Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 95, Nos 5 & 6, December 1985, pp. 439–446.

Investigations towards the synthesis of a CD-steroid intermediate

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MS received 3 May 1985; revised 24 June 1985

Abstract. The development of a new synthesis of 2,6,7,7a-tetrahydro-1β-hydroxy-4-formyl-7a-methylindene was undertaken involving the preparation of 2,6,7,7a-tetra-hydro-1β-hydroxy-4-methoxymethyl-7a-methylindene because of the erratic yield in the last oxidation step of the reported synthesis of the former compound. Although various attempts to prepare the latter were not successful, interesting rearrangement products, the dienone, 5,6,7,7a-tetrahydro-4,7a-dimethyl-5H-indene-1,5-dione and the tricyclic keto alcohol, 2,6-diketo-3-methyltricyclo(5,2,1,0)decan-8-ol, were obtained, the structures of which have been proved by spectral data. Mechanisms for the formation of these products have been proposed.

Keywords. Methylindene; synthesis; spectral data; dienone; tricyclic keto alcohol.

1. Introduction

In the synthesis of 2,6,7,7a-tetrahydro-1β-hydroxy-4-formyl-7a-methylindene (1a) (Banerjee *et al* 1976) and its optically active form (Banerjee *et al* 1983), considered to be an important synthon for the total synthesis of steroids, inconsistent yields were encountered in the last step involving oxidation of 1b to 1a by selenium dioxide. This prompted us to undertake the preparation of the methoxy compound (1d) that might be converted to 1a via the hydroxy compound (1c).

2. Results and discussion

For this purpose, the methoxyaminoketone (2a), the diaminoketone (2d) and the ethoxyaminoketone (2b) were prepared, as described below, and subjected to the annelation reaction with 2-methylcyclopentan-1,3-dione (5) under various conditions.

For the preparation of the first compound, 2-methoxyethyl bromide (Tallman 1934) was added to sodium acetylide, prepared by bubbling dry acetylene through sodamide in liquid ammonia, to get 4-methoxybut-1-yne (3) in 66% yield. Mannich reaction with the compound (3), formaldehyde and diethylamine gave the methoxydiethylamine (4), which was hydrated with mercuric sulphate and aq. H_2SO_4 to give the methoxyaminoketone (2a) in 25% yield. The structural assignment was supported by spectral data. The regioselectivity in the hydration reaction was presumably due to the following reasons. In the acetylenic amine (4), the C-3 is electron-deficient because of the relatively stronger inductive effect of the nitrogen of the aminomethylene compared to that of the oxygen of the methoxymethylene, the latter being separated by one extra

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methylene from the triple bond, and thus is open to attack by the nucleophilic hydroxyl ion, leading to the formation of the ketone (2a). The structure of the aminoketone (2a) was further confirmed by its preparation by the following unambiguous procedure, which incidentally proved to be a much better method because of the higher yield. The chloromethoxyketone (2e), obtained by the interaction of ethylene and β-methoxypropionylchloride in the presence of anhydrous $AlCl_3$, was treated with diethylamine in benzene to afford the aminoketone (2a) in 56% overall yield.

Various attempts, such as the Grignard reactions of 2-methoxyethylmagnesium bromide and vinylmagnesium bromide with 3-(diethylamino)-propionitrile and 3-methoxypropionitrile respectively gave back the starting compounds. The dichloroketone (2f) (Jones and Taylor 1961) also failed to react with methanol, but with diethylamine the required chloroaminoketone (2c) was obtained as the minor product, along with the second compound, the diaminoketone (2d) in larger quantity.

The third compound, the ethoxyaminoketone (2b) was prepared by the interaction of β-ethoxypropionylchloride and ethylene in the presence of anhydrous $AlCl_3$ to yield the chloroethoxyketone (2g) followed by its treatment with diethylamine in benzene.

The annelation reaction between the aminoketone (2a) and the dione (5) in xylene in the presence of pyridine followed by treatment with PTS (*p*-toluene sulphonic acid) gave the dienone (6) and the tricyclic keto-alcohol (7) (Danishefsky and Migdalof 1969a). The structure of the dienone (6) was confirmed by its spectral data and by its conversion to the known compound (8) (Banerjee *et al* 1976) by catalytic hydrogenation.

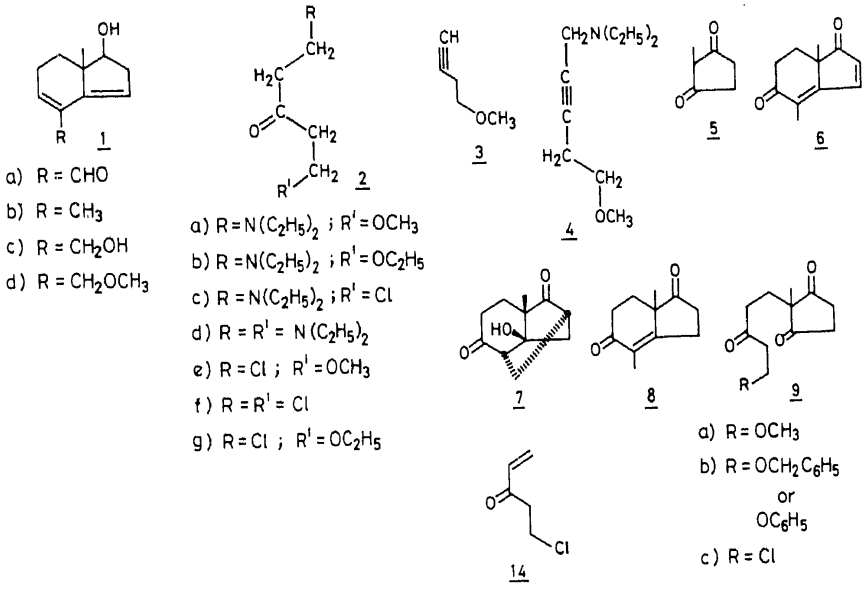
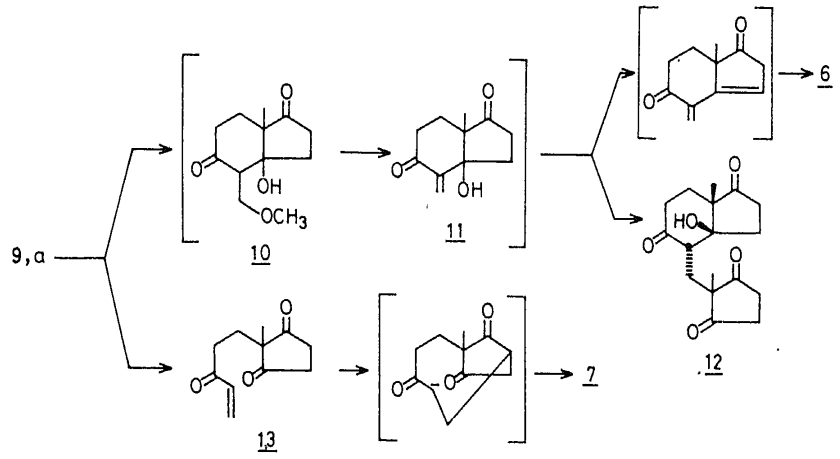


Chart 1.

The formation of the dienone (6) and the tricyclic keto alcohol (7) has been rationalised as follows (scheme 1). In the first case, the preliminary formation of the aldol (10), via the triketone (9a), has been envisaged, which on demethoxylation might give rise to the hydroxy enedione (11), the latter giving the dienone (6) by dehydration followed by isomerization. That the demethoxylation occurred in preference to the

dehydration was proved by trapping the intermediate (11) in the reaction of the triketone (9a) with one mole of the dione (5) in pyridine and benzene to give the hydroxy tetraketone (12)*. In the second case, it is presumed that the triketone (9a) undergoes demethoxylation to give the intermediate unsaturated triketone (13) which is converted to the tricyclic keto alcohol (7)* according to the mechanism, proposed by Danishefsky (Danishefsky and Migdalof 1969a), who had prepared the compound (13) by the condensation of the chlorovinyl ketone (14) and methyl cyclopentane dione (5). It may be mentioned that while the addition of the dione (5) to the intermediate (11) to give the hydroxytetraketone (12) is facile, similar addition to the intermediate (13) is not favoured because of the obvious preference to that of the Danishefsky pathway, mentioned earlier.



Scheme 1.

In the above mechanisms, the formation of the triketone (9a) has been assumed, the actual formation of which was realized when the condensation was carried out under milder conditions, viz, the treatment of the aminoketone (2a) with the dione (5) and pyridine in benzene at room temperature. Attempts to prepare the triketones (9a and 9b) by the individual addition of methanol, benzylalcohol and phenol to the mixture of the chlorotriketone (9c) and vinyl triketone (13) (Danishefsky and Migdalof 1969b) were futile.

Reactions with the diaminoketone (2d) or with the ethoxyaminoketone (2b) or with the triketone (9a) in place of 2a also resulted in the formation of the dienone (6) and the tricyclic keto alcohol (7).

3. Experimental

All boiling points and melting points are uncorrected. Anhydrous sodium sulphate has been used as the drying agent. The analytical data for compounds of series (2) are not

* Stereochemistry assigned to the racemic compounds (7) and (12) is based in analogy with that reported for a similar compound (Ramachandra and Kalyani Vijayan 1973).

reported as they are very labile. UV and IR spectra were determined on Shimadzu-180 and Perkin-Elmer 781 spectrophotometers. ^{1}H-NMR spectra were taken on Varian T-60 spectrometer. Chemical shifts reported are in δ values (ppm) relative to TMS as internal standard. The ^{13}C-NMR spectra were measured on a Brucker WH-270 spectrometer at 67·89 MHz in the pulsed mode. Mass spectra were determined on Atlas CH-4 spectrometer (70 eV).

3.1 4-*Methoxybut*-1-*yne* (3)

The acetylenic compound (3) was prepared by modifying a reported procedure (McCusker and Kroeger 1937). Sodium (9 g) was added in small portions to distilled liquid ammonia (≈ 550 ml), dry acetylene was then bubbled through it until a white suspension of sodium acetylide was formed. To this stirred suspension, 2-methoxyethylbromide (48 g) was slowly added dropwise and the stirring was continued for two hours with a stream of acetylene bubbling through the mixture. The ammonia was allowed to evaporate and a saturated solution of ammonium chloride was carefully added. The solution was chilled in a bath of ice-salt mixture and neutralized with 6N HCl. The product was collected after distillation by heating the reaction mixture on the waterbath, dried and redistilled to afford 20 g (66%) of the compound (3); b.p. 74–76° (reported 86–87°). IR (neat): ν_{max} 3300, 2850, 2150 cm^{-1}. ^{1}H-NMR (CCl_4): 1·9 (*t*, J = 2 Hz, 1H, C≡CH), 2·40 (*dt*, J = 2 Hz, 7 Hz, 2H, $-CH_2-C\equiv C$), 3·35 (*S*, 3 H, $-OCH_3$) and 3·45 (*t*, J = 7 Hz, 2H, OCH_2).

3.2 *N-diethylamino*-5-*methoxypent*-2-*yne* (4)

A mixture of 4-methoxybut-1-yne (3, 40 g), diethylamine (52 ml), acetic acid (30 ml), formalin (60 ml, 35% solution), cuprous chloride (0·8 g) and water (40 ml) was stirred under N_2 for 60 hr. The mixture was basified (pH > 13) with aq. NaOH, saturated with ammonium sulphate and extracted with ethylacetate (3 × 50 ml). The extract was washed with brine, dried and the solvent removed. The product (50 g, 63%) was isolated by distillation, b.p. 135–40°/60 mm. ^{1}H-NMR (CCl_4): 1·0 (*t*, J = 7 Hz, 6H, $-N-CH_2-\underline{CH_3}$), 2·4 (*m*, 6H, $-N-\underline{CH_2}-CH_3$ and $-\underline{CH_2}-CH_2-OCH_3$), 3·3 (*S*, 5H, $-OCH_3$ and $=C-\underline{CH_2}-N-$) and 3·35 (*m*, 2H, $-CH_2-O-$). (Found: C, 71·23; H, 11·40; N, 8·31. $C_{10}H_{19}NO$ requires: C, 70·96; H, 11·32; N, 8·28%.)

3.3 *N-diethylamino*-5-*methoxypentan*-3-*one* (2a)

3.3a *Preparation*: A mixture of the amine (4, 3·3 g), conc. H_2SO_4 (1·4 ml) and mercuric sulphate (0·25 g) in water (15 ml) was stirred under N_2 at RT for 15 hr. The mixture was basified (pH > 13) with aq. NaOH and extracted with ethylacetate after saturation with ammonium sulphate. The extract was washed with brine and then dried, the solvent removed and the product isolated by column chromatography (neutral alumina, ethylacetate-hexane, 3:1); yield, 930 mg (25%); b.p. 61–64°/50 mm; IR (neat): ν_{max} 1705 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 1·0 [*t*, J = 7 Hz, 6H, $-N(CH_2\underline{CH_3})_2$], 2·52 [*m*, 10H, $-\underline{CH_2}-N(\underline{CH_2}CH_3)_2$ and $-\underline{CH_2}-CO-\underline{CH_2}-$], 3·28 (*S*, 3H, OCH_3) and 3·64 (*t*, J = 7 Hz, 2H, OCH_2); Mass: M^+ *m/e* 187, *m/e* 86 (100%).

3.3b *Improved method*: To a stirred ice-cold mixture of diethylamine (1·46 g) in benzene (15 ml) 1-chloro-5-methoxypentan-3-one (2e; 1·5 g), whose preparation has

been described below, was added dropwise and left for 4 hr at 0°. The reaction mixture was basified (pH > 13) with dil. NaOH and extracted with ethylacetate. After removal of the solvent, the crude compound was distilled to get aminomethoxyketone (2a; 1·5 g, 81 %); b.p. 61–64°/50 mm.

1-Chloro-5-methoxypentan-3-one(2,e) and di-2-chloroethylketone (2f): To anhydrous $AlCl_3$(67 g), dissolved in dichloromethane (250 ml) and cooled to 0°, was added dropwise β-methoxypropionylchloride (56 g). Ethylene was bubbled through the mixture for 4–5 hr, the temperature being maintained between 0 and 5°. The reaction mixture was poured into crushed ice containing 100 ml of conc. HCl and extracted with dichloromethane. The organic layer was washed successively with water, $NaHCO_3$, water, brine and then dried. After removal of the solvent under reduced pressure, the crude compound was chromatographed over neutral alumina. The first fraction (hexane-benzene, 1:1) gave di-2-chloroethylketone (2f; 5·6 g) which was identified by comparison with an authentic sample (Jones and Taylor 1961), and the second fraction (hexane-chloroform, 1:3) gave the required methoxychloroketone (2e; 34·8 g, 68 %); b.p. 131–135°/5 mm; IR (neat); ν_{max} 1720 cm^{-1}; ^{1}H-NMR (CCl_4): 2·66 (*t*, *J* = 7 Hz, 2H, $COCH_2CH_2O$–), 2·93 (*t*, *J* = 6 Hz, 2H, $COCH_2CH_2Cl$), 3·33 (*S*, 3H, OCH_3), 3·53–3·8 (*m*, 4H, $-CH_2O-$ and $-CH_2Cl$).

3.3c *Attempted preparation of the aminoketone* (2a) *by a two-step conversion of the dichloroketone* (2f)—*1-Chloro-5-(diethylamino)pentan-3-one*(2c) *and di-2-(diethylamino) ethylketone*(2d): A mixture of dichloroketone (2f; 1·55 g), diethylamine (1·4 g) and benzene (25 ml) was stirred at 0° for 4 hr. The reaction mixture was basified with dil NaOH and extracted with benzene. After the removal of the solvent, the crude compound was chromatographed over neutral alumina. Elution with hexane-chloroform (1:1) gave the starting dichloroketone (0·79 g), elution with chloroform initially afforded the monoaminoketone (2c; 0·17 g, 9·1 %) and then the diaminoketone (2d; 0·53 g, 23 %), as the last fraction; IR (neat): ν_{max} 1710 cm^{-1}; ^{1}H-NMR (CCl_4): 1·97 (*t*, *J* = 7 Hz, 12H, methyl H), 2·32–2·76 (*m*, 16H, methylene H).

As the required monoaminoketone (2c) was obtained in very poor yield, the second step, i.e. treatment with methanol was not carried out.

3.4 *N-diethylamino-5-ethoxypentan-3-one* (2b)

β-Ethoxypropionylchloride was treated with ethylene in the presence of anhydrous $AlCl_3$ to get the chloroethoxyketone (2g; 53 %; IR (neat): ν_{max} 1715 cm^{-1}) which on treatment with diethylamine in benzene afforded (2b in 65 % yield. IR (neat); ν_{max} 1710 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 0·91–1·25 (*m*, 9H, $-N(CH_2CH_3)_2$ and $-OCH_2CH_3$), 2·28–2·60 (*m*, 10H, $-CH_2-N(CH_2CH_3)_2$ and $-CH_2COCH_2$) and 3·23–3·58 (*m*, 4H, $-CH_2-OCH_2CH_3$).

3.5 *5,6,7,7a-Tetrahydro-4,7a-dimethyl-5H-indene-1,5-dione*(6) *and 2,6-diketo-3-methyltricyclo*(5,2,1,0)*decan-8-ol* (7)

A mixture of the aminoketone (2a; 1·25 g), 2-methylcyclopentan-1,3-dione (5, 0·85 g), pyridine (1·75 ml) and xylene (10 ml) was heated under reflux for 20 hr. The mixture was diluted with chloroform and washed with dil. HCl, water, aq. $NaHCO_3$, water and brine. The chloroform was removed and PTS (1 g) was added to the xylene solution

which was then refluxed with a Dean-Stark attachment. After 4 hr, the solution was thoroughly washed with water, concentrated under vacuum and chromatographed over silica gel. Elution with chloroform initially gave 5,6,7,7a-tetrahydro-4,7a-dimethyl-5H-indene-1,5-dione (6, 0·71 g, 59 %) as the major product, which was further purified by a shortpath distillation; 136–140°/2 mm. UV (C_2H_5OH): λ_{max} 290 and 300 nm (ε 9300 and 11 000); IR (neat): ν_{max} 1710 and 1670 cm^{-1}; ^{1}H-NMR (CCl_4): 1·28 (*s*, 3H, CH_3), 1·88 (*s*, 3H, olefinic CH_3), 1·60–2·82 (*m*, 4H, $-CH_2-$), 6·32 (*d*, J = 3 Hz, 1H, olefinic α-H) and 7·06 (*d*, J = 3 Hz, 1H, olefinic β-H); Mass: M^+ *m/e* 176, *m/e* 161, *m/e* 133. (Found: C, 74·91; H, 6·90; $C_{11}H_{12}O_2$ requires C, 74·97; H, 6·86 %.)

Its structure was further confirmed by its conversion to the known compound (8) by the following procedure.

An ethanolic solution of the dienone (6, 260 mg) was hydrogenated over 5 % Pd-C catalyst (30 mg) for four hr when a little more than one equivalent of hydrogen was absorbed. The catalyst was filtered, the solution concentrated under vacuum and chromatographed over silica gel (hexane-ethylacetate, 1 : 1) when the compound (8) was obtained as a gummy material. The structure was confirmed by the direct comparison of the spectral data and by TLC with those of an authentic sample (Banerjee *et al* 1976).

Further elution with chloroform furnished the white crystalline compound (7, 0·12 g, 12 %), which was recrystallized from hexane-benzene; m.p. 170–171° (reported 172–174°, Danishefsky and Migdalof 1969a), IR (nujol): ν_{max} 3360, 1735 and 1690 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 1·13 (*s*, 3H, CH_3), 1·62–2·66 (*m*, 10H, methylenes and methine protons), 4·9 (*s*, 1H, OH, exchangeable with D_2O); Mass: M^+ *m/e* 194 and *m/e* 69 (base peak).

3.6 2-(5-*Methoxy*-3-*ketopentyl*)-2-*methylcyclopentan*-1,3-*dione* (9a)

3.6a *Preparation*: A mixture of the aminoketone (2a; 1·9 g), 2-methylcyclopentane-1,3-dione (5, 1·1 g), dry benzene (20 ml) and pyridine (2·5 ml) was stirred at RT for 24 hr. The solution was cooled, diluted with benzene, washed successively with dil. HCl, water, aq. $NaHCO_3$ and water and then dried. The solvent was removed under vacuum and the residue on distillation gave the pure methoxytriketone (9a; 1·54 g, 65 %); b.p. 176–183° (≈ 1 mm). IR (neat): ν_{max} 1750, 1710, 1705 and 1110 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 1·11 (*S*, 3H, CH_3), 1·92 (*t*, J = 7 Hz, 2H, $-\underline{CH}_2-C-CH_3$), 2·50 (*t*, J = 7 Hz, 2H, $-\underline{CH}_2-CH_2-C-CH_3$), 2·63 (*t*, J = 6 Hz, 2H, $OCH_2-\underline{CH}_2-$), 2·81 (*S*, 2H, ring methylene), 2·83 (*S*, 2H, ring methylene), 3·32 (*S*, 3H, OCH_3) and 2·62 (*t*, J = 6 Hz, 2H, $-OCH_2-$); ^{13}C-NMR ($CDCl_3$): 18·66 (*q*, CH_3), 27·77 (*t*, $\underline{CH}_2-C-CH_3$), 34·73 (*t*, ring methylenes), 37·07 (*t*, $-\underline{CH}_2-CH_2-C-CH_3$), 42·72 (*t*, $-OCH_2-\underline{CH}_2-$), 55·08 (*S*, $\underline{C}-CH_3$), 58·66 (*q*, OCH_3), 67·30 (*t*, $-OCH_2$), 208·16 (*S*, acyclic CO) and 215·77 (*S*, ring CO); Mass: M^+ *m/e* 266, *m/e* 211, *m/e* 125. (Found: C, 63.58; H, 8·00. $C_{12}H_{18}O_4$ requires C, 63·70; H, 8·02 %.)

3.6b *Attempted preparation of alkoxytriketones (9a and 9b) by another method. Reaction between the mixture of chlorotriketone (9c) and vinyl triketone (13) and different hydroxy compounds*: The mixture of triketones (9c and 13), prepared as per Danishefsky and Migdalof (1969b), except that DMSO was used as the solvent in place of monoglyme, was treated individually with one equivalent of the potassium salts of methanol, benzylalcohol and phenol in *t*-butanol at RT for 12 hr. The reaction mixtures were diluted with water, acidified with 2N HCl in the cold and extracted with ether. The

ether extracts were washed with aq. $NaHCO_3$, water and brine and then dried. After removal of the solvent the mixture of the unreacted triketones (9c and 13) and the hydroxy compounds (methanol, benzylalcohol and phenol) were obtained without a trace of any of the expected alkoxy triketones.

3.7 *3a,4,5,6,7,7a-Hexahydro-3a-hydroxy-4-(1',3'-diketo-2'-methylcyclopentano-2'-methylene)-7a-methylindene-1,5-dione* (12)

A mixture of the methoxytriketone (9a; 0·57 g), the dione (5, 0·28 g), pyridine (0·6 ml) and dry benzene (10 ml) was stirred at RT for 12 hr. The reaction mixture was diluted with benzene and washed successively with dil. HCl, water, aq. $NaHCO_3$ and water and dried. After removal of the solvent, the crude solid was crystallized from ethanol-hexane to give the pure compound (12, 0·61 g, 74%); m.p. 192–4°); IR (nujol): ν_{max} 3405, 1740, 1730 and 1710 cm^{-1}; ^{1}H-NMR (DMSO-d_6): 0·94 [*S*, 3H, $COC(\underline{CH}_3)CH$–OH], 1·06 [*S*, 3H, CO–$C(\underline{CH}_3)CO$], 1·32–2·78 (*m*, 15H, methylenes and methine protons) and 6·80 (*S*, 1H, OH, exchanges with D_2O); ^{13}C-NMR (DMSO-d_6): 11·84 [*q*, $-C(\underline{CH}_3)$–C–OH], 20·68 [*q*, CO–$C(\underline{CH}_3)$–CO], 23·07 (*t*, $-CH_2-\underline{CH}_2-C-CH_3$), 25·72(*t*, –CH–$\underline{CH}_2$–), 29·92((*t*, HO–C–$\underline{CH}_2$–), 32·64 (*t*, $-\underline{CH}_2-CH_2-C-CH_3$), 34·54 (*t*, HO–C–$CH_2-\underline{CH}_2$–), 36·15 (*t*, CO–$\underline{CH}_2-CH_2CO$), 36·69 (*t*, $COCH_2\underline{CH}_2CO$), 48·26 (*d*, CO–$\underline{CH}$–), 52·12 [*S*, HO–C–$\underline{C}(CH_3)$–CO], 53·54 [*S*, CO–$\underline{C}(CH_3)$–CO], 86·02 (*S*, –C–OH), 207·01 [*S*, $\underline{CO}$–$C(CH_3)$–$\underline{CO}$], 217·78 (*S*, $-CH_2-\underline{CO}$–CH) and 218·10 [*S*, $\underline{CO}$–$C(CH_3)$–C–OH]; Mass: M^+ *m/e* 306 (100%), *m/e* 288, *m/e* 260, *m/e* 194, *m/e* 181, *m/e* 125 and *m/e* 112. (Found: C, 66·7; H, 7·21. $C_{17}H_{22}O_5$ requires C, 66·65; H, 7·24%.)

3.8 *Reactions of (i) di-2-(diethylamino)ethylketone* (2d), *(ii) N-diethylamino-5-ethoxypentan-3-one* (2b) *and (iii) 2-(5-methoxy-3-ketopentyl)-2-methylcyclopentan-1,3-dione* (9a) *with the view to prepare the expected enedione* (1d)

(i) A solution of diaminoketone (2d; 0·23 g), the dione (5, 0·11 g), pyridine (0·23 ml) and xylene (20 ml) was refluxed for 16 hr. After the usual work-up, the crude compound was chromatographed over silica gel (hexane-chloroform, 1:1) when the dienone (6, 0·13 g, 77%) was obtained, b.p. 138°/2 mm.

(ii) A mixture of ethoxyaminoketone (2b; 1·5 g), the dione (5, 0·9 g), pyridine (1·75 ml) and xylene (10 ml) was refluxed for 20 hr. After the usual work-up, PTS (1·0 g) to the xylene solution was added and the mixture was heated under reflux for 4 hr. After work-up and purification by column chromatography (chloroform), the dienone (6, 0·62 g, 49%) and the tricyclic ketoalcohol (7, 0·31 g, 22%) were obtained.

(iii) Treatment of the triketone (9a) with (a) pyridine in xylene, (b) pyridine in xylene followed by PTS and (c) pyridine in benzene gave different mixtures of the dienone (6) and tricyclic ketoalcohol (7), except that in the last case only the compound (6) was formed.

Acknowledgements

One of the authors (RSB) wishes to thank the Department of Atomic Energy, Bombay and the Indian Institute of Science, Bangalore for financial assistance.

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