proportions of *cis*-2-pentene, *trans*-2-pentene and 1-pentene in the pentene.

Summary

1. The isomeric *cis*- and *trans*-2-pentenes have been synthesized from the pure *cis*- and *trans*-α-methyl-β-ethylacrylic acids. They have identical boiling points (35.4° at 740 mm.) but different refractive indices.

2. The diastereomeric *dl*-2,3-dibromopentanes obtained from the isomeric 2-pentenes by bromine addition have identical refractive indices but different boiling points, freezing points and densities.

3. Pentene prepared from 3-bromopentane appears to be the *trans* isomer, while that from 2-bromopentane is probably a mixture of *cis*-2-pentene, *trans*-2-pentene and 1-pentene. Pentene exposed to ultraviolet light is probably a mixture of these three hydrocarbons, also.

4. When hydrogen bromide in glacial acetic acid adds to the pure 2-pentenes, the resulting bromopentanes have different refractive indices.

5. The variation in the refractive index values of bromopentane mixtures obtained by other investigators when hydrogen bromide was added to different preparations of pentenes may be due to variable proportions of *cis*-2-pentene, *trans*-2-pentene and 1-pentene.

6. There is no experimental basis for the hypothesis of electronic isomerism of ethylene compounds.

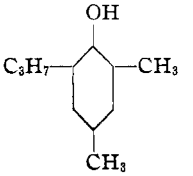
PASADENA, CALIF. RECEIVED JULY 6, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

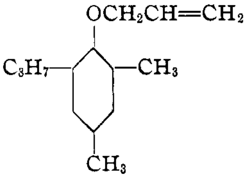
The Pyrolysis of Allyl 2,4,6-Trialkylphenyl Ethers

BY CHARLES D. HURD AND WILLIS A. YARNALL

Claisen, who discovered that allyl aryl ethers undergo rearrangement at 200–250° into *o*- or *p*-allylphenols, subjected allyl 2,4-dimethyl-6-propylphenyl ether (II) to similar thermal treatment in order to see if the rearrangement could be forced to the meta position. He found[1] that it could not, but he did encounter thermal instability in spite of the inability to rearrange. The products were stated to be the phenol (I), allene, diallyl and resinous matter. The yield of allene was reported to be 10%, and of diallyl 50%. Claisen believed that the gas was allene because it yielded a white precipitate with mercuric chloride solution. He demonstrated the absence of the isomeric methylacetylene by observing a non-reaction toward ammoniacal silver nitrate or cuprous chloride.



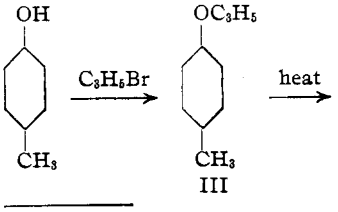
I



II

This problem was reinvestigated because it seemed unlikely that the gas was allene. The "equation type of mechanism" favors allene, to be sure, since $ArOC_3H_5$ differs from ArOH by C_3H_4. However, the formation of the phenol without allene is comparable to the pyrolytic formation of methane without allene from butylene,[2] or of propylene without allene from diallyl,[3] or of aniline without allene from diallylaniline.[4] Propylene was formed in each reaction. The last of these reactions is particularly striking since diallylaniline, $C_6H_5N(C_3H_5)_2$, may be regarded as the ammono analog of phenyl allyl ether. It decomposes at about 250° with the evolution of propylene. Therefore, it seemed reasonable to believe that Claisen's gaseous product was propylene also.

Any of the allyl 2,4,6-trialkylphenyl ethers should behave like II in this decomposition. Accordingly, allyl 2,6-dipropyl-4-methylphenyl ether (IX) was selected because it was more accessible than II. It was prepared from 2-propyl-4-methylphenol (V) which in turn was synthesized from *p*-cresol by the following sequence of steps.



III

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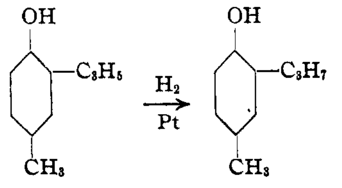
[1] (1) Claisen and Tietze, *Ann.*, **449**, 94 (1926).

[2] (2) Hurd and Spence, THIS JOURNAL, **51**, 3566 (1929); Hurd and Goldsby, *ibid.*, **56**, 1812 (1934).

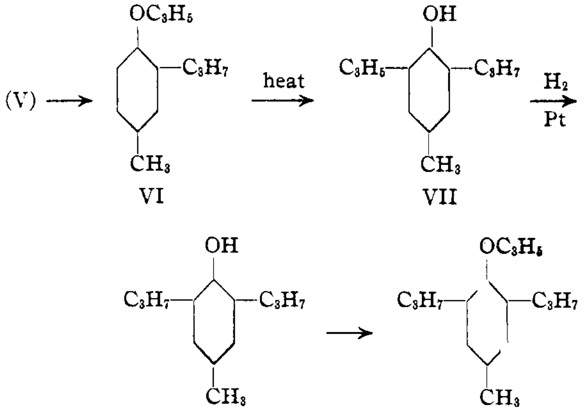
[3] (3) Hurd and Bollman, *ibid.*, **55**, 700 (1933).

[4] (4) Carnahan and Hurd, *ibid.*, **52**, 4586 (1930).



IV V

The hitherto unreported aryloxyacetic acid derivatives of IV and V were made by the reaction of the phenols with chloroacetic acid. The desired ether (IX) was prepared from V by these steps.

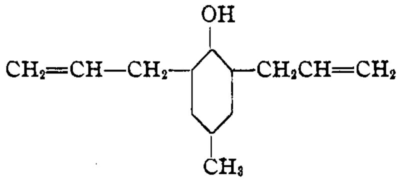


VI VII VIII IX

The last four compounds (VI–IX) were new.

The allyl ethers III, VI and IX were synthesized by a simple modification of Claisen's general method, which greatly increased the rapidity of the reaction and which gave somewhat higher yields. The modification consisted in taking allyl bromide, the phenol and sodium hydroxide in an aqueous–acetone (or alcohol) solvent. Claisen's reaction mixture was essentially anhydrous and the base was potassium carbonate instead of sodium hydroxide.

Higher-boiling polymers have long been noticed as concurrent reaction products during the pyrolytic rearrangement of allyl aryl ethers into allylphenols. Recently, the dimer of *o*-allylphenol was isolated[5] and characterized. In the present work it was established that the higher-boiling substances may include other compounds as well. Thus, during the rearrangement of allyl *p*-tolyl ether (III) into 2-allyl-4-methylphenol, it was observed that a definite amount of 2,6-diallyl-4-methylphenol (X) was among the reaction products.



X

For characterization it was hydrogenated to 2,6-dipropyl-4-methylphenol (VIII). This formation of X from III must speak for an intermolecular reaction mechanism, although the rearrangement itself (III to IV) has been shown[5] to be intramolecular.

It should be noted that phenols, related to the ethers, appeared among the pyrolytic products; thus, *p*-cresol from III, V from VI, and VIII from IX. This is in conformity with previous work.[6]

The gas which was evolved during pyrolysis of allyl 2,6-dipropyl-4-methylphenyl ether (IX) was propylene, as predicted. The quantity was comparable to Claisen's "allene" from allyl 2,4-dimethyl-6-propylphenyl ether, and the yield of diallyl was comparable also. The propylene was identified by bromine analysis. Instead of absorbing 2.0 equivalents of bromine as allene would require, the gas absorbed only 1.1 equivalents. The presence of some diallyl vapor in the propylene accounted for the fact that the value obtained was 1.1 instead of 1.0. Also, this contamination with diallyl explains the precipitate which Claisen obtained on treating the gas with mercuric chloride, and which led him to infer that the gas was allene. Diallyl and allene both give a heavy precipitate with mercuric chloride whereas pure propylene does not.

The small quantity of diallyl in the propylene prevented identification of the latter as propylene pseudo-nitrosite. Instead of obtaining crystals, m. p. 120°, from the reaction of the gas with nitrogen trioxide, an oil resulted. The same phenomenon was witnessed when a trace of diallyl was included with pure propylene. No difficulty was experienced in obtaining propylene pseudo-nitrosite from pure propylene or from a 3:2 mixture of propylene and allene. Also pure allene gas gave rise to its pseudo-nitrosite, m. p. 88°, smoothly.

Experimental Part

Allyl *p*-Tolyl Ether.— A mixture of 300 cc. of acetone, 400 cc. of water, 270 g. (2.5 moles) of *p*-cresol and

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(5) Hurd and Schmerling, THIS JOURNAL, **59**, 107 (1937).

(6) Hurd and Webb, *ibid.*, **58**, 2192 (1936).

102 g. of sodium hydroxide was made homogeneous by warming. One mole of allyl bromide was then added all at once through the attached reflux condenser. Vigorous refluxing and the separation into two layers occurred. One hundred cc. more of acetone was added and the remaining 1.5 moles of allyl bromide was dropped in during fifteen minutes. The mixture was left for two hours, then refluxed for one-half hour.

The upper layer (A) was separated. The lower aqueous layer was diluted with 300 cc. of water, and then extracted with two 50-cc. portions of petroleum ether. The extract, combined with (A), was washed with water, dried over potassium carbonate and distilled; yield, b. p. 97–98° (16 mm.), 280 g. From the aqueous portion, 50 g. of *p*-cresol was recovered. Therefore, the yield of the ether was 93%, based on the unrecovered cresol.

When Claisen's directions[7] were followed (including a ten-hour period of refluxing), the yield was 84%, based on the unrecovered cresol.

2-Allyl-4-methylphenol.—The liquid which remained after heating 280 g. of allyl *p*-tolyl ether for forty minutes at 200–208° (below b. p.) followed by forty minutes at 230° (boiling temperature) was extracted thrice with 20% potassium hydroxide solution (400, 100, 100 cc.). The alkaline extract was diluted and extracted with petroleum ether.

The alkali-soluble portion was dried and distilled under reduced pressure. About 10 cc. of *p*-cresol was collected first, then 163 cc. of 2-allyl-4-methylphenol, b. p. 115–118° (14 mm.); d^{20}_4 0.999; $n^{24}\mathrm{D}$ 1.5350.[8] To this, another 31 cc. was obtained from the alkali-insoluble fraction. The 194 g. is 69% of the theoretical. The phenol was soluble in 20% potassium hydroxide.

2-Allyl-4-methylphenoxyacetic Acid.—This derivative was prepared from *o*-allyl-*p*-cresol, chloroacetic acid and sodium hydroxide by the method of Koelsch.[9] The yield was 0.7 g. from 1 g., m. p. 124–125°. This acid did not decolorize bromine (in CCl_4), but it did show Baeyer's test ($KMnO_4 \longrightarrow MnO_2$) for unsaturation.

Neutr. Eq. Calcd. for $C_{11}H_{13}OCOOH$, 206. Found: 210.0, 207.5. *Anal.* Calcd. for $C_{12}H_{14}O_3$: C, 69.87; H, 6.85. Found: C, 69.39; H, 6.65.

2,6-Diallyl-4-methylphenol.—The alkali-insoluble portion (above), including the petroleum ether extract, was washed, dried, and thrice fractionated at 15 mm. From the original 80 cc. there were separated 31 cc. of 2-allyl-4-methylphenol (b. p. 116–118° (15 mm.); soluble in 20% alkali) and 15 cc. of 2,6-diallyl-4-methylphenol, b. p. 134–141° (15 mm.). The latter absorbed bromine readily.

This 15-cc. fraction was characterized as diallyl-*p*-cresol by hydrogenation to dipropyl-*p*-cresol. It was diluted with 15 cc. of methanol and 0.05 g. of platinum oxide catalyst[10] was added. Hydrogen was absorbed rapidly and exothermically during fifteen minutes. Distillation at 20 mm. yielded 4 cc. at 132–139°, 6 cc. at 139–145°, residue 2 cc. The refractive index, $n^{24}\mathrm{D}$ 1.5110, of the 6-cc. fraction checks with the value for pure 2,6-dipropyl-4-methylphenol (below). It did not absorb bromine. Also, in reaction with allyl bromide and alcoholic sodium hydroxide, it yielded the allyl ether (IX), b. p. 148–151° (22 mm.), $n^{25}\mathrm{D}$ 1.5002. The pyrolytic behavior of this ether was the same as that described below for IX.

2-Propyl-4-methylphenol (V).—This compound was prepared by hydrogenation of 2-allyl-4-methylphenol with the platinum oxide catalyst. About 0.1 g. of the catalyst was used for a 0.2-mole run, the phenol being diluted in an equal volume of alcohol. Heat was evolved during the hydrogenation. The catalyst maintained its activity for several runs. In all, 341 g. of allylcresol gave rise to 295 g. (86%) of the propylcresol, after distillation. The physical properties: b. p. 121–123 (18 mm.), d^{20}_4 0.983, $n^{23}\mathrm{D}$ 1.5238, compare with values in the literature.[11] The phenylurethan[12] melted at 100°.

2-Propyl-4-methylphenoxyacetic Acid.—This chloroacetic acid derivative was prepared in the customary manner with a yield of 0.5 g. from 1 g.; m. p. 114–115°. A mixed melting point determination with 2-allyl-4-methylphenoxyacetic acid revealed a lowering of 5°. The Baeyer unsaturation test was negative toward 0.06 g. of the substance but when 0.001 g. of 2-allyl-4-methylphenoxyacetic acid was added, there was an immediate brown coloration (MnO_2).

Neutr. Eq. Calcd. for $C_{11}H_{15}OCOOH$: 208. Found: 208, 207. *Anal.* (by M. A. Pollack) Calcd. for $C_{12}H_{16}O_3$: C, 69.2; H, 7.75. Found: C, 68.5; H, 7.48.

Allyl 2-Propyl-4-methylphenyl Ether (VI).—A homogeneous mixture of 152 g. (1.01 moles) of 2-propyl-4-methylphenol, 41 g. of sodium hydroxide and 150 cc. each of acetone and water was cooled to 0° and 123 g. of cold allyl bromide was added through a reflux condenser. Another 75-cc. portion of acetone was required to make the mixture homogeneous. At about 10° the solution became cloudy and two layers formed within five minutes. After fifteen minutes of refluxing, reaction was practically complete. Only 5 cc. of unreacted propylcresol was recovered from the aqueous layer. The yield of the desired ether in the insoluble layer was 153 g. or 82%. These physical constants were obtained: b. p. 123–124 (16 mm.), $n^{20}\mathrm{D}$ 1.5153, d^{20}_4 0.943.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.06; H, 9.46.

The ether was also prepared by Claisen's method, acetone and potassium carbonate, rather than aqueous acetone and sodium hydroxide. The yield, after ten hours of refluxing, was 73%.

2-Allyl-6-propyl-4-methylphenol (VII).—A bath maintained for forty-five minutes at 230° and then for thirty minutes at 275° was used to heat 141 g. of (VI). An atmosphere of nitrogen was maintained throughout. The maximum temperature of the reaction liquid was 252°. Three fractional distillations (at 17 mm.) of the product gave these fractions: (1) 121–124°, 22 cc. of V (soluble in 20% aq. KOH); (2) 124–138°, 8 cc., partially soluble in alkali; (3) 138–144°, 98 cc. (94 g.) of VII, insoluble in alkali; (4) higher-boiling residue, 15 cc. The yield of 2-

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[7] Claisen and Eisleb, *Ann.*, **401**, 36, 44 (1913).

[8] Claisen, *Ann.*, **441**, 44 (1913), reports b. p. 112 (12 mm.), d^{15}_4 1.006, $n^{16}\mathrm{D}$ 1.5424.

[9] Koelsch, THIS JOURNAL, **53**, 304 (1931).

[10] "Organic Syntheses," Coll. Vol. **I**, 1932, p. 53.

[11] V. Braun, Bayer and Blessing, *Ber.*, **57**, 392 (1924).

[12] Hill and Graf, THIS JOURNAL, **37**, 1840 (1915), reported a m. p. of 99°.

propyl-4-methylphenol (fractions 1 and 2) was 24%, and that of VII was 67%.

These physical properties were observed for 2-allyl-6-propyl-4-methylphenol: b. p. 135° (13 mm.), 140° (17 mm.), 145° (22 mm.); n^{20}_D 1.5235, n^{22}_D 1.5226; d^{20}_4 0.961. It was insoluble in 20% aqueous potassium hydroxide solution. An attempt to make the chloroacetic acid derivative (using alcoholic sodium hydroxide) was unsuccessful.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.0; H, 9.54. Found: C, 81.7; H, 9.40.

2,6-Dipropyl-4-methylphenol, VIII.—This phenol was prepared by hydrogenation of VII, with platinum oxide as catalyst. The yields were high. In a typical run 84 g. (b. p. 135–145° at 17 mm.) yielded 81 g. of product (b. p. 135–145° at 17 mm.), 62 g. of which distilled at 138–142° (17 mm.). Constants on the 138–142° fraction were: n^{25}_D 1.5122, d^{20}_4 0.950, m. p. 21°. No derivative could be obtained with chloroacetic acid, and no reaction occurred on heating with a mixture of phthalic anhydride and sulfuric acid. It was insoluble in aqueous or aqueous-alcoholic potassium hydroxide and it was inert toward bromine.

Anal. (Zerewitinoff). Calcd. for $C_{13}H_{19}OH$: OH, 1.00. Found: OH, 1.01, 1.08. (Combustion). Calcd. for $C_{13}H_{20}O$: C, 81.2; H, 10.54. Found: C, 80.9; H, 10.14.

Dinitrobenzoate of VIII.—Two grams of VIII, 2.3 g. of 3,5-dinitrobenzoyl chloride and 20 cc. of pyridine were refluxed for an hour and the product worked up in the usual way.[13] The 2,6-dipropyl-4-methylphenyl 3,5-dinitrobenzoate, after crystallization from alcohol, melted at 96° (light yellow needles).

Anal. (Dumas). Calcd. for $C_{20}H_{22}O_6N_2$: N, 7.26. Found: N, 7.41.

Allyl 2,6-Dipropyl-4-methylphenyl Ether, IX.—No reaction occurred between VIII, allyl bromide, acetone and potassium carbonate during a ten-hour refluxing period (Claisen's method). The modified method gave a 74% yield of IX.

Equivalent amounts of sodium hydroxide, allyl bromide (an excess taken), and VIII (80 cc.) were dissolved in 240 cc. of 95% ethanol. The mixture was refluxed for two hours. On working up the product (addition of water, separation of the insoluble layer, fractional distillation at 17 mm.) there was recovered 16 cc. of VIII (19% of the original), b. p. 135–145°, and there was obtained 55 cc. (74% yield) of IX, b. p. 147–154°. The residue was 10 cc. A fraction, b. p. 148° (15 mm.), possessed these constants: n^{25}_D 1.5020, d^{20}_4 0.915. The material absorbed bromine in quantity.

Anal. Calcd. for $C_{16}H_{24}O$: C, 82.6; H, 10.42. Found: C, 82.2; H, 10.24.

Pyrolysis of IX.—A quantity of the ether (10–15 g.) was placed in a 50-cc. distilling flask attached to the system shown in Fig. 1. The spiral condenser was cooled by crushed ice. The receiver, to collect the diallyl, was a side-arm test-tube cooled to −5° by ice and salt. The gas passed on through a mercury trap, and was collected in a 250-cc. bulb over 30% aqueous potassium hydroxide solution. Prior to a run, the atmosphere was completely displaced by carbon dioxide. At the end of the run, all of the gas was displaced into the 250-cc. bulb by the carbon dioxide stream, the manipulation being similar to that for the nitrometer in the familiar Dumas determination of nitrogen.

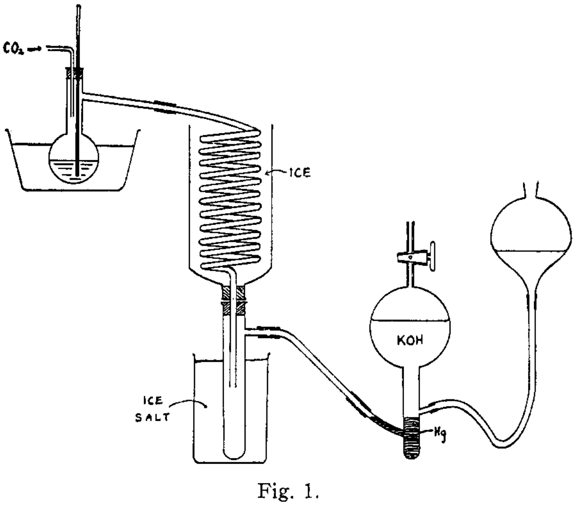

Fig. 1.

The reaction flask was heated to 220° by a salt-bath at 250°, at which time gas bubbles started to be evolved. Then, during twenty minutes, the bath temperature was raised to 290°. The reaction mixture turned brown and refluxed at 262–270° (inside temp.), at which stage the evolution of gas had ceased.

Four runs were made. A total of 49.5 g. of IX yielded these products: diallyl, 5 cc.; gas, 710 cc. (27°, 745 mm., vapor pressure of the potassium hydroxide solution at 27°, 21.3 mm.). Thus, about one-eighth of a mole of gas was formed per mole of the ether.

The diallyl was characterized by its typical odor, by physical constants (b. p. 60–63°, n^{20}_D 1.4060), and by conversion to diallyl tetrabromide, m. p. (and mixed m. p.) 53–55°. A few drops of diallyl added to mercuric chloride solution gave a heavy white precipitate. Propylene gave no precipitation after standing with mercuric chloride solution for a week.

The residues from the four runs were distilled *in vacuo*. There was obtained 21 cc. of VIII (b. p. 139–150° (18 mm.), n^{22}_D 1.5121), 4 cc. of substance boiling at 150–175°, n^{22}_D 1.5145, and a heavy, tarry residue. 3,5-Dinitrobenzoate of VIII was used for identification: m. p. and mixed m. p., 96°.

Identification of the Gas by Bromide–Bromate Titration.—The analytical method of Davis and co-workers[14] was used and the solutions made up as directed. The potassium bromide–bromate solution was 0.535 *N*. The method was tested on pure propylene and pure allene[15] before applying it on the gas from the reaction. The data are summarized in Table I.

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[13] Phillips and Keenan, This Journal, **53**, 1926 (1931).

[14] Davis, Crandall and Higbee, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 108 (1931).

[15] Prepared from dibromopropene and zinc dust: Hurd, Meinert and Spence, This Journal, **52**, 1143 (1930).

TABLE I

ANALYTICAL DATA

Gas	Volume cc., S.T.P.	Volume Moles	KBr-KBrO$_3$ soln. Cc.	KBr-KBrO$_3$ soln. Moles Br$_2$	Double bonds
Propylene	86	0.00384	14.56	0.00390	1.01
Allene	105	.00469	34.60	.00926	1.97
From Reaction	129	.00578	24.70	.00661	1.14
From Reaction	146	.00652	27.00	.00722	1.11

Pseudo-nitrosites.—Two hundred cc. of propylene gas was confined for one to two days in a tube with 0.5 cc. of liquid nitrogen trioxide and 3–4 cc. of absolute ether. The propylene pseudo-nitrosite[16] which separated was crystallized from ethyl acetate; m. p. 120°; yield 0.2 g. The crystals did not decompose in a week. Allene pseudo-nitrosite,[17] m. p. 88°, was prepared similarly in about 0.1-g. yield. These crystals decomposed within twenty-four hours. The precipitate which formed from 200 cc. of a 3:2 mixture of propylene and allene was 0.1 g. of propylene pseudo-nitrosite, m. p. 120°. In another experiment 2 drops of diallyl was added to the mixture of ether and nitrogen trioxide before absorbing 160 cc. of propylene gas. The pseudo-nitrosite obtained in this case was a yellow, non-crystallizable oil, n^{25}D 1.469.

Two 200-cc. samples of the gas from the reaction were treated similarly with the nitrogen trioxide reagent. Here, also, a yellow, non-crystallizable oil, n^{25}D 1.460, was obtained.

Summary

These new compounds have been prepared: 2,6-dipropyl-4-methylphenol, 2-allyl-6-propyl-4-methylphenol, allyl 2-propyl-4-methylphenyl ether, allyl 2,6-dipropyl-4-methylphenyl ether, 2,6-dipropyl-4-methylphenyl 3,5-dinitrobenzoate, 2-allyl-4-methylphenoxyacetic acid, and 2-propyl-4-methylphenoxyacetic acid.

During the rearrangement of allyl *p*-cresyl ether into 2-allyl-4-methylphenol, some 2,6-diallyl-4-methylphenol is formed concurrently.

Propylene, not allene, is the gas evolved during pyrolysis of allyl 2,6-dipropyl-4-methylphenyl ether.

EVANSTON, ILLINOIS RECEIVED JUNE 7, 1937

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[16] Demjanov, *J. Russ. Phys.-Chem. Soc.*, **33**, 275 (1901); *Chem. Zentr.*, **72**, II, 338 (1901).

[17] Demjanov and Ivanov, *Compt. rend. acad. sci.* (U. R. S. S.) [N. S.], **1**, 318 (1934); *C. A.*, **28**, 4374 (1934).

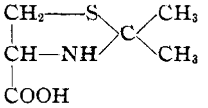
[CONTRIBUTION FROM THE BIOCHEMICAL RESEARCH FOUNDATION OF THE FRANKLIN INSTITUTE]

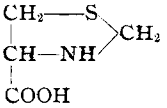
The Reaction of Cysteine with Acetone. A Note on the Titration of Cysteine by the Acetone–Hydrochloric Acid Method of Linderstrøm-Lang

BY GLADYS E. WOODWARD AND E. F. SCHROEDER

During the course of experiments on the enzymatic hydrolysis of glutathione,[1] it was observed that amino acid titrations performed on the reaction mixtures by the Linderstrøm-Lang acetone–hydrochloric acid method[2] were generally much lower than those carried out by other methods.[3,4] The results obtained with the former indicated that only one of the peptide linkages of the glutathione molecule was being hydrolyzed, while the latter methods gave values agreeing closely with the theoretical for complete hydrolysis of both linkages.

Further study of this anomalous situation has shown that cysteine, one of the constituent amino acids of the glutathione, reacts with acetone under the conditions of the titration to form the condensation product, 2,2-dimethylthiazolidine-4-carboxylic acid (I), which does not titrate in the Linderstrøm-Lang method. The structure of this compound, which could be isolated in good yield from cysteine–acetone reaction mixtures, is established by the following observations: (a) the empirical formula is $C_6H_{11}O_2NS$; (b) the amino group is absent, since the compound does not titrate with hydrochloric acid in the Linderstrøm-Lang method; (c) depression of the iodine uptake of the compound, as compared to cysteine, shows that the $-SH$ group also is bound; (d) after hydrolysis of the compound in aqueous solution, acetone and cysteine (as insoluble cystine) can be recovered in nearly quantitative, equimolar amounts.


I


II

The reaction between cysteine and acetone is analogous to that recently described by Schubert[5] and later characterized by Ratner and Clarke,[6] in which cysteine reacts with formaldehyde to yield thiazolidine-4-carboxylic acid (II).

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[1] Schroeder and Woodward, *J. Biol. Chem.*, in press.

[2] Linderstrøm-Lang, *Z. physiol. Chem.*, **173**, 32 (1928).

[3] Harris, *J Biol. Chem.*, **84**, 296 (1929).

[4] Linderstrøm-Lang, Weil and Holter, *Z. physiol. Chem.*, **233**, 174 (1935).

[5] Schubert, *J. Biol. Chem.*, **114**, 341 (1936).

[6] Ratner and Clarke, THIS JOURNAL, **59**, 200 (1937).