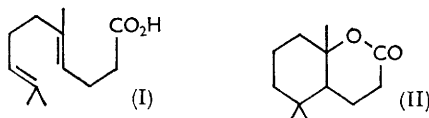


1004. Reduced Cyclic Compounds. Part IX.* The Preparation of *trans*-Deca-5,9-dienoic Acid and its Cyclisation to Δ^9 -Octal-1-one.

By M. F. ANSELL and J. W. DUCKER.

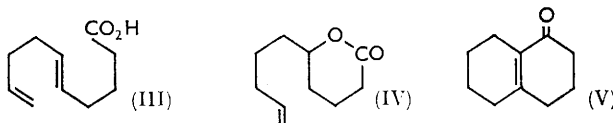
A one-stage conversion of an alkadienoic acid into a bicyclic ketone is reported.

THE cyclisation of olefinic acids to cycloalkenones is well known¹ and the "double cyclisation" of 8-phenyl-*trans*-oct-5-enoic acid and related compounds to tricyclic ketones has been reported.² The one-stage conversion of an alkadienoic acid into a bicyclic ketone has not previously been reported. Previous³ cyclisations of dienoic acids have yielded lactonic material; *e.g.*, geranylacetic acid (I) yields the lactone (II), intramolecular alkylation



occurring in preference to intramolecular acylation.⁴ Since the conditions for intramolecular alkylation are known⁵ to be that the double bonds must be 1,5 to each other and that one double bond must be triply substituted it was considered that with *trans*-deca-5,9-dienoic acid, in which the latter condition is not fulfilled, cyclisation to a bicyclic ketone should occur.

trans-Deca-5,9-dienoic acid was prepared by coupling of the Grignard reagent of 4-chlorobut-1-ene with 2,3-dichlorotetrahydropyran, followed by ring scission of the resulting 2-but-3'-enyl-3-chlorotetrahydropyran to *trans*-nona-4,8-dien-1-ol. This was converted by carboxylation of the Grignard reagent of the derived chloride into the required dienoic acid (III). Action of polyphosphoric acid on the acid (III) gave only 5-hydroxydec-8-enoic lactone (IV). Thus although, as expected, no intramolecular alkylation



occurred, neither had intramolecular acylation. When, however, the lactone was treated with polyphosphoric acid, a small yield of Δ^9 -octal-1-one (V) was obtained. The expected product, a Δ^5 - or Δ^6 -octalone, evidently isomerised to the conjugated ketone.

It was not possible to effect this cyclisation with polyphosphoric acid without isolating the lactone. When, however, *trans*-deca-5,9-dienoyl chloride was treated with aluminium chloride, the Δ^9 -octalone was obtained directly. This constitutes the first one-stage conversion of an alkadienoic acid into a bicyclic ketone.

EXPERIMENTAL

Refractive indices are at 20°.

2-But-3'-enyl-3-chlorotetrahydropyran.—A solution of 2,3-dichlorotetrahydropyran⁶ (0.8 mole) in ether (300 ml.) was added to a decanted solution of the Grignard reagent prepared

* Part VIII, *J.*, 1959, 2994.

¹ *Inter alia*, (a) Ansell and Brown, *J.*, 1958, 2955; (b) Riobe, *Compt. rend.*, 1958, **247**, 1016.

² Ansell and Brown, *J.*, 1958, 3956; Ansell and Ducker, preceding paper.

³ *Inter alia*, Stork and Burgstahler, *J. Amer. Chem. Soc.*, 1955, **77**, 5068; Tribolet, Gamboni, and Schinz, *Helv. Chim. Acta*, 1958, **41**, 1587.

⁴ Mondon and Teege, *Chem. Ber.*, 1958, **91**, 1014.

⁵ Schinz, Helg, Zobrist, Lauchenauer, Brack, Caliezi, Stauffacher, and Zweifel, *Helv. Chim. Acta*, 1956, **39**, 1269.

⁶ Crombie and Harper, *J.*, 1950, 1707.

from 1-chlorobut-3-ene ⁷ (91 g., 1.0 mole) in ether (600 ml.) at such a rate that steady refluxing was maintained. After being stirred for a further 30 min., the mixture was poured on ice (600 g.) and ammonium chloride (30 g.). The ethereal layer was separated and the aqueous layer extracted with ether (2 × 200 ml.). Distillation of the dried (MgSO₄) combined extracts gave *cis*- and *trans*-2-but-3'-enyl-3-chlorotetrahydropyran (87 g., 62%), b. p. 80—108°/13 mm., n_D 1.4685—1.4762. A redistilled sample had b. p. 85—86°/13 mm., n_D 1.4701 (Found: C, 61.7; H, 8.9; Cl, 20.1. C₉H₁₅ClO requires C, 61.9; H, 8.7; Cl, 20.4%).

trans-Nona-4,8-dien-1-ol.—A small amount of a solution of the above chloro-ether (44 g., 0.25 mole) in ether (100 ml.) was added to a stirred suspension of sodium sand (12.7 g., 0.55 g-atom) in ether (200 ml.). After a few minutes, reaction set in, and the remainder of the solution was then added at such a rate that vigorous refluxing was maintained. The mixture was then stirred at room temperature for 30 min. and sufficient water (*ca.* 200 ml.) then added to give two clear phases. The ethereal layer was separated and the aqueous phase extracted with ether (2 × 100 ml.). Distillation of the dried (MgSO₄) combined extracts gave *trans*-nona-4,8-dien-1-ol (29.4 g., 84%), b. p. 104—106°/14 mm., n_D 1.4618 (Found: C, 77.2; H, 11.2. C₉H₁₆O requires C, 77.1; H, 11.4%).

trans-1-Chloronona-4,8-diene.—Thionyl chloride (60 g., 0.5 mole) was added slowly to a stirred, boiling, solution of *trans*-nona-4,8-dien-1-ol (70 g., 0.5 mole) and pyridine (1 ml.) in benzene (500 ml.). The mixture was then boiled until evolution of gas ceased, cooled, and poured on ice. The organic layer was separated, washed with water, saturated sodium hydrogen carbonate solution and water, dried (MgSO₄), and distilled, to yield after removal of the solvent, *trans*-1-chloronona-4,8-diene (62.5 g., 79%), b. p. 84—85°/15 mm., n_D 1.4615 (Found: C, 68.4; H, 9.3; Cl, 22.5. C₉H₁₅Cl requires C, 68.1; H, 9.5; Cl, 22.4%).

trans-Deca-5,9-dienoic Acid.—This acid was prepared in 63.5% yield on a molar scale by carboxylation of the Grignard of *trans*-1-chloronona-4,8-diene (*cf.* preparation of hex-5-enoic acid ^{1a}) and had b. p. 98—100°/0.2—0.3 mm., n_D 1.4626 (Found: C, 71.6; H, 9.6. C₁₀H₁₆O₂ requires C, 71.4; H, 9.6%). The derived acid chloride (prepared by the action of oxalyl chloride ⁸) had b. p. 64—65°/0.3 mm., n_D 1.4670 (Found: C, 64.2; H, 8.3; Cl, 18.7. C₁₀H₁₅ClO requires C, 64.3; H, 8.0; Cl, 19.0%), and the derived amide [needles from light petroleum (b. p. 60—80°)] had m. p. 76—77° (Found: C, 71.8; H, 9.8; N, 8.6. C₁₀H₁₇NO requires C, 71.8; H, 10.2; N, 8.4%).

Action of Polyphosphoric Acid on trans-Deca-5,9-dienoic Acid.—This acid (1 g.) was treated with polyphosphoric acid (10 g.) at 70° for 25 min. by the general cyclisation procedure previously described.^{1a} Treatment of the crude product with Girard's reagent ⁹ did not afford a volatile ketone, but distillation of the non-ketonic fraction yielded 5-hydroxydec-8-enoic lactone (0.5 g.), b. p. 149—151°/18 mm., n_D 1.4660 (Found: C, 71.9; H, 9.5. C₁₀H₁₆O₂ requires C, 71.5; H, 9.5%), which was insoluble in sodium hydrogen carbonate solution but soluble in warm 2*N*-sodium hydroxide. The infrared spectrum of this compound showed absorption at 5.8 μ, indicating ¹⁰ a six-membered lactone, and at 6.1, 6.95, and 11.0 μ, indicating a terminal double bond.

Treatment of this lactone with polyphosphoric acid, as above, at 100° for 30 min. gave Δ⁹-octal-1-one (10% yield on 0.024-molar scale), b. p. 70—75°/0.5 mm., n_D 1.4901. The derived 2,4-dinitrophenylhydrazone (crimson laths from ethanol-chloroform) had m. p. and mixed m. p. 271—272° (decomp.) (for previously recorded constants see below).

Cyclisation of trans-Deca-5,9-dienoyl Chloride.—This acid chloride (0.038 mole) was cyclised with aluminium chloride in carbon disulphide (as described ^{1a} for the cyclisation of pent-4-enoyl chloride). Distillation gave Δ⁹-octal-1-one (17%), b. p. 65—70°/0.3 mm., n_D 1.4931 (lit.,¹¹ b. p. 85—92°/3 mm.). The 2,4-dinitrophenylhydrazone had m. p. and mixed m. p. 271—272° (decomp.) [lit., m. p. 266.5—267° (decomp.)]; the semicarbazone had m. p. and mixed m. p. 246—247° (lit.,¹¹ m. p. 242—243°); the oxime (needles from aqueous ethanol) had m. p. and mixed m. p. 148—149° (lit.,¹² m. p. 144—145°).

⁷ Roberts and Mazur, *J. Amer. Chem. Soc.*, 1951, **73**, 2509.

⁸ Bauer, *Oil and Soap*, 1946, **23**, 1.

⁹ Vogel, "Practical Organic Chemistry," Longmans, Green & Co., London, 1956.

¹⁰ Weisberger (ed.), "Techniques of Organic Chemistry," Vol. IX, Interscience Publ. Inc., New York, 1956.

¹¹ Bowman, Ketterer, and Chamberlain, *J. Org. Chem.*, 1953, **18**, 905.

¹² Cook and Lawrence, *J.*, 1937, 817.

The authentic specimens were obtained from Δ^9 -octal-1-one prepared by Huckel and Naab's method.¹³

The authors are indebted to the D.S.I.R. for an award (to J. W. D.) and to the University of London Central Research Fund for financial assistance.

QUEEN MARY COLLEGE, UNIVERSITY OF LONDON,
MILE END ROAD, LONDON, E.1.

[Received, May 9th, 1960.]

¹³ Huckel and Naab, *Annalen*, 1933, **502**, 136.
