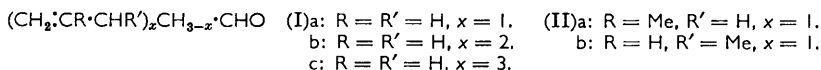


799. α -Allylated Acetaldehydes.

By R. F. WEBB, A. J. DUKE, and J. A. PARSONS.

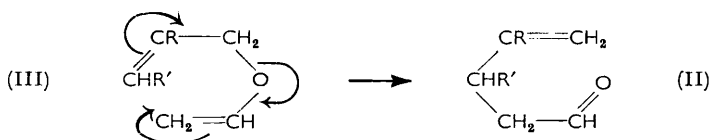
Preparative methods have been developed for mono-, di-, and tri-allylated acetaldehydes. Thermal rearrangement of allyl vinyl ethers in the condensed phase at $>\sim 160^\circ$ gives substantial amounts of the products of the aldol reaction, and also of the subsequent crossed Tischenko reaction, from the pent-4-enal initially produced.

THE rearrangement of allyl enol ethers to substituted pent-4-enals, originally observed by Hurd and Pollack,¹ has recently been developed by Brannock² into a preparative method for 2,2-dialkylpent-4-enals. We have employed comparable methods for the production of the allylated acetaldehydes (Ia—c) and (IIa and b), which differ from Brannock's products in having no substituents other than the allyl groups on the α -carbon atom.



Various improved methods have recently been described for the production of the starting materials, the allyl vinyl ethers.²⁻⁴ Thermal rearrangements of vinyl ether itself under pressure in the condensed phase at $\sim 200^\circ$, as described for the gas-phase rearrangement,¹ gave two condensation products (see below) of pent-4-enal at a rate comparable to that of the rearrangement. Rearrangement proceeds, however, smoothly and without the use of pressure, in an inert solvent at $110\text{--}140^\circ$, providing a convenient preparation of pent-4-enal (Ia). This procedure is also convenient for the production of allylacetaldehydes substituted in the allyl portion: compounds (IIa and b) have been obtained thus from 2-methylallyl and but-2-enyl vinyl ether. These ethers have been previously prepared and rearranged by the gas-phase procedure,⁵ but none of these products were characterised.

The infrared spectrum of the rearrangement product from but-2-enyl vinyl ether shows vinyl bands at 916 and 996 cm^{-1} , supporting a cyclic mechanism for the rearrangement of the allyl ethers of unconjugated aliphatic enols (III \rightarrow II), as is known to be characteristic of the rearrangements of allyl aryl ethers,⁶ *O*-allyl derivatives of acetoacetates⁶ and β -allyloxyacrylates.^{7 *}



The undistilled residue from a preparation of allyl vinyl ether by acid-catalysed pyrolysis of acetaldehyde diallyl acetal² was found to contain a large proportion of the triallyl compound (Ic). Gas-chromatography of the pyrolysate and of fractions subsequently distilled from the residue showed no mono- or di-allyl derivative (Ia or Ib) or intermediate allyl enol ethers, indicating that the successive steps in the series of reactions

* Pocker⁸ has shown the cyclic mechanism to apply in the rearrangement of allyl vinyl ether itself, by the use of isotopic labelling.

¹ Hurd and Pollack, *J. Amer. Chem. Soc.*, 1938, **60**, 1905.

² Brannock, *J. Amer. Chem. Soc.*, 1959, **81**, 3379.

³ Paul, Roy, Fluchaire, and Collardeau, *Bull. Soc. chim. France*, 1950, 121.

⁴ Weeks and Grant, B.P. 709,106; Adelman, *J. Amer. Chem. Soc.*, 1953, **75**, 2678; 1955, **77**, 1669; Watanabe and Conlon, *ibid.*, 1957, **79**, 2828.

⁵ Pollack, U.S.P. 2,870,201.

⁶ See Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 599.

⁷ Croxall and Van Hook, *J. Amer. Chem. Soc.*, 1950, **72**, 803.

⁸ Pocker, *Proc. Chem. Soc.*, 1961, 141.

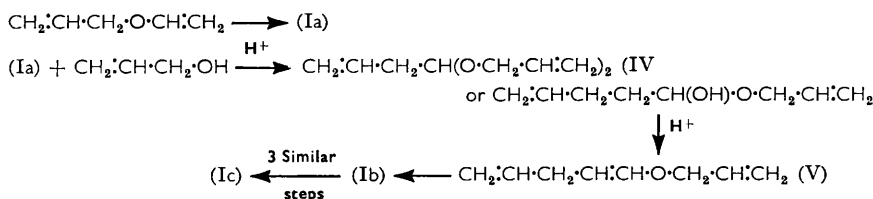
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α-Allylated Acetaldehydes.

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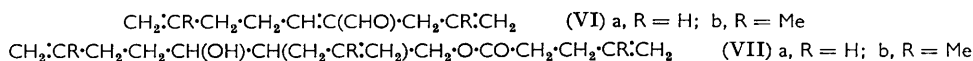
leading to compound (Ic) (see scheme) proceed progressively faster under the conditions employed. It is to be expected that increasing α -alkylation would increasingly favour elimination from the successive acetals (or hemi-acetals).⁹ The various acetals are rapidly interconverted at the temperatures employed, and the lower-boiling products (allyl vinyl ether and allyl alcohol) are removed by distillation while the higher allyl enol ethers are continuously returned to the high temperatures of the pyrolysis vessel for rearrangement.

This observation suggested preparative methods for compounds (Ib and c). Pyrolysis of pent-4-enal diallyl acetal (IV), while allyl alcohol was allowed to distil off as formed, gave essentially the former (Ib), accompanied by some of the latter (Ic). Subsequent return to the reaction mixture, of the mol. of allyl alcohol initially eliminated, while the pyrolysis was continued, produced the triallyl derivative (Ic). These procedures starting from pre-formed pent-4-enal were preferable to one-step procedures from the ether (III) or acetaldehyde diallyl acetal.



The infrared spectra of compounds (Ib and c) are surprisingly similar, the only significant differences being a peak at 860 cm^{-1} in the spectrum of the latter, and the differing intensities of the C-H stretching bands.

The by-products referred to above from the pyrolysis of allyl vinyl ether in undiluted form are the dehydrated aldol (VIa) of pent-4-enal (characterised by its infrared spectrum, molecular weight, and bromine number, and by the ultraviolet absorption of its 2,4-dinitrophenylhydrazone) and a hydroxy-ester, which from its molecular weight and degree of unsaturation may be the crossed Tischenko product (VIIa) from pent-4-enal and its aldol.¹⁰ The production of Tischenko-type products under purely thermal conditions has been reported,¹¹ benzaldehyde giving benzyl benzoate at $300\text{--}350^\circ$.



The same condensation products were produced in pyrolyses in sealed borosilicate-glass tubes and in a stainless-steel autoclave, making it probable that the reaction is thermal and not catalysed by the walls of the container. Uncatalysed aldol reactions have been observed,¹² but previous cases appear to have involved substantially more drastic conditions than ours. Condensations of the Doebner-Knoevenagel type involving highly activated methylene groups have been observed at low temperatures in the absence of catalysts.¹³

The same products arise on pyrolysis of pent-4-enal, a fact indicating that they are derived from the aldehyde. Comparable products (VIb and VIIb) were obtained on rearrangement in bulk of 2-methylallyl vinyl ether; in this case none of the uncondensed rearrangement product, 4-methylpent-4-enal, was observed. The presence of the ω -double bond is not necessary, as valeraldehyde undergoes similar changes at 200° , as judged by infrared spectra, at a rate only slightly slower than that for pent-4-enal.

⁹ Ref. 6, pp. 440—442.

¹⁰ For a survey of this type of reaction, see Kulpinski and Nord, *J. Org. Chem.*, 1943, **8**, 256.

¹¹ Lachman, *J. Amer. Chem. Soc.*, 1924, **46**, 720; Hurd and Bennett, quoted by Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalogue Company, New York, 1929, pp. 239—242.

¹² Engler and Dengler, *Ber.*, 1893, **26**, 1445; Hurd and Greengard, quoted by Hurd, ref. 11, pp. 255, 258.

¹³ Patai, Israeli, and Zabicky, *Chem. and Ind.*, 1957, 1671.

EXPERIMENTAL

Allyl Vinyl Ether (III; R = R' = H) and *2,2-diallylpent-4-enal* (Ic).—Allyl vinyl ether was produced by the methods of refs. 2 and 4 (Watanabe *et al.*). The transvinylation is improved in larger runs than that described by Watanabe and Conlon⁴ by adding the allyl alcohol slowly to a molar amount of refluxing butyl vinyl ether, while removing the product from the head of the column. Use of larger amounts of mercuric acetate catalyst permits faster distillation and reduces acetal formation.

The residue from a preparation by Brannock's method² from acetaldehyde diallyl acetal (1946 g.), after the head-temperature had finally risen sharply from 97° to >200°, was distilled *in vacuo*, giving 166 g. of distillate, boiling from 123°/15 mm. to 180°/5 mm. On fractionation this yielded *2,2-diallylpent-4-enal* (Ic) (69.8 g., 4.8%), b. p. 89°/10 mm., n_D^{25} 1.4695, d_{25}^{25} 0.883, spec. refraction 0.3156 (calc.¹⁴ 0.3147) [Found: C, 80.4; H, 9.6%; *M* (cryoscopic, in benzene), 157. C₁₁H₁₆O requires C, 80.4; H, 9.8%; *M*, 164] [orange-yellow *2,4-dinitrophenylhydrazone*, m. p. 150.5—151.5° (from ethanol) (Found: C, 59.2; H, 5.8; N, 16.1. C₁₇H₂₀N₄O₄ requires C, 59.2; H, 5.85; N, 16.3%)].

Pent-4-enal (Ia).—Dry 1-methylnaphthalene (200 ml.) was heated to 140° under a reflux condenser, and allyl vinyl ether (79 g.) was run in with stirring during 3—4 hr. The temperature of the refluxing liquid was then 110°, which rose to 129° after a further 10 hours' refluxing. The product was then rapidly distilled until the head-temperature reached 240°; the distillate was fractionated, giving *pent-4-enal* (63.4 g., 80.4%), b. p. 101—105°, n_D^{25} 1.4161 (lit.¹ b. p. 103—104°, n_D^{20} 1.4191, b. p.³ 102—105°).

3- and 4-Methylpent-4-enal.—Diethylene glycol ethyl ether was vinylated substantially by Reppe's procedure.¹⁵ Sodium (10% by wt. of the ether-alcohol) was dissolved in diethylene glycol ethyl ether, "Hyflo-Supercel" added, and the mixture refluxed while a mixture of equal parts of acetylene and nitrogen was passed in until the infrared spectrum of the liquid showed no hydroxyl absorption. The product was then added to a large volume of water and extracted continuously with ether. Evaporation of the extract and distillation of the residue gave *2-ethoxyethyl 2-vinyloxyethyl ether*, b. p. 189—192°, n_D^{25} 1.4277, d_{25}^{25} 0.941, spec. refraction 0.2731 (calc. 0.2746) (Found: C, 60.0; H, 10.0. C₈H₁₆O₃ requires C, 59.9; H, 10.1%). This was used to vinylate *2-methylallyl* and *but-2-enyl* alcohol by Watanabe and Conlon's procedure,⁴ and the products were rearranged by refluxing them in 1-methylnaphthalene (2 vol.) until the liquid temperature rose above 160° (about 6 hr.), at which stage the infrared spectra of the products in solution showed no peaks assignable to the vinyl ethers. The aldehydes were then distilled as for the unsubstituted *pent-4-enal* (see above). The yields, etc., of these products are recorded in the Table (C₈H₁₀O requires C, 73.4; H, 10.3%).

Substance	B. p.	Yield (%)	Yield		Spec. refraction		Found (%)	
			n_D^{25}	d_{25}^{25}	Found	Calc.	C	H
2-Methylallyl vinyl ether ...	89.5°	33	1.4188	0.8024	0.3143	0.3137	73.55	10.25
But-2-enyl vinyl ether	98.5	65	1.4168	0.8017	0.3134	0.3137	73.14	10.54
4-Methylpent-4-enal	128	87	1.4260	0.8544	0.2996	0.3005	73.0	10.3
3-Methylpent-4-enal	116	40	1.4211	0.8486	0.2985	0.3005	73.4	10.3

2,4-Dinitrophenylhydrazones were prepared from 3- and 4-methylpent-4-enals and, recrystallised from ethanol, had respectively m. p. 90.5° (Found: C, 51.6; H, 5.1; N, 20.1. C₁₂H₁₄N₄O₄ requires C, 51.8; H, 5.1; N, 20.1%) and m. p. 92.5° (Found: C, 51.4; H, 5.1; N, 20.0%).

2-Allyl- (Ib) and *2,2-Diallyl-pent-4-enal* (Ic).—*Pent-4-enal* (21.0 g., 0.25 mole), allyl alcohol (43.5 g., 0.75 mole), benzene (50 ml.), and toluene-*p*-sulphonic acid (250 mg.) were refluxed together under a 20 cm. Fenske column and partial-return head into a Dean-Stark trap. Water (4.5 ml.) was eliminated in 2 hr., after which distillate was taken off at the partial-return head at a reflux ratio of ~1:3. After all the benzene and uncombined allyl alcohol had been removed, the reflux ratio was increased to 1:5—10, and allyl alcohol was removed until the head-temperature rose above 100°. At this stage the liquid temperature was 173—176°. Distillation of the residue under reduced pressure gave *2-allylpent-4-enal* (16.0 g., 53%), b. p. (after refractionation) 51.5°/13 mm., n_D^{25} 1.4442, d_{25}^{25} 0.8600, spec. refraction 0.3090 (calc. 0.3087) (Found: C, 77.0; H, 9.6. C₈H₁₂O requires C, 77.3; H, 9.7%) [yellow *2,4-dinitrophenylhydrazone*, m. p. 104° (from ethanol) (Found: C, 55.6; H, 5.3; N, 18.2. C₁₄H₁₆N₄O₄ requires

¹⁴ All theoretical specific refractions are calculated by using the tables of Denbigh, *Trans. Faraday Soc.*, 1940, **36**, 936.

¹⁵ Reppe, I.G. *Farbenind. A.-G.*, G.P. 584,840.

C, 55.25; H, 5.3; N, 18.4%). 2,2-Diallylpent-4-enal (6.6 g.), b. p. 100—125°/16 mm., was also obtained (dinitrophenylhydrazone, m. p. and mixed m. p. 149—150°).

To produce the latter as the principal product, the combined distillates were returned to the reaction flask at the end of the pyrolytic stage, and the reaction cycle was repeated. In this case distillation gave, after 1—2 ml. of forerun, the triallyl compound (16.0 g., 39%), b. p. 95—97°/18 mm.

Condensation Products (VI) and (VII) from Pent-4-enal.—Allyl vinyl ether (68 g.) was heated in an autoclave at 190—210° for 3 hr. and the product was distilled, giving fractions: (1) (12.0 g.), b. p. 66—82°, (2) (9.8 g.), b. p. 82—99°, (3) (16.6 g.), b. p. 60—95°/15 mm., and (4) (7.0 g.), b. p. 85—138°/0.04 mm. From their infrared spectra, fractions (1) and (2) were substantially allyl vinyl ether [or (III), R = R' = H] and pent-4-enal [or (Ia)], respectively. Fraction 3, on redistillation, gave 2-allylhepta-2,6-dienal (VIa) (11.5 g., 18.6%), b. p. 92°/9.5 mm., n_D^{25} 1.4807, d_{25}^{25} 0.885, spec. refraction 0.321 (calc. 0.313) (Found: C, 79.1; H, 9.5%; M, 169; equiv. per double bond, 52, 53. C₁₀H₁₄O requires C, 79.9; H, 9.4%; M, 150; equiv. per double bond, 50). This gave a red 2,4-dinitrophenylhydrazone, m. p. 114.5—115.5° (from ethanol) (Found: C, 57.8; H, 5.3; N, 17.0. C₁₆H₁₈N₄O₄ requires C, 58.1; H, 5.5; N, 16.9%); λ_{\max} 373 (log ϵ 4.42) confirms its formulation as a conjugated aldehyde of the correct order of molecular weight, requiring $^{16} \lambda_{\max}$ ca. 373, (log ϵ ca. 4.46).

Redistillation of fraction 4 did not give sharp-boiling fractions, but 1.7 g. (2.5%) was obtained of boiling range 112—121°/0.12 mm., n_D^{25} 1.4797—1.4822, d_{25}^{25} 0.996, giving a positive reaction in the hydroxylamine—ferric ion test. The infrared spectrum of this material showed all the peaks required for 2-allyl-3-hydroxyhept-6-enyl pent-4-enoate (VIIa) (Found: C, 72.2; H, 9.5%; M, 272; equiv. per double bond, 79, 81; spec. refraction, 0.286. Calc. for C₁₅H₂₄O₃: C, 71.4; H, 9.58%; M, 252; equiv. per double bond, 84; spec. refraction, 0.291).

The corresponding fraction (VIIb), b. p. 200—215°/0.3 mm. (Found: C, 73.1; H, 10.65. Calc. for C₁₈H₃₀O₃: C, 73.4; H, 10.3%), was obtained on similar pyrolysis of 2-methylallyl vinyl ether.

Pyrolysis of Valeraldehyde.—Samples of valeraldehyde (1 ml.) were heated in a sealed tube for various periods at 200° ± 10°. Infrared spectra of the products after 45 min., 2 hr., and 8 hr. showed steadily increasing bands at 3500, 1695, and 1175 cm.⁻¹, assignable to $\alpha\beta$ -unsaturated aldehyde and hydroxy-ester, of slightly lower intensity than those observed during an identical pyrolysis of pent-4-enal. The bands at 2725 cm.⁻¹, due to the aldehydic protons, showed a continuous decrease.

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¹⁶ Johnson, *J. Amer. Chem. Soc.*, 1953, **75**, 2720.