## 66. *2-Phenylbutadiene from α-Methylstyrene.*

By E. G. E. Hawkins and R. D. Thompson.

The Prins reaction of α-methylstyrene, when carried out in acetic acid solution, has been found to give 3-phenylbut-2-enyl acetate, in addition to the 3-phenylbut-3-enyl acetate and 4-acetoxy-2-phenylbutan-2-ol previously reported. Pyrolysis of these phenylbutenyl acetates provides many by-products in addition to 2-phenylbutadiene, and a more satisfactory route to the diene involves catalytic dehydration of the isomeric phenylbutenols with iodine.

Conversion of the phenylbutenols into the corresponding chlorides and ethers has been studied. A second crystalline isomer of 2-phenylbutadiene dimer has been isolated.

It has been reported by Price *et al.*[1] that treatment of α-methylstyrene with paraformaldehyde in boiling acetic acid for three hours, followed by removal of half of the acid and further heating after addition of acetic anhydride, gives a 70% yield of 3-phenylbut-3-enyl acetate, which could be converted into 2-phenylbutadiene on pyrolysis. Other workers, by pyrolysis of phenylbutenyl acetate prepared in this way, have claimed diene yields of 34% [2] and " nearly quantitative " (on recycle).[3]

Repetition of the reaction between α-methylstyrene and paraformaldehyde, under the conditions used by Price *et al.*, was found to yield a 3—4 : 1 mixture of 3-phenylbut-3- and -2-enyl acetate, in addition to some of the presumed precursor, 4-acetoxy-2-phenylbutan-2-ol, through its incomplete dehydration, and residues. Proof of the structure of the 3-phenylbut-2-enyl acetate, which was separated from its lower-boiling isomer by fractional distillation, was based on spectroscopic evidence together with the results of ozonolysis (to give acetophenone) and hydrogenation (to 3-phenylbutyl acetate). In view of the evidence of St. Pfau and Plattner [4] that dehydration of 1,3-diols (including 3-phenylbutane-1,3-diol) by acetic anhydride yields only βγ-unsaturated alcohols, the production of the ester of this αβ-unsaturated alcohol is unexpected: however, it was confirmed that dehydration of 4-acetoxy-2-phenylbutan-2-ol by acetic anhydride yielded a similar mixture of phenylbutenyl acetates.

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[1] Price, Benton, and Schmidle, *J. Amer. Chem. Soc.*, 1949, **71**, 2860.

[2] Grummitt and Leaver, *J. Amer. Chem. Soc.*, 1952, **74**, 1595.

[3] Meek, Merrow, Ramey, and Cristol, *J. Amer. Chem. Soc.*, 1951, **73**, 5563.

[4] St. Pfau and Plattner, *Helv. Chim. Acta*, 1932, **15**, 1250.

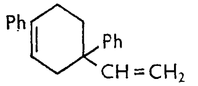
When α-methylstyrene and paraformaldehyde were heated for 1 hr. in acetic acid alone the product consisted of a mixture of the phenylbutenyl acetates and the glycol acetate, together with some of the free phenylbutenols.

Pyrolysis of the phenylbutenyl acetates, either separately or as a mixture, proved to be an unsatisfactory method of preparing 2-phenylbutadiene. These esters were dropped, either neat or in a diluent, down a heated glass or stainless steel tube, in a nitrogen atmosphere, and even when an inert column packing (glass beads) and optimum temperature (425—475°) and contact time were used, yields of diene never exceeded *ca.* 40%. The phenylbutadiene was always accompanied by α-methylstyrene and higher-boiling materials. Replacement of the inert column packing by active materials (*e.g.*, alumina or phosphoric acid on kieselguhr) led to a mixture of aromatic hydrocarbons, including ethylbenzene, cumene, naphthalene, and biphenyl.

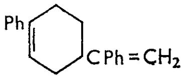
When mixed phenylbutenyl acetates, containing some of the free alcohols and glycol acetate, was recycled to the pyrolysis system (glass beads) a number of times and the final products were fractionated these contained, in addition to acetic acid, 2-phenylbutadiene, and unchanged material, also α-methylstyrene, 1-methylindene, acetophenone, 2-phenylbut-3-en-2-ol, and phenylbutadiene dimers, as well as a number of unidentified materials and polymeric residue. The 1-methylindene probably arose by cyclisation of a phenylbutenol or its ester, but in order to cast light on the sources of the other by-products of pyrolysis a number of related compounds were individually pyrolysed under similar, non-catalysed conditions.

Both 3-phenylbut-3- and -2-en-1-ol underwent a reverse Prins reaction, the latter more sluggishly, at 450—550°, to give mainly α-methylstyrene and formaldehyde, whilst 2-phenylbut-3-en-2-ol yielded a mixture including acetophenone and 1-methylindene and much polymeric material. The glycol acetate (4-acetoxy-2-phenylbutan-2-ol) also provided a mixture which contained some α-methylstyrene and acetic acid but whose largest constituent (40—45%) was 2-phenylbut-3-en-2-ol: its formation implied that loss of acetic acid from the primary acetate group was faster under these conditions than the dehydration of the tertiary alcohol. The free glycol, at 500°, also gave small quantities of α-methylstyrene but, surprisingly, was converted mainly into acetophenone: ethylene could not be detected in the exit gases, although either it or ethanol might have been expected.

Formation of 2-phenylbutadiene dimers under the conditions of pyrolysis is not unexpected: the monomer dimerises even at *ca.* 0°, and more rapidly at higher temperatures. Alder and Haydn,[5] who had previously noted the ease of dimerisation of this diene, isolated only one, (I), of the four possible isomers as a crystalline product. In the present work it was found that although compound (I), m. p. 61—62°, was the major constituent a second crystalline component (II), m. p. 56·5—58°, could be separated: its structure was confirmed by spectroscopic study and by dehydrogenation to 4-α-methylbenzylbiphenyl which was synthesised for comparison.



(I)



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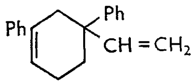

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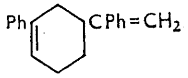

(IV)

Attempts were also made to obtain 2-phenylbutadiene by preparation and dehydrochlorination of the isomeric 4-chloro-2-phenylbutenes. Reaction of 3-phenylbut-3-en-1-ol with thionyl chloride in (i) dimethylaniline at 0°, (ii) benzene under reflux, and (iii) dimethylaniline and benzene at 0° gave some of the corresponding chloride, but the crude product was unstable on distillation and yielded varying amounts of 2-phenylbutadiene and its dimers on fractionation. Goering, Nevitt, and Silversmith's method,[6] namely,

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[5] Alder and Haydn, *Annalen*, 1950, **570**, 201.

[6] Goering, Nevitt, and Silversmith, *J. Amer. Chem. Soc.*, 1955, **77**, 4042.

reaction in ether at room temperature, gave 70—75% yields of the chloride. This reaction afforded also a small amount of 3-phenylthiophen, identified by synthesis. 3-Phenylbut-2-en-1-ol was similarly converted into its chloride, which appeared to be even more unstable than its isomer.

Dehydrochlorination of 4-chloro-2-phenylbut-1-ene by basic reagents proved difficult. It did not react with potassium hydroxide or sodium methoxide at room temperature, and only slightly under reflux. Use of sodium butoxide in boiling butan-1-ol led to decomposition, but little 2-phenylbutadiene was isolated: the main products were the diene dimer and butyl phenylbutenyl ether. Dimethylaniline at 300° and solid potassium hydroxide at 170° also had little effect, but yields of 50—60% of phenylbutadiene were obtained by use, at 140°, of sodium dissolved in diethylene glycol. By contrast, it has been reported [7] that 3-chloro-3-phenylbut-1-ene is dehydrochlorinated to 2-phenylbutadiene when heated with pyridine.

The most convenient route to 2-phenylbutadiene involved dehydration of the isomeric phenylbutenols or 3-phenylbutane-1,3-diol by heating them with catalytic amounts of iodine. Yields of the monomeric diene were usually 80—85%; it was free from α-methylstyrene, and the only other product appeared to be the diene dimer (as residue). 3-Phenylbut-2-en-1-ol is dehydrated, under these conditions, more rapidly than its isomer, whilst by suitable choice of column take-off temperature during the dehydration of the glycol a mixture of the intermediates, 3-phenylbut-3- (70%) and -2-en-1-ol (30%), was obtained in the distillate.

Treatment of 2-phenylbut-3-en-2-ol with dilute sulphuric acid provided mainly di-(3-phenylbut-2-enyl) ether; the intermediate alcohol, 3-phenylbut-2-en-1-ol, formed by anionotropic rearrangement of the tertiary alcohol, was also found in the product, and its acetate was obtained when the sulphuric acid was replaced by a mixture of acetic acid and anhydride. When ethanol was used as reaction solvent the major product was the ethyl ether of 3-phenylbut-2-en-1-ol. Examination by gas-phase chromatography showed that the latter alcohol with ethanol in the presence of hydrochloric acid gave 4-ethoxy-2-phenylbut-1-ene (*ca.* 12%) and *cis*- and *trans*-4-ethoxy-2-phenylbut-2-ene (88%). 3-Phenylbut-3-en-1-ol, when treated similarly, was partially converted into 3-phenylbut-2-en-1-ol and its ethyl ethers. Hydrogenation of the mixed ether isomers yielded solely ethyl 3-phenylbutyl ether, identical with a sample synthesised from 3-phenylbutyl chloride and sodium ethoxide.

In the absence of a reactive solvent acid-catalysed reaction of the phenylbutenols gave a high-boiling product. Although this gave no ether band in its infrared spectrum it was shown to be di-(3-phenylbut-2-enyl) ether (*a*) by synthesis from 3-phenylbut-2-enyl chloride and sodium 3-phenylbut-2-enyl oxide, and (*b*) by hydrogenation of it and the synthetic ether to the same di-(3-phenylbutyl) ether (having an ether band in the infrared spectrum) which was also obtained, in poor yield, by Williamson synthesis.

3-Phenylbut-3-en-1-ol with formic acid provided the formate in good yield, whereas 3-phenylbut-2-en-1-ol, under similar conditions, gave a poor yield of ester together with high-boiling ethers.

## EXPERIMENTAL

*Reaction of α-Methylstyrene, Paraformaldehyde, and Acetic Acid.*—(*a*) (Cf. ref. 1.) Paraformaldehyde (110 g.), α-methylstyrene (354 g.), and acetic acid (1 l.) were heated together under reflux for 3 hr., part of the acetic acid (500 c.c.) was evaporated at normal pressure and replaced by acetic anhydride (500 c.c.), and heating was continued for a further 3 hr. The crude phenylbutenyl acetate (262 g.), b. p. 130—150°/15 mm., was separated by flash distillation. A number of similar batches were combined and fractionated in a 4 ft., helices-packed, heated column, to give main fractions: (i) (*ca.* 75%) b. p. 135°/13 mm., $n_D^{20}$ 1·5233; (ii) (*ca.* 25%) b. p. 144—145°/13 mm., $n_D^{20}$ 1·5335.

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[7] Marvel and Woolford, *J. Org. Chem.*, 1958, **23**, 1658.

Fraction (i) was 3-phenylbut-3-enyl acetate (Found: C, 75·5; H, 7·4. Calc. for $C_{12}H_{14}O_2$: C, 75·8; H, 7·4%): the presence of vinyl and acetate groups was confirmed by the infrared spectrum, and ozonolysis yielded formaldehyde (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 163—166°). Hydrolysis with aqueous-alcoholic potassium hydroxide yielded 3-phenylbut-3-en-1-ol, b. p. 130—131°/13 mm., $n_D^{20}$ 1·5581 (Found: C, 79·9; H, 8·2. Calc. for $C_{10}H_{12}O$: C, 81·1; H, 8·1%), which provided a 3,5-*dinitrobenzoate*, m. p. 77—78° (from ethanol) (Found: C, 59·3; H, 4·2; N, 7·8. $C_{17}H_{14}N_2O_6$ requires C, 59·7; H, 4·1; N, 8·2%), and a *phenylurethane*, m. p. 46—48° (Found: C, 76·1; H, 6·5; N, 5·1. $C_{17}H_{17}NO_2$ requires C, 76·4; H, 6·4; N, 5·2%). Hydrogenation of the alcohol (5 g.) in the presence of Adams catalyst gave 3-phenylbutanol (4·5 g.), b. p. 117—120·5°/12 mm., $n_D^{20}$ 1·5190 (3,5-dinitrobenzoate, m. p. and mixed m. p. 73—74°).

Fraction (ii) consisted of 3-phenylbut-2-enyl acetate; its infrared and ultraviolet spectra were in agreement with this, and ozonolysis gave acetophenone (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 242—244°). Hydrolysis yielded 3-*phenylbut*-2-*en*-1-*ol*, b. p. 142—145°/15 mm., $n_D^{20}$ 1·5698 (Found: C, 79·9; H, 8·2%), which afforded a 3,5-*dinitrobenzoate*, m. p. 143—145° (from acetone) (Found: C, 59·6; H, 4·14; N, 8·2%), and a *phenylurethane*, m. p. 80—82° (from ethanol–light petroleum) (Found: C, 76·2; H, 6·6; N, 5·1%). Catalytic hydrogenation gave, as before, 3-phenylbutanol, $n_D^{20}$ 1·5181 (3,5-dinitrobenzoate as above).

(*b*) α-Methylstyrene (118 g.), paraformaldehyde (36 g.), and acetic acid (333 c.c.) were heated under reflux for 1 hr., the acid removed under reduced pressure, and the residue fractionated. There were obtained (i) α-methylstyrene (6·0 g.), (ii) fractions (48·4 g.) consisting of a mixture of 3-phenylbut-3- and -2-enyl acetate together with some of the corresponding alcohols and 4-methyl-4-phenyl-1,3-dioxan (7%), (iii) 4-acetoxy-2-phenylbutan-2-ol (68·4 g.), b. p. 160—165°/13 mm., $n_D^{20}$ 1·5147 (Found: C, 69·3; H, 7·8. Calc. for $C_{12}H_{16}O_3$: C, 69·2; H, 7·7%), and (iv) high-boiling materials (7·7 g.).

Hydrolysis of 4-acetoxy-2-phenylbutan-2-ol (100 g.) yielded the corresponding glycol (60·5 g.), b. p. 167°/12 mm., $n_D^{20}$ 1·5393 (Found: C, 72·9, 72·8; H, 8·5, 8·6. Calc. for $C_{10}H_{14}O_2$: C, 72·3; H, 8·4%), which provided a *monophenylurethane*, m. p. 110—112° (from benzene–light petroleum) (Found: C, 72·0; H, 6·7; N, 5·0. $C_{17}H_{19}NO_3$ requires C, 71·6; H, 6·7; N, 4·9%). An attempt to prepare the 3,5-dinitrobenzoate of this glycol brought about dehydration and there was isolated the slightly impure derivative of 3-phenylbut-2-en-1-ol, m. p. 136—138°, undepressed on admixture with an authentic sample (Found: C, 60·0; H, 4·3; N, 8·0%).

*Pyrolysis of Phenylbutenyl Acetates.*—(*a*) The acetate (usually 25 g.) (3-phenylbut-3- or -2-enyl or the mixed ester) was allowed to drop slowly, in a stream of nitrogen, into a 2 ft. tube (of glass or stainless steel), which was heated in a furnace: the tube temperature was recorded by means of a thermocouple. The tube was packed to various depths, with glass beads, porcelain saddles, or activated alumina, and experiments were made with different temperatures and feed rates. The products, condensed in a carbon dioxide-cooled receiver, were distilled and examined spectroscopically. Selected results are given in Table 1.

TABLE 1.

| Isomer used * | Wt. (g.) | Diluent | Length packed † (in.) | Temp. | Time (min.) | Product (g.) Phenylbutadiene ‡ | Product (g.) High-boiling material |
|---|---|---|---|---|---|---|---|
| 3 | 25 | — | 24 | 400° | 85 | 0·9 | 18·3 |
| 3 | 25 | — | 7½ | 450 | 70 | 5·5 | 13·4 |
| 3 | 25 | — | 24 | 475 | 20 | 7·2 | 10·2 |
| 3 | 25 | — | 1½ | 500 | 65 | 7·2 | 13·6 |
| 2 | 25 | — | 1½ | 500 | 110 | 7·7 | 8·0 |
| 3 | 25 | — | 1½ | 550—575 | 25 | 5·1 | 12·4 |
| 3 | 25 | Benzene (20 g.) | 7½ | 400 | 105 | 0·5 | 23·6 |
| 3 | 25 | ,, | 7½ | 450 | 120 | 5·5 | 11·9 |
| 2 | 25 | ,, | 7½ | 450 | 65 | 7·7 | 9·8 |
| 3 | 25 | Benzene | 7½ | 450 | 150 | 6·0 | 13·1 |

* 3 = 3-Phenylbut-3-enyl acetate; 2 = 3-Phenylbut-2-enyl acetate. † Beads.
‡ Contains α-methylstyrene in varying amounts.

Addition of various metal salts or antioxidants to the feed did not appreciably reduce the proportion of high-boiling products. When the tube contained activated alumina as packing the product at 300—450° was cumene (in low yield), containing ethylbenzene and α-methylstyrene; at 550—600° naphthalene and biphenyl were formed.

(*b*) Mixed isomers of phenylbutenyl acetate were pyrolysed in batches of 400 g. in a tube at 450° containing 7½ in. of glass beads (reaction time *ca.* 4½ hr.). The product was flash-distilled: the portion boiling at <100°/15 mm. was fractionated to separate it into acetic acid, α-methylstyrene, and 2-phenylbutadiene, and the material (A) with b. p. between that of the diene and 100°/15 mm. was set aside. The material with b. p. 100—200°/15 mm. was recycled for pyrolysis, after being made up with fresh ester; after three recycles it was set aside (B). All the residual material (b. p. >200°/15 mm.), containing polymers, was discarded. The material was refractionated, with results as in Table 2. Many of these fractions were complex mixtures, (A + B) not resolved by gas-phase chromatography, but the main constituents were evaluated by this means and by their infrared spectra. Fraction 1 consisted largely of 2-phenylbutadiene, fractions 9—11 of 4-methyl-4-phenyldioxan (present in the feed), and fractions 11—13 of unchanged phenylbutenyl acetates.

TABLE 2.

| Fr. | B. p./13 mm. | Wt. (g.) | $n_D^{20}$ | Fr. | B. p./13 mm. | Wt. (g.) | $n_D^{20}$ |
|---|---|---|---|---|---|---|---|
| 1 | 64—71° | 13·5 | 1·5445 | 7 | 100—112° | 9·7 | 1·5579 |
| 2 | 71—75 | 5·0 | 1·5445 | 8 | 112—118 | 11·7 | 1·5565 |
| 3 | 75—80 | 7·2 | 1·5480 | 9 | 118—122 | 17·9 | 1·5470 |
| 4 | 80—87 | 26·7 | 1·5558 | 10 | 122—124 | 20·5 | 1·5425 |
| 5 | 87—95 | 7·5 | 1·5529 | 11 | 124—132 | 14·2 | 1·5385 |
| 6 | 95—100 | 32·4 | 1·5459 —1·5465 | 12 | 132—140 | 13·7 | 1·5380 |
|  |  |  |  | 13 | 140—155 | 4·0 | 1·5480 |

Fraction 4 was redistilled to give 1-methylindene, b. p. 199—200°, $n_D^{20}$ 1·5535, identical spectroscopically (infrared) with material, b. p. 81—85°/11 mm., synthesised by reaction of indan-1-one with methylmagnesium iodide. The product of this Grignard reaction was separated by fractionation into 1-methylindene, 1-methylindanol, and unchanged indan-1-one. Catalytic hydrogenation (Adams catalyst) of a portion of fraction 4 yielded 1-methylindane, b. p. 68—72°/13 mm., $n_D^{20}$ 1·5200, identified by its infrared spectrum.

Fraction 6 was refractionated, to give 2-phenylbut-3-en-2-ol, b. p. 212—215°, $n_D^{20}$ 1·5445, identical spectroscopically (infrared) with that obtained by pyrolysis of 4-acetoxy-2-phenylbutan-2-ol (see below).

Redistillation of the stored 2-phenylbutadiene, obtained from this series of pyrolyses, left a residue of dimer which had b. p. 210—220°/14 mm. Fractional crystallisation from ethanol and methanol yielded three batches (A), (B), and (C) of solid. (A) had m. p. 61—62° (Found: C, 92·3, 92·2; H, 7·65, 7·7. Calc. for $C_{20}H_{20}$: C, 92·3; H, 7·7%), and its ultraviolet and infrared spectra were in agreement with the structure of the dimer isolated by Alder and Haydn,[5] 1,4-diphenyl-4-vinylcyclohex-1-ene. When heated for 10 hr. at 320° with 5% palladium–charcoal it gave *p*-terphenyl, m. p. 210—212° (from chloroform) (Found: C, 94·2; H, 6·1. Calc. for $C_{18}H_{14}$: C, 93·9; H, 6·1%), identified spectroscopically.

Solid (B) had m. p. 56·5—58° (Found: C, 91·9; H, 7·6%). Its infrared spectrum disclosed an αα-disubstituted vinyl group, and ultraviolet spectroscopy indicated a vinylbenzene system. It was shown to be α-(4-phenylcyclohex-3-enyl)styrene (II) by dehydrogenation, as above, to 4-*α-methylbenzylbiphenyl*, m. p. 61·5—63° (from methanol) (Found: C, 93·0; H, 7·0. $C_{20}H_{18}$ requires C, 93·0; H, 7·0%), which was synthesised, for comparison, by the following steps: (i) Friedel–Crafts reaction between benzoyl chloride and biphenyl[8] gave 4-benzoylbiphenyl, m. p. 100—101°; (ii) reaction of this with methylmagnesium iodide[9] provided 4-biphenylyl-α-methylbenzyl alcohol, m. p. 102—104°; (iii) dehydration with sulphuric acid in acetic acid[9] gave α-4-biphenylylstyrene, m. p. 95—96°; and (iv) catalytic hydrogenation of this olefin (Adams catalyst) gave 4-α-methylbenzylbiphenyl, m. p. and mixed m. p. 62—63° (identical spectra).

Compound (C) had m. p. 40—44°, and was shown spectroscopically to be a 7 : 3 mixture of (A) and (B) although attempts at separation by crystallisation failed.

In addition to materials (A—C) a non-crystalline portion remained, but dehydrogenation gave a product in which only *p*-terphenyl could be identified.

[8] Schlenk and Bergmann, *Annalen*, 1928, **463**, 120.
[9] Schlenk and Bergmann, *Annalen*, 1928, **464**, 22.

*Pyrolysis of* 3-*Phenylbut*-3-*en*-1-*ol*.—The alcohol (25 g.) was dropped through a 2 ft. tube, containing 7½ in. of glass beads and heated to 450°, during 1 hr., and the condensed product distilled. The distillate (16·1 g.), b. p. 53°/12 mm., $n_D^{20}$ 1·5380, was shown spectroscopically to be α-methylstyrene. During the pyrolysis and distillation paraformaldehyde crystallised on the colder surfaces.

*Pyrolysis of* 3-*Phenylbut*-2-*en*-1-*ol*.—Use of the above conditions led to little reaction, but when the column temperature was raised to 550° the phenylbutenol (15 g.) yielded paraformaldehyde and fractions: (i) (3·2 g.) b. p. <55—60°/12 mm., $n_D^{20}$ 1·5346; (ii) (1·0 g.) b. p. 60—80/12 mm., $n_D^{20}$ 1·5502; (iii) (1·4 g.) b. p. 80—122°/12 mm., $n_D^{20}$ 1·5620; (iv) (3·3 g.) b. p. 122—137°/12 mm., $n_D^{20}$ 1·5633; and residue (1·1 g.). Spectroscopy showed that fractions (i) and (ii) contained α-methylstyrene, biphenyl, 1-methylindene, and other aromatic hydrocarbons, whilst fraction (iv) was unchanged phenylbutenol.

*Pyrolysis of* 2-*Phenylbut*-3-*en*-2-*ol*.—The alcohol (15 g.), pyrolysed over glass beads at 550°, yielded fractions shown spectroscopically to contain acetophenone and 1-methylindene; much dark red residue (7·2 g.), remained.

*Pyrolysis of* 4-*Acetoxy*-2-*phenylbutan*-2-*ol*.—The glycol monoacetate (300 g.) was pyrolysed in the system described above, at 500°, during 9⅓ hr. Distillation of the product yielded acetic acid (32 g.), α-methylstyrene (33·5 g.), a fraction (87·0 g.), b. p. 97—98°/12 mm., $n_D^{20}$ 1·5331—1·5341, and a residue (23·2 g.). Redistillation of part of the above fraction yielded 2-phenylbut-3-en-2-ol, b. p. 148—149°/100 mm., $n_D^{20}$ 1·5330 (Found: C, 80·7; H, 8·1. Calc. for $C_{10}H_{12}O$: C, 81·1; H, 8·1%), which gave a *phenylurethane* (in low yield on long heating with phenyl isocyanate), m. p. 107—108·5° (Found: C, 76·4; H, 6·4; N, 5·1. $C_{17}H_{17}NO_2$ requires C, 76·4; H, 6·4; N, 5·2%), and the 3,5-dinitrobenzoate, m. p. and mixed m. p. 141—143°, of 3-phenylbut-2-en-1-ol. Catalytic hydrogenation (Adams catalyst) provided 2-phenylbutan-2-ol, b. p. 94—96°/13 mm., $n_D^{20}$ 1·5200, identified spectroscopically.[10]

For comparison, 2-phenylbut-3-en-2-ol was synthesised from vinylmagnesium chloride and acetophenone in tetrahydrofuran.[7] Distillation of the product gave fractions containing mixtures of acetophenone and the alcohol in varying proportions: the purest sample, b. p. 97°/12 mm., $n_D^{20}$ 1·5336, contained 95% of the phenylbutenol and 5% of acetophenone.

*Pyrolysis of* 3-*Phenylbutane*-1,3-*diol*.—The glycol (11 g.) was dropped at 500° during 115 min., through the above column. Distillation of the product gave: (i) (1·4 g.) b. p. 50—75°/12 mm., $n_D^{20}$ 1·5364; (ii) (3·0 g.), b. p. 75—90°/12 mm., $n_D^{20}$ 1·5345; (iii) (2·5 g.) b. p. 90—160°/12 mm., $n_D^{20}$ 1·5354; and residue (0·5 g.). Infrared spectroscopy showed that fraction (i) contained α-methylstyrene (65%) and acetophenone (35%) (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 249°), fraction (ii) was mainly acetophenone (95%), and fraction (iii) was the glycol.

*Pyrolysis of Dimers of* 2-*Phenylbutadiene*.—(i) 1,4-Diphenyl-4-vinylcyclohex-1-ene (16 g.), pyrolysed at 550—560° during 65 min., gave a product which by fractionation and infrared spectroscopy was shown to contain 2-phenylbutadiene, 1-methylindene, biphenyl, and *p*-terphenyl.

(ii) Crude mixed isomers, treated similarly, gave a similar product, but in addition to *p*-terphenyl, m. p. 210—212° (Found: C, 94·2; H, 6·1. Calc. for $C_{18}H_{14}$: C, 93·9; H, 6·1%), there was also isolated *m*-terphenyl, m. p. 83—84° (from methanol) (Found: C, 94·1; H, 6·0%), identified spectroscopically.

*Conversion of Phenylbutenols into their Chlorides*.—(a) 3-*Phenylbut*-3-*en*-1-*ol*. (i) The alcohol (50 g.) was added, during 1 hr., to thionyl chloride (42 g.) in ether (150 c.c.) at room temperature, and stirring continued for a further ½ hr. The solvent was evaporated and the product flash-distilled: the distillate (48·2 g.) had b. p. 100—120°/11 mm. Redistillation gave 4-*chloro*-2-*phenylbut*-1-*ene* (42·1 g.), b. p. 106—107°/11 mm., $n_D^{20}$ 1·5504 (Found: C, 72·65; H, 6·7. $C_{10}H_{11}Cl$ requires C, 72·1; H, 6·6%).

(ii) Repetition of experiment (i) on half the scale, up to the end of the reaction with thionyl chloride, was followed by washing of the ethereal solution with water and sodium hydrogen carbonate solution, and storage for 2 days over anhydrous sodium sulphate and solid sodium hydrogen carbonate. Distillation then gave 2-phenylbutadiene (8·5 g.), $n_D^{20}$ 1·5469, and its dimers (5·7 g.), but no chloride.

(iii) Repetition of experiment (i) on double the scale yielded, on final distillation, 2-phenylbutadiene (20 g.), 4-chloro-2-phenylbut-1-ene (52 g.), and a fraction (6 g.), b. p. 110—120°/11 mm., which crystallised on storage. Recrystallisation from light petroleum (b. p.

[10] Hawkins, *J.*, 1949, 2076.

60—80°) and methanol gave 3-phenylthiophen, m. p. 88—90° (Found: C, 75·0; H, 5·2; S, 19·4. Calc. for $C_{10}H_8S$: C, 75·0; H, 5·0; S, 20·0%). 3-Phenylthiophen was synthesised for comparison by heating 2-phenylbutadiene (22 g.) and sulphur (16 g.) at 200° for 6½ hr.: in addition to polymer (26 g.), there was obtained a distillate (5·9 g.) which after several recrystallisations from ethanol had m. p. and mixed m. p. 92—94° (lit.,[11] 91·5—92°) (Found: C, 75·1; H, 5·0; S, 19·9%).

Decomposition with formation of 2-phenylbutadiene and its dimers occurred on reaction of the phenylbutenol with thionyl chloride in *NN*-dimethylaniline at 0°, in benzene under reflux, or in *NN*-dimethylaniline and benzene at 0°.

(b) 3-*Phenylbut*-2-*en*-1-*ol*. The alcohol (75 g.) was added to thionyl chloride (63 g.) in ether (225 c.c.) as above. Flash-distillation of the product gave a distillate (79·5 g.), b. p. 100—118°/11 mm., which on fractionation yielded 1-chloro-3-phenylbut-2-ene (25·7 g.), b. p. 97—110°, $n_D^{20}$ 1·5580. Other products, including 2-phenylbutadiene and its dimer, were also obtained.

*Dehydrochlorination of* 4-*Chloro*-2-*phenylbut*-1-*ene*.—The chloride (8·3 g.) was added to a solution from sodium (1·25 g.) in diethylene glycol (20 c.c.) and the mixture heated, at 100—140°, under a packed column at reduced pressure: the low-boiling product (b. p. 55—60°/11 mm.) was removed as rapidly as possible. Redistillation yielded 2-phenylbutadiene (3·8 g.), b. p. 57—59°/11 mm., $n_D^{20}$ 1·5480.

Other attempts at dehydrochlorination gave either no or little reaction: these included the use of potassium hydroxide, in methanol at 35° and fused (at 160°), sodium methoxide solution under reflux, and dimethylaniline at 150°. Sodium n-butoxide solution at 180° gave a mixture including a fraction shown spectroscopically to contain an ether group.

*Dehydration of Phenylbutenols, etc., with Iodine*.—(a) 3-*Phenylbut*-3-*en*-1-*ol*. The alcohol (10 g.) was heated at *ca.* 140—150° with a crystal of iodine under a heated, helices-packed column at reduced pressure. Wet phenylbutadiene was taken off as formed: after drying there was obtained pure 2-phenylbutadiene (6·9 g.), b. p. 59—60°/12 mm., $n_D^{20}$ 1·5461, with residue (2·0 g.).

(b) 3-*Phenylbut*-2-*en*-1-*ol*. The alcohol was treated as above, to give finally 2-phenylbutadiene (7·2 g.) and residue (1·9 g.).

(c) 3-*Phenylbutane*-1,3-*diol*. (i) The glycol (10 g.) was dehydrated as above, except that material with b. p. $<$140°/10 mm., was removed rapidly through a column. The distillate (6·6 g.), b. p. 120—140°/10 mm., $n_D^{20}$ 1·5530, was found, by infrared spectroscopy, to contain 3-phenylbut-3- (70%) and 3-phenylbut-2-en-1-ol (30%); there was a residue (1·4 g.).

(ii) Repetition of the above experiment, but under the conditions of (a) and (b) with a low temperature of take-off, led to the conversion of the glycol (10 g.) into 2-phenylbutadiene (6·5 g.) and residue (1·9 g.).

(d) 4-*Acetoxy*-2-*phenylbutan*-2-*ol*. Dehydration of the glycol acetate (10 g.) under similar conditions to (c, i) gave a distillate (7·7 g.), b. p. 115—140°/10 mm., $n_D^{20}$ 1·5297, shown spectroscopically to consist of 4-acetoxy-2-phenylbut-1-ene (70%), 4-acetoxy-2-phenylbut-2-ene (20%), and glycol acetate (10%).

*Ethyl Phenylbutenyl Ethers*.—(a) *From* 3-*phenylbut*-2-*en*-1-*ol*. (i) The alcohol (40 g.) and ethanol (100 c.c.), containing a few drops of hydrochloric acid, were heated together under reflux for 3 hr. After working up there was obtained an ethyl phenylbutenyl ether (29·9 g.), b. p. 118°/11 mm., $n_D^{20}$ 1·5268; its infrared spectrum showed an absence of hydroxyl and the presence of an ether group, mainly with unsaturation of the type $CRR'{:}CHR''$ but having *ca.* 5% of type $CH_2{:}CRR'$.

(ii) Reaction as in experiment (i) but on half the scale and with heating continued for 16 hr. gave fractions (i) (1·4 g.) b. p. 60—110°/11 mm., $n_D^{20}$ 1·5385, (ii) (3·0 g.) b. p. 110—116°/11 mm., $n_D^{20}$ 1·5189, (iii) (6·2 g.) b. p. 116—120°/11 mm., $n_D^{20}$ 1·5235; (iv) (1·6 g.) b. p. 120—125°/11 mm., $n_D^{20}$ 1·5224, and (v) (0·2 g.) b. p. 215—220°/11 mm., and a residue (2·8 g.). Examination of fractions 2—4 spectroscopically and fractions 2 and 3 by gas chromatography showed that they contained three isomeric ethyl ethers, *i.e.*, *cis*- and *trans*-1-ethoxy-3-phenylbut-2-ene and 4-ethoxy-2-phenylbut-1-ene: the first two (the major constituents) had similar infrared spectra; the third occurred to the extent of *ca.* 12%.

(b) *From* 3-*phenylbut*-3-*en*-1-*ol*. The phenylbutenol (10 g.) was heated with acidified ethanol for 18 hr.; spectroscopy showed the main fractions obtained [(1·5 g.) b. p. 113—

[11] Broun and Voronkov, *J. Gen. Chem.* (*U.S.S.R.*), 1947, **17**, 1162.

117°/11 mm., $n_D^{20}$ 1·5268; (4·1 g.) b. p. 117—120°/11 mm., $n_D^{20}$ 1·5338] to be mixtures of unchanged phenylbutenol (25%) with 1-ethoxy-3-phenylbut-2-ene.

(c) *From* 2-*phenylbut*-3-*en*-2-*ol.* Similar treatment again yielded 1-ethoxy-3-phenylbut-2-ene, b. p. 120—124°/12 mm., $n_D^{20}$ 1·5273.

The mixed isomers from experiment (a, ii) were hydrogenated over Adams catalyst to yield 1-*ethoxy*-3-*phenylbutane*, b. p. 100—100·5°/11 mm., $n_D^{20}$ 1·4879, uniform on gas chromatography (Found: C, 80·2; H, 10·1. $C_{12}H_{18}O$ requires C, 80·9; H, 10·1%), and identical spectroscopically with a synthetic sample. The latter was obtained by heating 3-phenylbutyl chloride (7·2 g.) with sodium ethoxide (from 3 g. of sodium in 50 c.c. of ethanol) and toluene (50 c.c.) for 58 hr. The 1-ethoxy-3-phenylbutane (3·1 g.) finally obtained had b. p. 100—101·5°/11 mm., $n_D^{20}$ 1·4875 (Found: C, 81·15; H, 10·0%), and was uniform on gas chromatography.

*Di*(*phenylbutenyl*) *Ether*.—(a) *From* 2-*phenylbut*-3-*en*-2-*ol.* The alcohol (5 g.) and 1% hydrochloric acid (40 c.c.) were heated together on the water-bath for 1½ hr. and the cooled product was extracted with ether. Final distillation yielded unchanged phenylbutenol and a fraction (2·3 g.), b. p. 215—220°/12 mm., $n_D^{20}$ 1·5842 (Found: C, 85·3; H, 7·9. $C_{20}H_{22}O$ requires C, 86·3; H, 7·9%), having only weak ether bands (infrared spectrum) but with a double bond conjugated with an aromatic ring (ultraviolet spectrum). The infrared spectrum also indicated that unsaturation was not of the $CRR'{:}CH_2$ type, in agreement with the product's being di-(3-phenylbut-2-enyl) ether. Catalytic hydrogenation (Adams catalyst) yielded di-(3-phenylbutyl) ether, identical with that synthesised as below.

(b) *From* 3-*phenylbut*-2-*en*-1-*ol.* The alcohol (10 g.), 1% hydrochloric acid (20 c.c.), and dioxan (5 c.c.) were heated on the steam-bath for 4 hr. Working up gave di-(3-phenylbut-2-enyl) ether (4·5 g.), identically spectroscopically with that above, and a residue (3·0 g.).

(c) *From* 3-*phenylbutane*-1,3-*diol.* The glycol (10 g.) and 20% sulphuric acid (25 c.c.) were heated under reflux for 3½ hr. Final distillation yielded the di(phenylbutenyl) ether (2·2 g.), b. p. 220—240°/12 mm., $n_D^{20}$ 1·5920, and higher-boiling materials (4·2 g.).

(d) *Synthetic.* Sodium (0·6 g.) was dissolved in 3-phenylbut-2-en-1-ol (20 c.c.) and toluene (25 c.c.) under reflux, and 1-chloro-3-phenylbut-2-ene (4·0 g.) added gradually. Heating at 70° and stirring were continued for 2 hr., *ca.* 80% of the sodium alkoxide being utilised. Distillation of the product gave a major fraction (8·3 g.), b. p. 200—230°/11 mm., which on redistillation provided fractions: (i) (2·7 g.) b. p. 203—215°/11 mm., $n_D^{20}$ 1·5903; and (ii) (2·9 g.) b. p. 215—225°/11 mm., $n_D^{20}$ 1·5845. The infrared spectra showed that fraction (i) was largely the di(phenylbutenyl) ether, but contained some dimer of 2-phenylbutadiene, whereas (ii) was the pure ether, identical with that from (a), (b), and (c) above.

The synthetic di(phenylbutenyl) ether, after hydrogenation (Adams catalyst), yielded the *di*(*phenylbutyl*)*ether*, b. p. 215—225°/12 mm., $n_D^{20}$ 1·5379 (Found: C, 85·0; H, 9·1. $C_{20}H_{26}O$ requires C, 85·1; H, 9·2%), $\nu_{max.}$ 1125 cm.$^{-1}$ (ether).

The saturated ether was also obtained in poor yield (0·5 g.) by heating 1-chloro-3-phenylbutane (5 g.) with a solution from sodium (0·3 g.) in 3-phenylbutanol (5 g.) and toluene (25 c.c.) under reflux for 24 hr.

*Reaction of Phenylbutenols with Formic Acid*.—(a) 3-*Phenylbut*-3-*en*-1-*ol.* The alcohol (10 g.) and formic acid (4 g.) were heated together at 130° for ¼ hr. and the product distilled to give fractions: (i) (8·6 g.) b. p. 118—122°/12 mm., $n_D^{20}$ 1·5367; (ii) (1·0 g.) b. p. 130—150°/12 mm., $n_D^{20}$ 1·5367; and a residue (0·2 g.). Fraction (i) was 3-*phenylbut*-3-*enyl formate* (Found: C, 75·15; H, 7·0. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%), having an infrared spectrum consistent with the presence of a $CH_2{:}CRR'$ system and a formate group.

(b) 3-*Phenylbut*-2-*en*-1-*ol.* The alcohol (10 g.) was treated in the same way as its isomer (above). There were obtained fractions: (i) (2·0 g.) b. p. 125—130°/12 mm., $n_D^{20}$ 1·5458; (ii) (2·9 g.) b. p. 190—225°/12 mm., $n_D^{20}$ 1·5340; and a residue (3·2 g.). Spectroscopically, fraction (i) was shown to consist of the phenylbutenyl formate, but (ii) was unidentified.

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