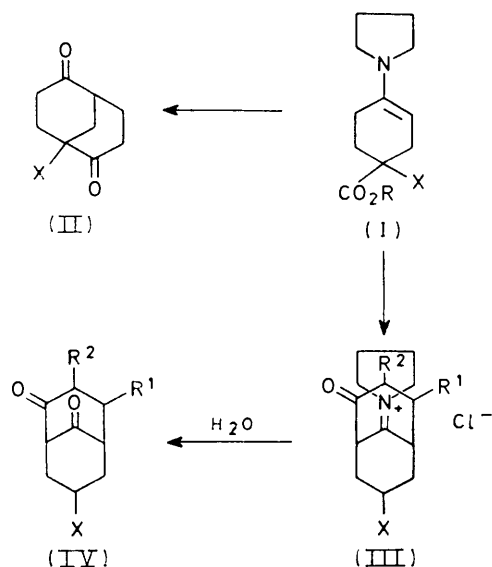


Enamine Chemistry. Part XX.¹ Reactions of $\alpha\beta$ -Unsaturated Acid Chlorides. Synthesis of Alkyl 2,6-Dioxobicyclo[3.3.1]nonane-1-carboxylates, Alkyl 2,9-Dioxobicyclo[3.3.1]nonane-7-carboxylates, and 2,9-Dioxobicyclo[3.3.1]nonane-7-carbonitriles

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Reactions of the pyrrolidine enamines of dialkyl 4-oxocyclohexane-1,1-dicarboxylates with acryloyl chloride give alkyl 2,6-dioxobicyclo[3.3.1]nonane-1-carboxylates, whereas the pyrrolidine enamines of ethyl 4-oxocyclohexane-1-carboxylate and ethyl 1-cyano-4-oxocyclohexane-1-carboxylate give ethyl 2,9-dioxobicyclo[3.3.1]nonane-7-carboxylates and 2,9-dioxobicyclo[3.3.1]nonane-7-carbonitriles, respectively. The reasons for this change in the course of the reaction are discussed. Distillation of the proline enamine of diethyl 4-oxocyclohexane-1,1-dicarboxylate gives a pyrrolo[1,2-*a*]indole derivative.

We have previously reported² the synthesis of alkyl 2,4,6-trioxoadamantane-1-carboxylates by the reaction of dialkyl 4-(pyrrolidin-1-yl)cyclohex-3-ene-1,1-dicarboxylates (I; X = CO₂R) with crotonoyl and methacryloyl chlorides in boiling benzene. The corresponding reaction with acryloyl chloride surprisingly failed to yield an adamantane derivative and no other identifiable products were isolated.



SCHEME 1

Further work has now shown that an intramolecular cyclisation can occur in the reaction with acryloyl chloride, but only after elimination of one of the geminal alkoxy-carbonyl groups in the enamine (I; X = CO₂R). The product obtained on hydrolysis of the enamine function has been shown to be the alkyl 2,6-dioxobicyclo[3.3.1]nonane-1-carboxylate (II; X = CO₂R) rather than the expected alkyl 2,9-dioxobicyclo[3.3.1]nonane-7-carboxylate (IV) (Scheme 1). The latter structure was ruled out by comparison of the ethyl ester with authentic ethyl 2,9-dioxobicyclo[3.3.1]nonane-7-carboxylate (IV; X = CO₂Et, R¹ = R² = H), obtained by reaction of acryloyl chloride with ethyl 4-(pyrrolidin-1-yl)cyclohex-3-ene-1-carboxylate (I; X = H, R = Et). That the two products were not epimers of

(IV) was shown by the failure of sodium ethoxide to effect interconversion. However treatment of the product (II) with concentrated hydrochloric acid resulted in decarboxylation to give bicyclo[3.3.1]nonane-2,6-dione. The change in the course of the reaction can be attributed to a change in the magnitude of the two competing destabilising steric effects which influence the conformations of the intermediate iminium salts [*viz.* A^(1,3) strain³ versus 1,3-diaxial strain] (see ref. 2). The 3-oxoprop-2-enyl substituent, introduced into the enamine at C-3 by reaction with acryloyl chloride, is forced into an equatorial orientation by the steric requirements of the axial ester group at C-1, thus preventing intramolecular cyclisation onto the regenerated enamine position at C-5. Elimination of the axial ester group removes these 1,3-diaxial interactions, and the A^(1,3) interactions between the α -methylene group of the pyrrolidine ring, and the oxopropenyl group forces the latter into an axial orientation and results in cyclisation onto the more reactive carbanionic centre generated at C-1 rather than onto the enamine position at C-5 (Scheme 2). When the temperature of the reaction was lowered, so as to prevent this decarboxylation, only intermolecular reaction with a second molecule of enamine occurred, to give the bis-compound (VI).

In an attempt to decrease the 1,3-diaxial interactions, and thus allow formation of adamantane derivatives from acryloyl chloride or give increased yields with crotonoyl and methacryloyl chlorides, the corresponding reaction with ethyl 1-cyano-4-(pyrrolidin-1-yl)cyclohex-3-ene-1-carboxylate (I; X = CN) has been investigated. The large ester group would be expected to take up an equatorial orientation and the lower steric requirements of the cyano-group might then allow the oxopropenyl group to become axially oriented and thus permit cyclisation to an iminoadamantane. However, the reactions with acryloyl, crotonoyl, and methacryloyl chlorides now gave only the corresponding 2,9-dioxobicyclo[3.3.1]nonane-7-carbonitriles (IV; X = CN). It appears that the increased electron-withdrawing power of the cyano-group results in preferential decarboxylation of the ester *before* the oxopropenyl substituent has been introduced, otherwise the bicyclic 2,6-dione (II; X =

* P. W. Hickmott, H. Suschitzky, and R. Urbani, *J.C.S. Perkin I*, 1973, 2063.

³ F. Johnson, *Chem. Rev.*, 1968, **68**, 375.

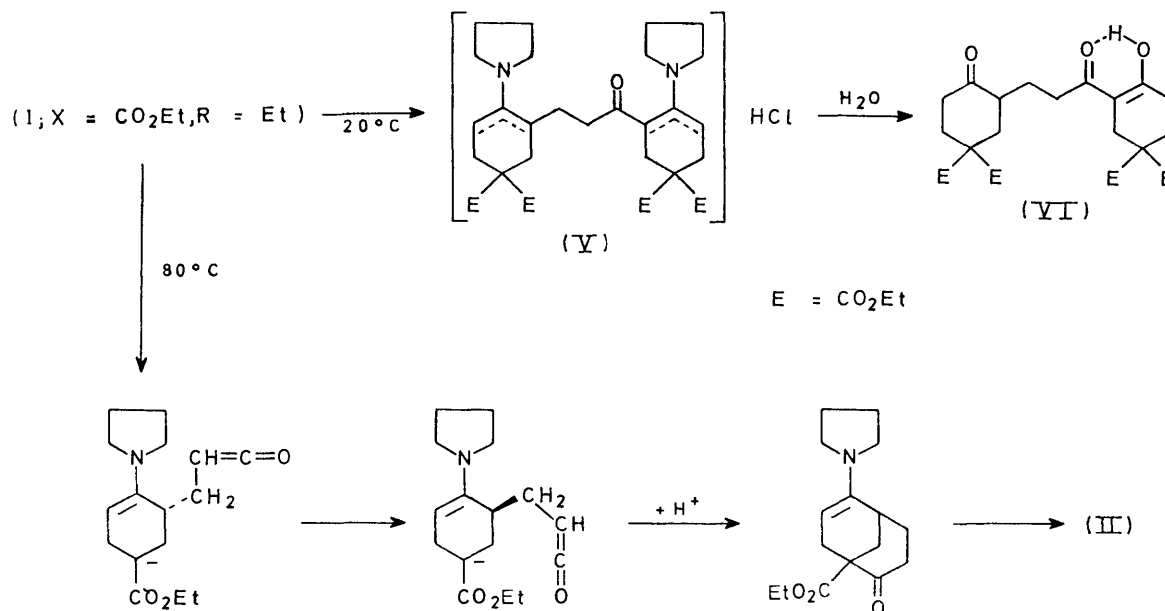
¹ Part XIX, P. W. Hickmott, P. J. Cox, and G. A. Sim, *J.C.S. Perkin I*, 1974, 2544.

CN) or the adamantane derivative would be formed. This ready decarboxylation was confirmed by treatment of the enamine with a trace of toluene-*p*-sulphonic acid in boiling benzene. Only 4-oxocyclohexyl cyanide was isolated on hydrolysis, in quantitative yield.

Finally, an attempt has been made to increase the $A^{(4,9)}$ interactions by introduction of a substituent at the α -position of the pyrrolidine ring, and thus force the oxopropenyl substituent into an axial orientation in the reaction with acryloyl chloride. However, treatment of the proline enamine (VII) of diethyl 4-oxocyclohexane-1,1-dicarboxylate with either acryloyl or crotonyl

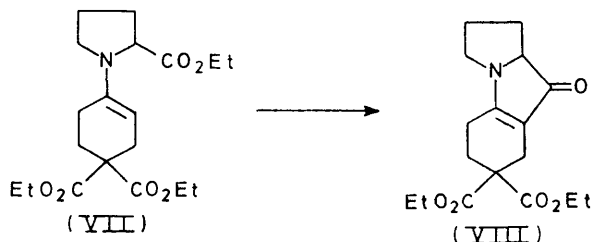
of which was purified by preparative t.l.c. on silica (eluant benzene-acetone, 9:1) to give *ethyl 2,6-dioxobicyclo[3.3.1]nonane-1-carboxylate* (0.17 g, 12%) (Found: C, 64.7; H, 7.0%; M^+ , 224. $C_{12}H_{16}O_4$ requires C, 64.3; H, 7.15%; M , 224); ν_{CO} (film) 1735 and 1700 cm^{-1} ; τ ($CDCl_3$) 5.78 (q, J 7 Hz, CH_2-CH_3), 8.75 (t, J 7 Hz, CH_2-CH_3), and 6.9—8.1 (11 H, complex methylene envelope).

Methyl 2,6-Dioxobicyclo[3.3.1]nonane-1-carboxylate (II; $X = CO_2Me$).—(a) 4-Oxocyclohexane-1,1-dicarboxylic acid⁵ (10 g) was heated under reflux with methanol (100 ml) and a catalytic amount of concentrated sulphuric acid for 20 h. The solvent was removed *in vacuo* and the residue extracted with ether. The extract was washed with



SCHEME 2

chloride resulted in no reaction. During this investigation it was found that distillation of the crude enamine (VII) resulted in cyclisation to the pyrrolo-[1,2-*a*]indole derivative (VIII), in good yield, and the scope of this reaction is being further studied.



EXPERIMENTAL

Ethyl 2,6-Dioxobicyclo[3.3.1]nonane-1-carboxylate (II; $X = CO_2Et$).—Acryloyl chloride (4.62 g) in dry benzene (30 ml) was added dropwise to diethyl 4-(pyrrolidin-1-yl)cyclohex-3-ene-1,1-dicarboxylate⁴ (I; $X = CO_2Et$, $R = Et$) (15.05 g) in boiling benzene (250 ml) during 1 h, and the mixture was heated under reflux for 20 h. The precipitate was collected, washed with dry benzene, and hydrolysed by stirring with cold water (150 ml) for 3 h. Extraction with ether gave the crude product as an oil (4 g), a portion (0.5 g)

n-sodium hydroxide (10 ml) and water (10 ml), dried ($MgSO_4$), and distilled to give *dimethyl 4-oxocyclohexane-1,1-dicarboxylate* (8 g, 75%), b.p. 102° at 60 N m^{-2} (Found: C, 55.9; H, 6.45%; M^+ , 214. $C_{10}H_{14}O_6$ requires C, 56.1; H, 6.55%; M , 214); ν_{CO} (film) 1735br cm^{-1} ; τ ($CDCl_3$) 6.2 ($2 \times OCH_3$) and 7.56 (s, CH_2). The ketone was heated under reflux with pyrrolidine (6 ml) and toluene-*p*-sulphonic acid (0.2 g) in benzene (100 ml) under a Dean-Stark head for 3 h. Distillation gave dimethyl 4-(pyrrolidin-1-yl)cyclohex-3-ene-1,1-dicarboxylate (9 g, 56%), M^+ 267; ν_{max} (film) 1650 (C:C) and 1740 (C:O) cm^{-1} ; τ ($CDCl_3$) 5.8br (=CH), 6.33 (s, $2 \times OCH_3$), 7.03 (m, CH_2-N-CH_2), and 7.2—8.4 (complex).

(b) Treatment of the foregoing enamine with acryloyl chloride (as above) gave *methyl 2,6-dioxobicyclo[3.3.1]nonane-1-carboxylate* as an oil (Found: C, 62.6; H, 6.8%; M^+ , 210. $C_{11}H_{14}O_4$ requires C, 62.9; H, 6.7%; M , 210); ν_{CO} (film) 1740—1700 cm^{-1} ; τ ($CDCl_3$) 6.23 (s, CH_3) and 7.0—8.0 (complex).

Bicyclo[3.3.1]nonane-2,6-dione.—Ethyl 2,6-dioxobicyclo[3.3.1]nonane-1-carboxylate (0.3 g) in glacial acetic acid (1 ml) and water (0.36 ml) was heated under reflux with concentrated hydrochloric acid (0.36 ml) for 11 h. The solvent was evaporated off and the residue purified by

⁴ H. Stetter and H. G. Thomas, *Chem. Ber.*, 1968, **101**, 1115.

⁵ T. Kutsuma and S. Sugawara, *Tetrahedron*, 1958, **3**, 175.

preparative t.l.c. on silica (eluant benzene-acetone, 9 : 1) to give bicyclo[3.3.1]nonane-2,6-dione as a waxy solid (0.075 g, 37%), m.p. and mixed m.p. 140.5–141.5° (from 1 : 1 benzene-cyclohexane) (lit.,^{6b} 141°) (Found: M^+ , 152.0837. Calc. for $C_9H_{12}O_2$: M , 152.0838), identical (i.r. and n.m.r.) with authentic material⁶ [ν_{CO} (Nujol) 1700 cm^{-1} (sharp); τ ($CDCl_3$) 7.0–8.0 (complex)].

Ethyl 2,9-Dioxobicyclo[3.3.1]nonane-7-carboxylate (IV; X = CO_2Et , $R^1 = R^2 = H$).—(a) Ethyl 4-oxocyclohexane-1-carboxylate⁷ (20 g), pyrrolidine (8 ml), and toluene-*p*-sulphonic acid (0.2 g) in benzene (100 ml) were heated under reflux for 20 h under a Dean-Stark head. Distillation gave ethyl 4-(pyrrolidin-1-yl)cyclohex-3-ene-1-carboxylate (15 g, 56%), M^+ 223; ν_{max} (film) 1735 (C:O) and 1645 (C:C) cm^{-1} ; τ ($CDCl_3$) 5.87 (q, $CH_2 \cdot CH_3$, and =CH), 6.92 (m, $CH_2 \cdot N \cdot CH_2$), 8.75 (t, $CH_2 \cdot CH_3$), and 7.5–8.6 (complex, CH_2).

(b) Acryloyl chloride (2.03 g) in dry benzene (30 ml) was added dropwise to the foregoing enamine (5 g) in boiling benzene (150 ml) and the mixture was heated under reflux for 20 h. The precipitate was hydrolysed with cold water (100 ml) for 3 h, and the crude oil (3.1 g) was extracted with ether and purified by preparative t.l.c. on silica (eluant benzene-acetone, 9 : 1) to give *ethyl 2,9-dioxobicyclo[3.3.1]nonane-7-carboxylate* (1.54 g, 32%) (Found: C, 64.35; H, 7.1%; M^+ , 224. $C_{12}H_{16}O_4$ requires C, 64.3; H, 7.15%; M , 224; ν_{CO} (film) 1705–1740 cm^{-1} ; τ ($CDCl_3$) 5.88 (q, $CH_2 \cdot CH_3$) and 6.7–8.2 (complex, CH_2). Hydrolysis of the bicyclic dione (0.3 g) by heating under reflux with glacial acetic acid (1 ml), water (0.36 ml), and concentrated hydrochloric acid (0.36 ml) for 11 h gave β -(2-oxo-5-carboxycyclohexyl)propionic acid, identical with authentic material.⁸

Ethyl 4-Methyl-2,9-dioxobicyclo[3.3.1]nonane-7-carboxylate (IV; X = CO_2Et , $R^1 = Me$, $R^2 = H$).—Treatment of ethyl 4-(pyrrolidin-1-yl)cyclohex-3-ene-1-carboxylate with crotonoyl chloride (as above) gave *ethyl 4-methyl-2,9-dioxobicyclo[3.3.1]nonane-7-carboxylate* (13%) (Found: C, 65.4; H, 7.4%; M^+ , 238. $C_{13}H_{18}O_4$ requires C, 65.55; H, 7.65%; M , 238; ν_{CO} (film) 1730 cm^{-1} ; τ ($CDCl_3$) 5.9 (q, $CH_2 \cdot CH_3$), 6.8–8.2 (complex, CH_2), and 8.6–9.2 (2 \times CH_3).

2,9-Dioxobicyclo[3.3.1]nonane-7-carbonitrile (IV; X = CN, $R^1 = R^2 = H$).—(a) Ethyl 3-bromopropionate (100 g) was added dropwise to ethyl cyanoacetate (31.2 g) and sodium (12.7 g) in ethanol (500 ml) at 0 °C during 1 h. The mixture was heated under reflux for 20 h and filtered, and the filtrate was evaporated to dryness. Water (100 ml) was added to the residue and the mixture was extracted with ether (2 \times 100 ml). The extract was dried ($MgSO_4$) and distilled to give *diethyl 4-cyano-4-ethoxycarbonylheptanedioate* (60 g, 60%), b.p. 178° at 133.4 N m^{-2} (Found: C, 57.4; H, 7.3; N, 4.6%; M^+ , 313. $C_{15}H_{23}NO_6$ requires C, 57.5; H, 7.4; N, 4.5%; M , 313; ν_{max} (film) 2260 (C:N) and 1745 (C:O) cm^{-1} ; τ ($CDCl_3$) 5.8 (q, $CH_2 \cdot CH_3$), 8.7 (m, $CH_2 \cdot CH_3$), and 7.2–8.0 (complex, CH_2).

(b) The foregoing triester (75 g) was added to an aqueous ethanolic solution (500 ml) of sodium hydroxide (19.6 g) at 23 °C and left at ambient temperature for 20 h. The solvent was evaporated off *in vacuo* and the residue acidified with concentrated hydrochloric acid; the resulting oil was extracted with ether to give *4-cyano-4-ethoxycarbonylheptanedioic acid* (40 g, 65%) (Found: C, 51.2; H, 5.9; N, 5.4%; M^+ , 257. $C_{11}H_{15}NO_6$ requires C, 51.4; H, 5.8; N, 5.5%;

M , 257; ν_{max} (film) 2260 (C:N) and 1700–1745 (C:O) cm^{-1} ; τ ($CDCl_3$) –1.7br (CO_2H), 5.80 (q, $CH_2 \cdot CH_3$), 8.73 (t, $CH_2 \cdot CH_3$), and 7.2–8.0 (complex, CH_2).

(c) The dicarboxylic acid (42.3 g) was added to acetic anhydride (153 ml) and pyridine (15.3 ml) and heated under reflux for 2 h. The mixture was filtered and the filtrate evaporated to dryness, and the residual black oil was distilled to give *ethyl 1-cyano-4-oxocyclohexane-1-carboxylate* (16 g, 50%), b.p. 130° at 33.4 N m^{-2} (Found: C, 61.7; H, 6.6; N, 7.3%; M^+ , 195. $C_{10}H_{13}NO_3$ requires C, 61.6; H, 6.7; N, 7.2%; M , 195; ν_{max} (film) 2240 (C:N) and 1735 (C:O) cm^{-1} ; τ ($CDCl_3$) 5.87 (q, $CH_2 \cdot CH_3$), 8.75 (t, $CH_2 \cdot CH_3$), and 7.0–8.3 (complex, CH_2). The ketone (14 g) was converted into the enamine by heating with pyrrolidine (7 ml) and toluene-*p*-sulphonic acid (0.2 g) in toluene (100 ml) for 20 h under a Dean-Stark head and then for a further 24 h under a molecular sieve (4 Å). Evaporation of the solution and distillation of the residue gave ethyl 1-cyano-4-(pyrrolidin-1-yl)cyclohex-3-ene-1-carboxylate (I; X = CN) (4 g, 22.5%), b.p. 128° at 40 N m^{-2} , M^+ 248; ν_{max} (film) 2220 (C:N), 1730 (C:O), and 1645 (C:C) cm^{-1} ; τ ($CDCl_3$) 5.77 (q, $CH_2 \cdot CH_3$), 6.53 (=CH), 6.92 (m, $CH_2 \cdot N \cdot CH_2$), 8.83 (t, $CH_2 \cdot CH_3$), and 7.2–8.4 (complex, CH_2).

(d) Treatment of a boiling solution of the enamine (I; X = CN) (2.5 g) in dry benzene (100 ml) with acryloyl chloride (0.96 g) as described in previous experiments gave *2,9-dioxobicyclo[3.3.1]nonane-7-carbonitrile* (0.56 g, 29%) (Found: C, 67.4; H, 6.3; N, 7.7%; M^+ , 177.0790. $C_{10}H_{11}NO_2$ requires C, 67.8; H, 6.2; N, 7.9%; M , 177.0790; ν_{max} (film) 2270 (C:N) and 1720 (C:O) cm^{-1} ; τ ($CDCl_3$) 6.5–8.0 (complex, CH_2).

4-Methyl-2,9-dioxobicyclo[3.3.1]nonane-7-carbonitrile (IV; X = CN, $R^1 = Me$, $R^2 = H$).—In the same way as before, treatment of a boiling solution of the enamine (I; X = CN) (2.82 g) in dry benzene (100 ml) with crotonoyl chloride (1.25 g) gave *4-methyl-2,9-dioxobicyclo[3.3.1]nonane-7-carbonitrile* (0.45 g, 20%), m.p. 88° (Found: C, 69.2; H, 6.7; N, 7.2%; M^+ , 191.0944. $C_{11}H_{13}NO_2$ requires C, 69.2; H, 6.8; N, 7.3%; M , 191.0946; ν_{max} (Nujol) 2270 (C:N) and 1720 (C:O) cm^{-1} ; τ ($CDCl_3$) 8.85 (d, CH_3) and 6.9–8.1 (complex, CH_2). Heating the bicyclic dione (0.3 g) with glacial acetic acid (1 ml), water (0.36 ml), and concentrated hydrochloric acid (0.36 ml) under reflux for 11 h, removal of the solvent, and preparative t.l.c. gave β -methyl- β -(2-oxo-5-carboxycyclohexyl)propionic acid (0.202 g, 56%), M^+ 228.0895; ν_{CO} (Nujol) 1700 cm^{-1} ; τ ($CDCl_3$) 0.31 (s, CO_2H), 9.0 (m, CH_3), and 6.9–8.2 (CH_2).

3-Methyl-2,9-dioxobicyclo[3.3.1]nonane-7-carbonitrile (IV; X = CN, $R^1 = H$, $R^2 = Me$).—Under the same conditions treatment of the enamine (I; X = CN) (2.5 g) in boiling benzene (100 ml) with methacryloyl chloride (1.1 g) gave *3-methyl-2,9-dioxobicyclo[3.3.1]nonane-7-carbonitrile* (0.7 g, 33%) (Found: C, 69.1; H, 6.8; N, 7.1%; M^+ , 191.0944. $C_{11}H_{13}NO_2$ requires C, 69.2; H, 6.8; N, 7.3%; M , 191.0946; ν_{max} (Nujol) 2270 (C:N) and 1720 (C:O) cm^{-1} ; τ ($CDCl_3$) 9.33 (d, CH_3) and 7.4–9.0 (complex, CH_2).

4-Oxocyclohexyl Cyanide.—Ethyl 1-cyano-4-(pyrrolidin-1-yl)cyclohex-3-ene-1-carboxylate (I; X = CN) (1 g) in benzene (20 ml) was heated under reflux in the presence of a crystal of toluene-*p*-sulphonic acid for 20 h. The solvent was removed *in vacuo* and the residual oil hydrolysed with ice-cold water (40 ml) for 3 h. Extraction with ether gave

⁶ (a) J. P. Schaefer and L. M. Honig, *J. Org. Chem.*, 1968, **33**, 2655; (b) H. Meerwein and W. Schurmann, *Annalen*, 1913, **398**, 196.

⁷ L. N. Owen and P. A. Robins, *J. Chem. Soc.*, 1949, 327.

⁸ H. Stetter and H. G. Thomas, *Chem. Ber.*, 1966, **99**, 920.

4-oxocyclohexyl cyanide (0.5 g, 100%), purified by preparative t.l.c. on silica (eluant benzene-acetone, 9:1), M^+ 123.0682; $\nu_{\max.}$ (film) 2 250 (C:N) and 1 718 (C:O) cm^{-1} ; τ (CDCl_3) 6.7–8.1 (m).

Diethyl 3-[β -(5,5-Bisethoxycarbonyl-2-oxocyclohexyl)propionyl]-4-oxocyclohexane-1,1-dicarboxylate (VI).—Acryloyl chloride (0.77 g) in dry benzene (30 ml) was added dropwise to diethyl 4-(pyrrolidin-1-yl)cyclohex-3-ene-1,1-dicarboxylate (I; X = CO_2Et , R = Et) (5 g) in benzene (150 ml) at ambient temperature during 1 h, and the resulting suspension was heated under reflux for 20 h. The precipitate (V) was collected,* washed with dry benzene, and stirred with ice-cold water (50 ml) for 3 h. Extraction with ether (3 \times 50 ml) gave the *product* (VI) (1.3 g, 29%) as an oil (Found: C, 60.55; H, 7.3%; M^+ , 538. $\text{C}_{27}\text{H}_{38}\text{O}_{11}$ requires C, 60.2; H, 7.1%; M , 538); ν_{CO} (film) 1 730 and 1 600 br cm^{-1} ; τ (CCl_4) —5.73 (s, enolic OH), 5.82 (q) and 8.75 (q) ($\text{CH}_2\cdot\text{CH}_3$), and 7.0–8.0 (complex, CH_2).

Diethyl 2,3,5,6,7,8,9,9a-Octahydro-9-oxo-1H-pyrrolo[1,2-a]-indole-7,7-dicarboxylate (VIII).—Diethyl 4-oxocyclohexane-1,1-dicarboxylate (9.68 g) and ethyl pyrrolidine-2-carboxylate (5.6 g) were heated under reflux under a molecular

sieve (4 Å) for 20 h. Removal of the solvent *in vacuo* gave crude diethyl 4-(2-ethoxycarbonylpyrrolidin-1-yl)cyclohex-3-ene-1,1-dicarboxylate (VII) (13.2 g). Distillation of the crude enamine (10.8 g) gave the *pyrrolo[1,2-a]indole* (VIII) (5 g, 52%), b.p. 175° at 1.33 N m^{-2} (Found: C, 63.5; H, 7.4; N, 4.25%; M^+ , 321.1576. $\text{C}_{17}\text{H}_{23}\text{NO}_5$ requires C, 63.5; H, 7.2; N, 4.4%; M , 321.1581); $\nu_{\max.}$ (film) 1 730 and 1 670 (C:O) and 1 590 (C:C) cm^{-1} ; $\lambda_{\max.}$ (MeOH) 332 nm (ϵ 6 320); τ (CDCl_3) 5.83 (q, $\text{CH}_2\cdot\text{CH}_3$), 8.81 (t, $\text{CH}_2\cdot\text{CH}_3$), and 6.0–8.4 (complex, CH_2). Treatment of the enamine (VII) with acryloyl or crotonoyl chloride in boiling benzene gave diethyl 4-oxocyclohexane-1,1-dicarboxylate and ethyl pyrrolidine-2-carboxylate, derived by hydrolysis of the enamine, as the only identified products.

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* The filtrate was not examined further since any adamantane derivative or bicyclic dione (IV) would have been precipitated from the benzene solution as the corresponding iminium salt.