Ring Expansion. Part I. The Dienone–Phenol Rearrangement of spiro[5 : 5]*Undeca-*1 : 4*-diene-*3*-one.*

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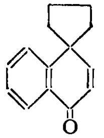
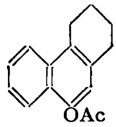
A convenient synthesis of *spiro*[5 : 5]undecan-3-one from *cyclo*hexanone and vinyl cyanide is given. The spiran was converted into the dienone, which readily rearranged in acetic anhydride–sulphuric acid with simultaneous ring expansion, yielding 2′-acetoxybenzo*cyclo*heptene.

Arnold, Buckley, and Dodson (*J. Amer. Chem. Soc.*, 1950, **72**, 3153) have shown that the unsaturated *spiro*-ketone (I) rearranges in acid, with ring expansion, to the phenanthrene derivative (II). We wished to learn whether a six-membered ring could be expanded similarly in good yield to form a seven-membered ring; for this purpose *spiro*[5 : 5]undecan-3-one appeared to be a suitable starting material.

Bruson and Riener (*ibid.*, 1942, **64**, 2850) found that the addition of vinyl cyanide to *cyclo*hexanone in the presence of Triton B afforded, along with mono- and tetrakis-cyanoethyl derivatives of *cyclo*hexanone, 9% of 2 : 2-bis-2′-cyanoethyl*cyclo*hexanone. We have raised this yield to a reproducible 18—20% by addition of only a limited quantity of vinyl cyanide. Recently, in a work available to us only in abstract, Levina, Shusherina, and Kaminskaya (*Doklady Akad. Nauk S.S.S.R.*, 1952, **86**, 79; *Chem. Abs.*, 1953, **47**, 4849) reported a 40% yield of the biscyanoethyl ketone by the use of 1% of dry sodium hydroxide as catalyst: we have been unable to duplicate their results and have consistently obtained intractable polymers.



(I)



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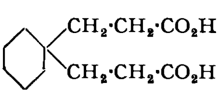

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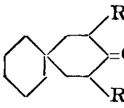
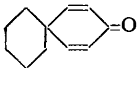
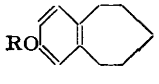


(IV)

Alkaline hydrolysis of 2 : 2-bis-2′-cyanoethyl*cyclo*hexanone followed by Wolff-Kishner reduction afforded the acid (III), which on esterification and Dieckmann ring closure gave ethyl 3-oxo*spiro*[5 : 5]undecane-2-carboxylate (IV; R = H, R′ = CO_2Et). Hydrolysis then furnished the *spiro*-ketone (IV; R = R′ = H). Bromination of the ketone in acetic acid containing hydrobromic acid resulted in a dibromo-derivative which must be *cis*-2 : 4-dibromo*spiro*[5 : 5]undecan-3-one (IV; R = R′ = Br) since the carbonyl absorption is at the position (1756 cm.$^{-1}$) expected (Corey, *J. Amer. Chem. Soc.*, 1954, **76**, 175) for a carbonyl group in a *cyclo*hexane ring sterically hindered by two equatorially substituted bromine atoms. Elimination of hydrogen bromide by boiling collidine yielded low-melting dienone (V) which was purified by chromatography. This rearranged smoothly at room temperature in acetic anhydride containing a drop of sulphuric acid, to yield the acetate (VI; R = Ac) which was readily hydrolysed to 2′-hydroxybenzo*cyclo*heptene identical with an authentic sample kindly provided by Professor V. Prelog.

(V)





(VI)

Refluxing the dibromo-ketone (IV; R = R′ = Br) with 2 : 4-dinitrophenylhydrazine in acetic acid for ten minutes under nitrogen afforded the 2 : 4-dinitrophenylhydrazones of 4-bromo*spiro*[5 : 5]undec-1-en-3-one and the dienone (V). The former derivative was smoothly converted into the latter after a further fifteen minutes' refluxing under the same conditions.

EXPERIMENTAL

2 : 2-*Bis-2′-cyanoethyl*cyclo*hexanone.*—Vinyl cyanide (90 g.) was added during 80 min. to a vigorously stirred solution of Triton B (10 g.) in *cyclo*hexanone (180 g.) at 30—35°. The mixture was acidified, filtered, washed several times with water, and distilled, giving fractions : (i) *cyclo*hexanone; (ii) b. p. 150—190°/1 mm. (21 g.), largely 2-2′-cyanoethyl*cyclo*hexanone; (iii) b. p. 214—216°/1 mm., crystallised from benzene–light petroleum to furnish 2 : 2-bis-2′-cyanoethyl*cyclo*hexanone (61 g.), m. p. 63° (Found : C, 70·9; H, 7·7. Calc. for $C_{12}H_{16}ON_2$: C, 70·5; H, 7·9%) [*semicarbazone*, m. p. 196° (from ethanol) (Found : N, 26·5. $C_{13}H_{19}ON_5$ requires N, 24·0%)].

cyclo*Hexanone*-2 : 2-*bis*-β-*propionic Acid.*—Hydrolysis of the dicyanide (15 g.) with boiling aqueous potassium hydroxide afforded the diacid, m. p. 136° (lit., 141°) (16 g.) (Found : C, 59·4; H, 7·6. Calc. for $C_{12}H_{18}O_5$: C, 59·6; H, 7·5%).

cyclo*Hexane*-1 : 1-*bis*-β-*propionic Acid.*—The foregoing acid (49 g.), potassium hydroxide (20 g.), and 85% hydrazine (23 c.c.) were refluxed for 8 hr. in ethylene glycol (250 c.c.), then the condenser was removed and the temperature allowed to rise to 200° by distillation of all the water. After 3·5 hr. at 200° the solution was cooled, acidified, and extracted with ether to yield crude *cyclo*hexane-1 : 1-bis-β-propionic acid (39 g.), which was esterified without purification to the *diethyl* ester (44 g.), b. p. 207—208°/19 mm. (Found: C, 67·5; H, 9·9; OEt, 15·8. $C_{16}H_{28}O_4$ requires C, 67·6; H, 9·9; 2OEt, 15·9%).

Ethyl 3-*oxo*spiro[5 : 5]*undecane*-2-*carboxylate.*—The ester (9·7 g.) was added slowly to a rapidly stirred suspension of sodium (0·77 g.) in toluene (30 c.c.) at 110—115°. After 5 hr. the solution was cooled in ice, then added to cold 10% aqueous acetic acid. The toluene layer was separated, washed successively with water, aqueous sodium carbonate, and water, dried (Na_2SO_4), and distilled to furnish *ethyl* 3-*oxo*spiro[5 : 5]*undecane*-2-*carboxylate* (4·0 g., 51%), b. p. 160°/20 mm. (Found : C, 70·6; H, 9·3. $C_{14}H_{22}O_3$ requires C, 70·6; H, 9·3%). The ultra-violet absorption spectrum, in ethanol, showed a maximum at 256 mμ (log ε 3·95).

spiro[5 : 5]*Undecan*-3-*one.*—The *spiro*-keto-ester (1·5 g.), when refluxed for 12 hr. in 50% aqueous ethanol (10 c.c.) containing concentrated hydrochloric acid (2 c.c.), yielded the *spiro*-ketone (0·73 g.), b. p. 135—140°/14 mm., characterised as its 2 : 4-*dinitrophenylhydrazone*, m. p. 121° (Found : C, 58·9; H, 6·5; N, 16·2. $C_{17}H_{22}O_4N_4$ requires C, 59·0; H, 6·4; N, 16·2%).

cis-2 : 4-*Dibromo*spiro[5 : 5]*undecan*-3-*one.*—The *spiro*-ketone (0·7 g.) in acetic acid (3 c.c.) decolorised bromine (1·36 g.) in acetic acid (3 c.c.) instantly, and after the addition of hydrobromic acid (1 c.c.) the whole was kept overnight. Dilution with water, followed by extraction with ether, furnished the cis-*dibromo*-spiro-*ketone* (1·3 g., 93%), m. p. 132° (from ether) (Found C, 40·8; H, 5·0. $C_{11}H_{16}OBr_2$ requires C, 40·8; H, 5·0%).

spiro[5 : 5]*Undeca*-1 : 4-*dien*-3-*one.*—The dibromo-*spiro*-ketone (1·3 g.) and collidine (3 c.c.) were gently boiled for 4 min., then cooled, and the collidine hydrobromide was filtered off. The filtrate was taken up in ether, washed twice with 5% hydrochloric acid, dried (Na_2SO_4), and concentrated. The crude product (0·8 g.) after chromatography over activated alumina afforded the *spiro*-dienone (250 mg.), m. p. 82°, with a maximum in the ultra-violet at 235 mμ (log ε 4·2). Its 2 : 4-*dinitrophenylhydrazone*, crystallised from ethanol–chloroform, had m. p. 163—164° (Found : C, 59·2; H, 5·2. $C_{17}H_{18}O_4N_4$ requires C, 59·6; H, 5·3%) and showed maxima in the ultra-violet at 257 and 395 mμ (log ε 4·15 and 4·44 respectively).

2′-*Hydroxybenzo*cyclo*heptene.*—One drop of concentrated sulphuric acid in acetic anhydride (2 c.c.) was added to the *spiro*-dienone (0·15 g.) in acetic anhydride (7 c.c.). After 7 hr. water (25 c.c.) was added and the solution was set aside at 0° for 12 hr. The precipitated 2-*acetoxybenzo*cyclo*heptene* (90 mg.) had m. p. 61—62° after crystallisation from ethanol (Found : C, 76·3; H, 8·1. $C_{15}H_{16}O_2$ requires C, 76·4; H, 7·9%). Mild alkaline hydrolysis of the acetate furnished 2′-hydroxybenzo*cyclo*heptene, m. p. 72° [from light petroleum (b. p. 60—80°)] (Found : C, 81·8; H, 8·8. Calc. for $C_{11}H_{14}O$: C, 81·5; H, 8·7%). The phenol and its acetate gave undepressed mixed m. p.s with authentic specimens (Prelog, Ruzicka, and Metzler, *Helv. Chim. Acta*, 1947, **30**, 1883).

4-*Bromo*spiro[5 : 5]*undec*-1-*en*-3-*one.*—The dibromo-*spiro*-ketone (130 mg.) in acetic acid (5 c.c.) was added to a hot solution of 2 : 4-dinitrophenylhydrazine (80 mg.) in acetic acid (3 c.c.), then heated for 10 min. in nitrogen. On cooling, the orange 2 : 4-*dinitrophenylhydrazone* (65 mg.) of 4-bromo*spiro*[5 : 5]undec-1-en-3-one separated (m. p. 157°), which was crystallised from chloroform–ethanol for analysis (Found : C, 48·3; H, 4·6; N, 13·3. $C_{17}H_{19}O_4N_4Br$ requires C, 48·2; H, 4·5; N, 13·2%). The ultra-violet absorption spectrum showed max. at 256 and 375 mμ (log ε 4·1 and 4·4 respectively). Concentration of the acetic acid mother-liquors and addition of two drops of water furnished *spiro*[5 : 5]undeca-1 : 4-dien-3-one 2 : 4-dinitrophenylhydrazone (43 mg.), m. p. 163—164°, undepressed in m. p. by the sample prepared as above.

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