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A NOVEL ONE STEP SYNTHESIS OF A DIHYDROPENTALENE†

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Abstract—1, 4-Dipyrrolidinocyclohexa-1, 3-diene **4** reacts with dimethyl acetylenedicarboxylate in an unexpected manner to produce the substituted dihydropentalene **6**.

The reaction of cyclic enamines (e.g. 1-pyrrolidinocyclohexene **1**) with dimethyl acetylenedicarboxylate constitutes a well-employed double ring expansion procedure[1] to give in the case shown the substituted cyclooctadiene **3** via the bicyclo[4,2,0]octene intermediate **2**. We proposed to extend this process by attempting a cognate quadruple ring expansion on the bisenamine 1, 4-dipyrrolidinocyclohexa-1, 3-diene **4** in the hope of achieving a direct route to the substituted dihydro[10]annulene **5**. In the event the yellow product obtained in fair yield had the molecular formula $C_{16}H_{19}O_4$ and its spectroscopic properties, particularly the ^1H NMR spectrum (one vinylic proton and two neighbouring allylic CH_2 groups) pointed strongly to the bicyclic fulvene structure of the dihydropentalene **6**. The formation of this product may be rationalised by assuming that the double ring expansion process on the bisenamine (**4**) takes place normally to give the highly substituted cyclooctatriene **7**. This then undergoes a transannular Michael-type reaction to give the zwitterionic bicyclo[3,3,0]octane intermediate **8** which, by elimination of the elements of pyrrolidine, is transformed into the dihydropentalene **6**. Oxidation of **6** with bromine in carbon tetrachloride, NBS or DDQ in benzene gave an intense blue-green product which was too unstable to be purified. Its electronic spectrum (578, 480, 327 and 278 nm in $CHCl_3$) suggested that it was probably the pentalene[2] derived from **6**.

Treatment of **6** with methanolic hydrogen chloride regioselectively removed one of the carbomethoxy groups without affecting the enamine functionality. The low coupling constant ($J = 1.2$ Hz) between the vinylic protons thus generated, strongly suggested the structure **9** for this product. Treatment with aqueous sodium hydroxide did hydrolyse the enamine function to give the diacid **10** and this product was used to confirm the carbon skeleton of **6**. Catalytic hydrogenation of **10** gave the ketodiacid **11** which was electrolytically bis-decarboxylated[3] to give the unsaturated ketone **12**. Hydro-

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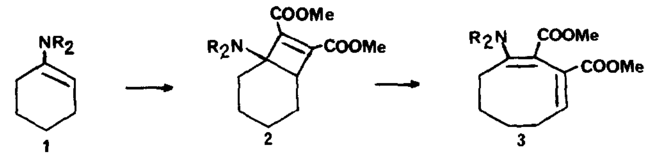
†Dedicated to the memory of Frantisek Sorm.



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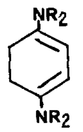

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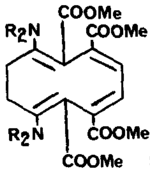

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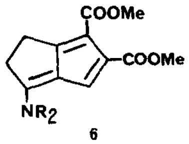

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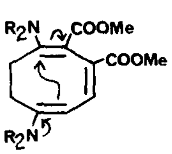

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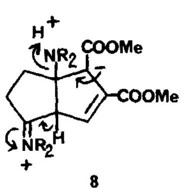

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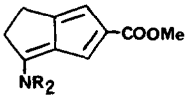

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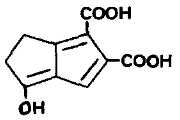

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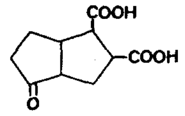

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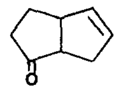

12

(NR_2 = Pyrrolidino)

genation of the semicarbazone of **12** gave the saturated derivative which was converted directly into the 2, 4-dinitrophenylhydrazone. Direct comparison with the two corresponding derivatives of bicyclo[3,3,0]octan-2-one showed their identity.

EXPERIMENTAL

The IR spectra were measured on a Perkin-Elmer 225 spectrometer, UV spectra were run in ethanol on a Unicam SP 800 spectrometer, ^1H NMR spectra were determined in $CDCl_3$ on a Varian HA 100 spectrometer and mass spectra were obtained on an AEI MS 12 instrument. Melting points were taken on a Kofler hot-stage apparatus and analyses were determined by the microanalytical staff of the University of Glasgow.

Bis-enamines of cyclohexane-1, 4-*dione*

To a solution of cyclohexane-1, 4-dione (10.8 g) in benzene (300 ml) was added pyrrolidine (24.6 ml) and the solution refluxed under oxygen-free nitrogen under a Soxhlet apparatus containing 5 Å molecular sieves for 2 hr. Evaporation gave crude 1, 4-dipyrrolidinocyclohexa-1, 3-diene m.p. 134–138° with sublimation. It could not be purified without the occurrence of extensive oxidation.[4] The more stable 1, 4-dimorpholino-compound,[5] prepared in similar fashion (5 hr reflux time), could be purified by vacuum sublimation m.p. 124–126° (Found: C, 67.43; H, 8.72; N, 11.23; $C_{14}H_{22}N_2O_2$ requires C, 67.17; H, 8.86; N, 11.19%), λ_{max} 311 nm (ϵ 13,400); ν_{max} (Nujol) 1648, 1628s, 1592 cm^{-1}; δ 4.91 (2H, s, 2 × =CH), 3.85–3.55 (8H, m, 4 × OCH_2), 2.95–2.65 (8H, m, 4 × NCH_2), 2.32 (4H, s, 2 × CH_2).

2, 3-*Dicarbomethoxy* - 6 - *pyrrolidinobicyclo*[3,3,0]*octa* - 1, 3, 5 - *triene* **6**

To a solution of crude 1, 4-dipyrrolidinocyclohexa-1, 3-diene (21.8 g) in hot oxygen-free toluene was added dimethyl acetylenedicarboxylate (25 ml) and the solution refluxed under nitrogen for 25 hr. Evaporation to 100 ml and cooling the red solution to 0°, filtration and washing with cold benzene gave pale yellow crystals of **6** (63%) m.p. 190–191° after crystallisation from ethyl acetate (Found: C, 66.22; H, 6.40; N, 4.80; M^+ 289. $C_{16}H_{19}NO_4$ requires C, 66.42; H, 6.62; N, 4.84%; M 289) λ_{max} 278 (ϵ 27,200), 326 nm (ϵ 33,400); ν_{max} ($CHCl_3$) 1710, 1693, 1602 cm^{-1}; δ 6.49 (1H, s, =CH), 3.76 (3H, s, $COOCH_3$), 3.72 (3H, s, $COOCH_3$) 3.6 – 3.2 (4H, m, 2 × NCH_2), 2.71 (4H, bs, 2 × CH_2), 2.15 – 1.8 (4H, m, 2 × pyrrolidine CH_2). The corresponding morpholino-compound prepared in the same manner crystallised from ethyl acetate m.p. 189–190° (Found: M^+ 305. $C_{16}H_{19}NO_5$ requires M 305).

3-*Carbomethoxy* - 6 - *pyrrolidinobicyclo*[3,3,0]*octa* - 1, 3, 5 - *triene* **9**

The bicyclooctatriene (**6**; 1.44 g) was refluxed with methanolic hydrogen chloride (60 ml) for 10 hr. The solution was evaporated to 10 ml, ice (50 g) added and the solution basified with 4*M* sodium hydroxide. The precipitate was filtered, washed with water, dried (87%) and purified by vacuum sublimation m.p. 207–209° (Found: C, 72.81; H, 7.17; N, 5.95. $C_{14}H_{17}NO_2$ requires C, 72.70; H, 7.40; N, 6.06%), ν_{max} (Nujol) 1686, 1604 cm^{-1}; δ 6.68 (1H, d, *J* 1.2 Hz, =CH), 6.02 (1H, d, *J* 1.2 Hz, =CH), 3.75 (3H, s, $COOCH_3$) 3.7 – 3.3 (4H, m, 2 × NCH_2), 3.1 – 2.5 (4H, m, 2 × CH_2), 2.2 – 1.7 (4H, m, 2 × pyrrolidine CH_2).

Degradation of **6** *to bicyclo*[3,3,0]*octan*-2-*one*

The bicyclooctatriene (**6**, 2.89 g) was heated under reflux for 2 hr with 0.5*N* sodium hydroxide (40 hr). The solution was reduced to one third of its bulk and concentrated hydrochloric acid added to precipitate the dicarboxylic acid (**10**, 80%) which was crystallised from methanol–ethyl acetate, m.p. 196–198° (Found: C, 57.41; H, 3.89. $C_{10}H_8O_5$ requires C, 57.70; H, 3.87%). This diacid (**10**; 950 mg) was hydrogenated in ethanol (250 ml) using 10% Pd/C (100 mg) and the product **11** electrolytically decarboxylated[3] at a Pt electrode in aqueous pyridine. The resulting crude bicyclo[3,3,0]oct - 6 - en - 2 - one **12** was converted into its semi-carbazone (33% from **10**) m.p. 142–144° from methyl acetate–diisopropyl ether (Found: C, 60.39; H, 7.33; N, 22.59; M^+ 179. $C_9H_{13}N_3O$ requires C, 60.31; H, 7.31; N, 23.19%. M 179). This semicarbazone (58 mg) in ethanol (5 ml) was hydrogenated with 10% Pd/C (10 mg) to give the semicarbazone of bicyclo[3,3,0]octan - 2 - one m.p. 168–170° after crystallisation from methyl acetate–diisopropyl ether and vacuum sublimation (Found: C, 59.47; H, 8.50; N, 23.14; M^+ 181, $C_9H_{15}N_3O$ requires C, 59.64; H, 8.34; N, 23.19%; M 181). The semicarbazone was converted to the 2, 4-dinitrophenylhydrazone m.p. 104.5–105.5° after crystallisation from ethanol–diisopropyl ether (Found: M^+ 304, $C_{14}H_{16}N_4O_4$ requires M^+ 304). Both derivatives were identical by spectroscopic and mixed melting point comparison with the corresponding derivatives of authentic bicyclo[3,3,0]octan - 2 - one.

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