108–109°. After three recrystallizations 0.3 g. of phenylurethan was obtained from 0.5 g. of phenol. The C-alkylation product recovered from the γ-phenylallylation of 2,6-diallylphenol was hydrogenated to give a product whose phenylurethan also melted at 108–109°.

Anal. Calcd. for $C_{28}H_{33}NO_2$: C, 80.92; H, 8.00. Found: C, 80.89; H, 7.95.

A sample of 2,6-dipropylphenol[4] was treated with γ-phenylallyl bromide according to the procedure used to prepare γ-phenylallyl 2,6-diallylphenyl ether. The alkali-insoluble product here also rearranged during distillation, b.p. 170–180° (0.5–1 mm.). A yield of 80% of the rearranged material was isolated. The 2,6-dipropyl-4-(γ-phenylallyl)-phenol obtained thus was hydrogenated according to the procedure outlined above giving an authentic sample of 2,6-dipropyl-4-(γ-phenylpropyl)-phenol, b.p. 170–180° (0.5–1 mm.), n^{20}D 1.5448. The phenylurethan prepared from this material melted at 108–109° and did not depress the melting point of the phenylurethan of the hydrogenated product from the rearrangement.

Allyl 2-(α-Phenylallyl)-phenyl Ether.—To a solution of 2.7 g. (0.115 mole) of sodium in 100 ml. of absolute methanol was added 24.0 g. (0.115 mole) of 2-(α-phenylallyl)-phenol[12] and the solution allowed to stand at room temperature for 48 hours. The reaction mixture was treated in the manner described for earlier ethers and allyl 2-(α-phenylallyl)-phenyl ether crystallized from methanol, m.p. 40–41°, weight 13.6 g. (47%).

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.37; H, 7.25. Found: C, 86.45; H, 7.21.

2-Allyl-6-(α-phenylallyl)-phenol.—Twelve grams (0.48 mole) of the above ether was mixed with 50 ml. of dimethylaniline and heated at 200° for three hours. The cooled reaction mixture was diluted with 100 ml. of petroleum ether and extracted several times with dilute sulfuric acid, then with water and finally dried over anhydrous magnesium sulfate. The phenol distilled at 155–158° (0.5–1 mm.), n^{20}D 1.5843, weight 7.41 g. (62%).

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.37; H, 7.25. Found: C, 86.11; H, 7.39.

The phenylurethan of this phenol was prepared in the standard manner,[11] m.p. 101–102°.

Anal. Calcd. for $C_{25}H_{23}NO_2$: C, 81.27; H, 6.27. Found: C, 80.43; H, 6.14.

An identical product was obtained by the formation of γ-phenylallyl 2-allylphenyl ether from 2-allylphenol[4] and its rearrangement in dimethylaniline by the procedure described above.

2,4-Dipropyl-6-(α-phenylpropyl)-phenol.—A sample of 2-allyl-6-(α-phenylallyl)-phenol was hydrogenated under the conditions described for the preparation of 2,6-dipropyl-4-(γ-phenylpropyl)-phenol. The 2-propyl-6-(α-phenylpropyl)-phenol distilling at 152–154° (0.5–1 mm.) was obtained in 93% yield. The sodium salt of this phenol was treated in absolute methanol with allyl bromide according to the procedure used to prepare γ-phenylallyl 2,6-diallylphenyl ether. The ether obtained was rearranged by distillation, b.p. 151–154° (0.5–1 mm.), yield 63%. The 2-propyl-4-allyl-6-(α-phenylpropyl)-phenol was treated with hydrogen in the manner discussed above and 81% of 2,4-dipropyl-6-(α-phenylpropyl)-phenol, b.p. 145–150° (0.5–1 mm.), was obtained.

Anal. Calcd. for $C_{21}H_{28}O$: C, 85.09; H, 9.52. Found: C, 85.14; H, 9.36.

Treatment of 0.5 g. of the above phenol with phenyl isocyanate gave, after four recrystallizations from hexane, 0.2 g. of phenylurethan, m.p. 136.5–137.5°.

Anal. Calcd. for $C_{28}H_{33}NO_2$: C, 80.92; H, 8.00. Found: C, 80.76, H, 7.90.

The melting point of a mixture (approx. 50–50) of this phenylurethan with that of 2,6-diallyl-4-(γ-phenylallyl)-phenol was 100–123°.

Preparation and Rearrangement of Allyl 2-Allyl-6-(α-phenylallyl)-phenyl Ether.—An 0.08-mole batch of 2-allyl-6-(α-phenylallyl)-phenol was allowed to react with allyl bromide according to the method described for preparation of allyl 2-(α-phenylallyl)-phenyl ether. The reaction mixture was worked up as usual and the ether which could not be distilled was isolated in crude state, n^{20}D 1.5670, in 82% yield by evaporation of the dry petroleum ether solution under reduced pressure (1–2 mm.) for several hours at room temperature. This crude ether showed no absorption in the region from 3040–3700 cm.$^{-1}$ whereas 2,6-diallyl-4-(γ-phenylallyl)-phenol has a strong absorption band at 3460 cm.$^{-1}$.

Fourteen grams (0.048 mole) of this crude ether was heated in 50 ml. of dimethylaniline at 210° for three hours. The cooled reaction mixture was diluted with 100 ml. of petroleum ether, extracted with several portions of dilute sulfuric acid and washed with water. The resultant solution was extracted with one 50-ml. and three 25-ml. portions of Claisen alkali. The phenolic materials were isolated from the alkaline extracts by careful acidification with hydrochloric acid in the cold followed by extraction with petroleum ether. The petroleum ether solution was washed with water and dried. The product, b.p. 170–200° (0.5–1 mm.), n^{20}D 1.5888, weighed 5.97 g. (42% calculated from the crude ether).

Anal. Calcd. for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.87; H, 7.76.

A phenylurethan was prepared from 0.5 g. of this phenolic mixture but only 0.1 g. of a pure product, m.p. 136–137°, could be obtained. This did not depress the melting point of an authentic sample of 2,6-diallyl-4-(γ-phenylallyl)-phenol.

The phenolic product was hydrogenated then under conditions given for preparation of 2,6-dipropyl-4-(γ-phenylpropyl)-phenol. From 0.5 g. of this material 0.5 g. of a phenylurethan mixture, m.p. 100–130°, was obtained. Fractional crystallization from hexane gave two fractions, one weighing 0.15 g., m.p. 135–137°, the second weighing 0.05 g., m.p. 107.5–109°. The first showed no melting point depression when mixed with an authentic sample of the phenylurethan from 2,4-dipropyl-6-(α-phenylpropyl)-phenol. The second gave similar results when mixed with the phenylurethan from 2,6-dipropyl-4-(γ-phenylpropyl)-phenol.

Attempted Preparation of Allyl 2,6-Di-(α-phenylallyl)-phenyl Ether.—A sample of γ-phenylallyl 2-(α-phenylallyl)-phenyl ether, m.p. 65–70°, was obtained by treatment of 2-(α-phenylallyl)-phenol with γ-phenylallyl bromide under the conditions described earlier. Rearrangement of this ether was accomplished by heating 35 g. in 200 ml. of dimethylaniline at 210° for three hours. The 2,6-di-(α-phenylallyl)-phenol, b.p. 205–220° (0.5–1 mm.), n^{20}D 1.6100, weighed 16.9 g. (48%). This phenol was very difficultly soluble in Claisen alkali and failed to give a color with ferric chloride. When this material was treated with allyl bromide under the stand-

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[11] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 136.

[12] L. Claisen and E. Tietze, *Ber.*, **58**, 275 (1925).

ard conditions there was obtained, after numerous extractions with Claisen alkali, a small amount of liquid, $n^{20}D$ 1.5808. Since the refractive index was not altered by heating the compound at 200° for several hours this was assumed to be C-alkylation product. No further study of the substance was made.

CORVALLIS, OREGON

[CONTRIBUTION FROM THE PITTSBURGH CONSOLIDATION COAL COMPANY, RESEARCH AND DEVELOPMENT DIVISION]

Silica–Alumina Catalyzed Isomerization–Disproportionation of Cresols and Xylenols

BY IRENE PIGMAN, ELSIO DEL BEL AND M. B. NEUWORTH

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Vapor phase isomerization–disproportionation of the isomeric cresols and xylenols in the presence of synthetic silica–alumina catalyst is described. At a maximum conversion temperature of 344° silica–alumina shows a very high selectivity for isomerization–disproportionation of methyl groups in alkyl phenols. The detailed product distribution was determined with varying depths of conversion. From the nature of the primary isomerization products, evidence is presented for the stepwise shift of methyl groups. The effect of steric hindrance on the isomerization and disproportionation reactions is discussed.

The aluminum chloride-catalyzed isomerization of *p*-cresol to *m*-cresol was first reported by Norris and Turner.[1] Baddely[2] described the $AlCl_3$ catalyzed isomerization of *o*-, *m*- and *p*-cresol and a number of individual xylenols at temperatures from 125–135°. Quantitative data were presented on the rate of isomerization of *p*-cresol. Since a minimum of one mole of aluminum chloride was used per mole of alkyl phenol, the actual compounds studied were aryloxy aluminum chlorides. Baddely concluded that *o*-cresol does not isomerize or form from the isomerization of *m*- or *p*-cresol. Meissner and French[3] re-examined the aluminum chloride-catalyzed isomerization–disproportionation of the isomeric cresols. They found that all three cresols isomerize using a molar excess of aluminum chloride and suggested that Baddely's conclusions regarding *o*-cresol were based on inadequate analytical procedures.

Aluminum fluoride was used by Nickels[4] for vapor phase isomerization–disproportionation of *o*-cresol. Given[5] described the vapor phase isomerization–disproportionation of cresols and xylenols over silica–alumina type catalysts using relatively large quantities of steam as a diluent at temperatures from 360–400°. Detailed product distribution was not presented.

Our investigation covers vapor phase silica–alumina catalyzed isomerization–disproportionation of the individual isomeric cresols and xylenols at lower temperatures. Complete product distribution will be presented as determined by infrared absorption analysis. An attempt will be made to account for the variations in product distribution with depth of conversion in terms of a mechanistic picture of methyl group migration.

Experimental

The pure compounds, except *p*-cresol, were purchased from Reilly Tar and Chemical Co. in a purity of 90–98%. Synthetic *p*-cresol was obtained from Hercules Powder Co. The compounds were further purified by precise fractionation, a heart cut being retained in each case.

The catalyst was synthetic silica–alumina Grade 111 obtained from Davison Chemical Co. The average analysis is 88% silica and 12% alumina. The average surface area is 372 m.²/g.

The experimental apparatus was similar in design to the apparatus previously described[6] for thermal cracking of alkyl phenols. It consisted of a precision liquid feeder, stainless steel reactor 1″ × 36″, and a product recovery system. Nitrogen gas was used as an inert diluent.

Fresh catalyst was used for each experiment. A 30-minute lineout period was employed at the beginning of each run. The condensed liquid product was transferred with benzene. The benzene solution was dried azeotropically and distilled into seven alkyl phenol cuts on a precision fractionation column. The cuts were analyzed for phenol, *o*-, *m*-, *p*-cresol, the six isomeric xylenols, 2,4,6- and 2,3,6-trimethylphenol using a modification of the infrared method of Friedel.[7]

Analyses were made on a Baird double beam spectrophotometer using NaCl optics. The remaining C_9-phenols boiling above 3,4-xylenol were determined as a group by distillation using acenaphthene as a backing liquid. The fraction of the products boiling above acenaphthene was reported as residue. Carbon was determined by difference. The gas was analyzed by a gravimetric method described by Barthauer, *et al.*[8]

Discussion of Results

The results of the conversion of the three isomeric cresols at 344° are shown in Table I. One striking fact is the greater lability of the methyl group in the cresols as compared with the corresponding xylenes.[9] Temperatures in excess of 450° would be required to obtain the same conversion of xylenes at an equivalent space rate. The amount of isomerization varied from 29.0 to 39.4% of the converted

TABLE I

CONVERSION OF THE ISOMERIC CRESOLS

Experimental Conditions: temperature, 344°; partial pressure of alkyl phenol, 0.4 atm.; vapor minute space velocity (VMSV), 7.0 min.⁻¹; liquid hourly space velocity (LHSV), 0.4 hr.⁻¹.

Starting isomer	*o*-Cresol	*m*-Cresol	*p*-Cresol
Conversion, wt. %	50	43	87
Compn. of converted products, wt. %			
Phenol	27.8	17.3	20.4
Cresols (isom.)	29.0	35.2	39.4
Xylenols (disprop.)	28.7	17.2	21.9
Neutrals	0.5	2.5	0.5
Residue	4.9	21.4	14.0
Carbon	8.7	6.4	3.4
Gas	0.1	..	..

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