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SPIRO-COMPOUNDS, SYNTHESIS AND CATALYTIC DEHYDROGENATION OF SUBSTITUTED SPIRO[5,5] UNDECANES

A. MITRA* and M. DUTTA GUPTA
Department of Chemistry, University of Kalyani, Kalyani, Nadia, West Bengal, India

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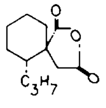
Abstract—Catalytic dehydrogenation of 1-propyl-8,9-benzospiro[5,5]undecane-7-ol (**5**: R = H), and 1-propyl-3'-methyl-8,9-benzospiro[5,5]undecane-7-ol (**5**: R = Me) has been carried out to study the effect of a bulky alkyl group on the ring in the ring transformation of the spiro[5,5]undecane system. The catalytic dehydrogenation of the spiro-compound **5**(R = H) gave phenanthrene and 1-ethylpyrene (minor product) and spiro compound **5**(R = Me) gave only 3-methylphenanthrene. For the synthesis of **5** (R = H or Me), the anhydride (**1**) of 1-carboxy-2-propylcyclohexane-1-acetic acid was condensed with benzene and toluene to give **2** (R = H or Me) which was reduced catalytically to **3**(R = H or Me). Intramolecular acylation of **3**(R = H or Me) gave the spiroketone (**4**: R = H or Me) which was reduced to **5**(R = H or Me).

A study of the dehydrogenation of a large number of synthetic alicyclic polynuclear hydrocarbons has thrown light on the molecular rearrangement during catalytic dehydrogenation. Ring transformation[1-5] has been noted during catalytic dehydrogenation of a large number of spirans. During the catalytic dehydrogenation of spiro[5,5]undecanes containing 1-alkyl (Me or Et) substituent in the spirocyclohexane ring, the loss of one C atom occurred with formation of substituted phenanthrenes.[6,7] In these cases, ring fission takes place away from the alkyl substituent and the alkyl group present in the spirocyclohexane ring is not eliminated. Thus it was considered worthwhile to see whether a n-propyl substituent present in 1-position of the ring of the spiro[5,5]undecane system has any effect on the course of ring transformation during catalytic dehydrogenation. Consequently we synthesised 1-propyl-8,9-benzospiro[5,5]undecane-7-ol (**5**: R = H), and 1-propyl-3'-methyl-8,9-benzospiro[5,5]undecane-7-ol (**5**: R = Me).

Spiro compound **5**(R = H) gave phenanthrene and a small amount of 1-ethylpyrene while compound **5**(R = Me) gave only 3-methylphenanthrene. In both the cases the n-propyl group was eliminated and loss of another C atom was observed in the final product while in the case of compound **5**(R = H), the isolation of some 1-ethylpyrene indicated no loss of carbon and some cyclodehydrogenation. Probably the spirocyclohexane ring underwent fission near the heavy propyl group with the formation of an intermediate which by angular cyclisation formed a partly reduced 4-butylphenanthrene (**A**). This during further dehydrogenation mainly eliminated a 4-Bu group and partly underwent cyclodehydrogenation to afford 1-ethylpyrene. Formation of new rings by cyclodehydrogenation under conditions of catalytic dehydrogenation has been observed.[8-10] An alkyl group (–CH_3) at 3'-position prevented the cyclodehydrogenation of the 4-Bu group in the intermediate.



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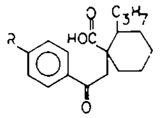

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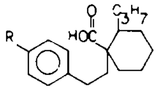

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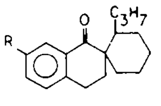

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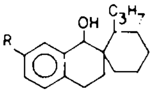

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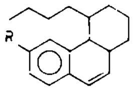

A

For the synthesis of 1-propyl-8,9-benzospiro[5,5]undecane-7-ol (**5**: R = H), the anhydride (**1**) of 1-carboxy-2-propylcyclohexane-1-acetic acid was condensed with benzene to give a single keto acid $\alpha\alpha$-(2'-propylcyclohexane)-β-benzoylpropionic acid (**2**: R = H) which showed its CO absorption at 1700 cm^{-1} in its IR spectrum. The keto-acid reacted with salicylaldehyde to give a pyrylium salt. This indicates the presence of a keto methylene group and as such excludes its alternative structure. The keto-acid was reduced by catalytic hydrogenation to give $\alpha\alpha$-(2'-propylcyclohexane)-γ-phenylbutyric acid (**3**: R = H) which showed CO absorption at 1680 cm^{-1} in its IR spectrum. The reduced acid was converted into its methyl ester which showed characteristic absorption at 1750 cm^{-1} (C=O of ester) in its IR spectrum. Intramolecular acylation of **3**(R = H) gave 1-propyl-8,9-benzospiro[5,5]undecane-7-one (**4**: R = H). This spiro ketone showed absorption at 1680 cm^{-1} in its IR spectrum characteristic of such a 6-membered cyclic ketone. It showed no absorption for acid OH. The spiro ketone (**4**: R = H) was reduced to 1-propyl-8,9-benzospiro[5,5]undecane-7-ol (**5**: R = H). Absorption at 3400 cm^{-1} in its IR spectrum indicated an OH group formed by the reduction of the keto group.

In a similar manner, 1-propyl-3'-methyl-8,9-

benzospiro[5,5]undecane-7-ol (5: R = Me) was synthesised from anhydride 1 by condensation with toluene. The keto acid 2(R = Me) showed its CO absorption at 1700 cm^{-1} in its IR spectrum. This keto acid reacted with salicylaldehyde to form a pyrylium salt indicating the presence of a keto methylene group. This keto acid (2: R = Me) was reduced to αα-(2'-propylcyclohexane)-γ-(p-tolyl)-butyric acid (3: R = Me) which showed absorption at 1690 cm^{-1} for acid CO in its IR spectrum. The methyl ester showed its absorption at 1750, 1225, 1150 cm^{-1} in IR spectrum. The acid chloride of 3(R = Me) on intramolecular acylation gave 1-propyl-3'-methyl-8,9-benzospiro[5,5]undecane-7-one (4: R = Me). Absorption at 1680 cm^{-1} in its IR spectrum was indicative of such a 6-membered ketone. The spiro ketone (4: R = Me) was reduced to 1-propyl-8,9-benzospiro[5,5]undecane-7-ol (5: R = Me). Absorption at 3400 cm^{-1} in its IR spectrum indicated an OH group formed by the reduction of the keto group present in 4(R = Me).

EXPERIMENTAL

All m.ps are uncorrected. UV spectra were measured in 95% EtOH solns with a Beckman DU-2 spectrophotometer. IR spectra were recorded by CDRI Lucknow. Microanalyses were performed by Alfred Bernhardt, Microanalytsches Laboratorium, West Germany.

The 1-carboxy-2-n-propylcyclohexane-1-acetic acid was prepared from 2-n-propylcyclohexanone and ethyl cyanoacetate.[11-13]

The potassium salt of 2-carbethoxycyclohexanone from 2-carbethoxycyclohexanone (170 g; 1 mole) and K(39 g; 1 mole) in ice-cool dry benzene (400 ml) was heated on a steam bath with n-propyl iodide (160 g) for 12 hr. The usual work up gave 2-carbethoxy-2-n-propylcyclohexanone (152 g), b.p. 136–138°/4.5 mm. (Found: C, 67.79; H, 8.38. $C_{12}H_{20}O_3$ requires: C, 67.89; H, 9.50%); semicarbazone, m.p. 128–9° from MeOH (Found: C, 58.02; H, 8.57; N, 15.56. $C_{13}H_{23}O_3N_3$ requires: C, 57.97; H, 8.61; N, 15.60%).

A mixture of 2-carbethoxy-2-propylcyclohexanone, conc HCl, AcOH, H_2O (1:2:2:2) was refluxed on a sandbath for 18 hr. The usual work up gave 2-propylcyclohexanone in 79.5% yield, b.p. 96–100°/20 mm. (lit.[14,15] b.p. 83–84°/13 mm); semicarbazone, m.p. 132–33° from MeOH (lit.[14] m.p. 133–34°) (Found: C, 60.97; H, 9.68; N, 21.17. Calc. for $C_{10}H_{19}N_3O$: C, 60.88; H, 9.71; N, 21.30%).

Ethyl 2-propylcyclohexylidene cyanoacetate. A mixture of 2-propylcyclohexanone (42 g, 0.39 mole), ethyl cyanoacetate (40 g, 0.39 mole), NH_4OAc (4 g), AcOH (8 g) and dry benzene (45 ml) was heated on an oil bath at 160–165° for 24 hr. The usual work up gave ethyl 2-propylcyclohexylidene cyanoacetate (54 g), b.p. 135–137°/0.4 mm (Found: C, 71.28; H, 8.91; N, 5.81. $C_{14}H_{21}NO_2$ requires: C, 71.45; H, 9.00; N, 5.95%).

1-*Carboxy-2-propylcyclohexane*-1-*acetic acid.* A soln of KCN (40 g) in water (90 ml) was added to ethyl 2-propylcyclohexylidene cyanoacetate (64 g) in EtOH (300 ml). The mixture was allowed to stand at room temp. for 6 days. The alcohol was distilled off and the dark residue was hydrolysed with a mixture of conc. HCl and AcOH by heating under reflux for 30 hr. The solid acid separated on cooling and the mother liquor gave more on dilution. It was dissolved in Na_2CO_3 (charcoal) and was precipitated with conc. HCl. The crude acid, m.p. 127–28° crystallised from benzene–pet ether (40–60°) as a colourless powder (30 g), m.p. 143–145°; IR (KBr) 1710, 1690 cm^{-1} (C=O of acid) (Found: C, 63.19; H, 8.79. $C_{12}H_{20}O_4$ requires: C, 63.13; H, 8.83%).

The diethyl ester of the acid from the acid chloride and dry EtOH crystallised from acetone–petroleum (40–60°) as colourless needles, m.p. 132–133° (Found: C, 67.80; H, 9.81. $C_{16}H_{28}O_4$ requires: C, 67.57; H, 9.93%).

The dicarboxylic acid (28 g) was refluxed with Ac_2O (95 ml) for 6 hr. The anhydride (1) was collected as viscous liquid (18 g) at 150–155°/0.8 mm.

The anhydride (1; 1.9 g), aniline (1 ml) and dry benzene (7 ml) were refluxed on a steam bath for 4 hr. The solids which separated on cooling were collected and washed with dil. HCl. The anilic acid crystallised from benzene, m.p. 134°. (Found: C, 71.43; H, 8.12; N, 4.71. $C_{18}H_{25}O_3N$ requires: C, 71.25; H, 8.36; N, 4.62%).

αα-(2'-Propylcyclohexane)-β-benzoylpropionic acid (2: R = H). Powdered anhyd. $AlCl_3$ (33 g) was gradually added to a soln of 1 (25 g) in dry benzene (160 ml) cooled in ice with constant stirring. The mixture was kept at room temp. for 12 hr and warmed at 60–65° for 0.5 hr. The product was decomposed with ice and conc. HCl and the excess C_6H_6 was removed by steam. The residue was collected, dissolved in hot dil. Na_2CO_3aq and filtered. After the acidification with HCl and extraction with Et_2O, the organic phase was washed with water, dried (Na_2SO_4) and the solvent removed. The residual thick oil crystallised from benzene–petroleum (60–80°) in colorless needless, m.p. 131–33°. The mother liquor afforded more of 2 (R = H) collected at 180–190°/1.0 mm as a thick colorless oil (20 g) which crystallised from benzene-petroleum (60–80°) in colorless needless m.p. 131–33°; IR (Nujol) 1700 cm^{-1} (C=O of acid); UV (EtOH) 250 nm (Found: C, 74.77; H, 8.31. $C_{18}H_{24}O_3$ requires: C, 74.97; H, 8.39%).

Pyrylium derivative of 2(R = H). A mixture of 2(R = H; 0.19 g) and salicylaldehyde (0.19 g) in dry EtOH (10 ml) was saturated with dry HCl at 0° and kept for 3 days in a refrigerator. The crimson red ppt of the pyrylium salt was collected, washed with EtOH and dried in vacuum. It was readily soluble in alkali and did not melt upto 290°.

αα-(2'-Propylcyclohexane)-γ-phenylbutyric acid (3: R = H). Compound 2(R = H; 14 g) was hydrogenated on Pd–C (2 g, 10%) at 50° and 3 atm in glacial AcOH (100 ml) containing a few drops of $HClO_4$ for 10 hr. The catalyst was filtered off and usual work up gave an oil. The oil was dissolved in dil. $NaHCO_3$aq, acidified and the precipitated reduced acid was taken up in Et_2O washed with H_2O, dried (Na_2SO_4) and the solvent removed. The residual oil (12 g) distilled as a thick colourless liquid at 189–200°/0.5 mm, which readily solidified. It crystallised from MeOH as colourless needles, m.p. 172–173°; IR (Nujol) 1680 cm^{-1} (C=O of acid); UV (EtOH) 261 nm (Found: C, 78.91; H, 9.62. $C_{18}H_{26}O_2$ requires: C, 78.79; H, 9.55%).

The acid (3: R = H) was converted into its methyl ester by diazomethane in ether. After the usual work up it gave an oil which was purified by chromatographic separation over alumina with hexane. It distilled at 117–120°/0.2 mm as a colorless oil, IR (neat) 1750 (C=O of ester), 1250, 1150 cm^{-1} (C–O of ester) (Found: C, 79.01; H, 10.10. $C_{19}H_{28}O_2$ requires: C, 79.12; H, 9.79%).

1-*Propyl*-8,9-*benzo*-7-*ketospiro*[5,5]*undecane* (4: R = H). Compound 3(R = H); (4 g) was added to a mixture of polyphosphoric acid (P_2O_5, 40 g; H_3PO_4, 25 ml, 85%) and heated on a steam bath with stirring for 3 hr. The mixture was poured into crushed ice and allowed to stand. It was thoroughly extracted with Et_2O, washed with H_2O and then with alkali and finally with H_2O. It was dried (Na_2SO_4) and the solvent removed. The spiro-ketone (3 g) purified by chromatographic fractionation over alumina with hexane, distilled at 136–140°/0.5 mm. IR (film) 1680 cm^{-1} (C=O of keto); UV (EtOH) 230 (4.15), 266 (2.36 nm) (Found: C, 84.20; H, 9.53. $C_{18}H_{24}O$ requires: C, 84.32; H, 9.44%).

1-*Propyl*-8,9-*benzospiro*[5,5]*undecane*-7-*ol* (5: R = H). Compound 4 (R = H; 1.6 g) in dry THF (20 ml) was added in portions to a suspension of LAH(2 g) in dry THF (20 ml) cooled in ice. It was gently refluxed for 2 hr. Water was added to the cooled mixture and the spiro-ol collected in Et_2O, dried (Na_2SO_4) and solvent removed. The residual thick oil (1.2 g) distilled at 155°/0.5 mm; IR (film) 3400 cm^{-1} (OH stretching).

Catalytic dehydrogenation of 1-*propyl*-8,9-*benzospiro*[5,5]*undecane*-7-*ol* (5: R = H). Compound 5(R = H; 1.0 g) was heated with 10% Pd–C catalyst (0.1 g) in a sealed tube at 360–380° for 24 hr. The product was extracted with Et_2O, dried (Na_2SO_4) and the solvent removed. The residual oil was separated by chromatographic fractionation on alumina with hexane. The white solids (homogeneous in TLC) with bluish violet fluorescence obtained from the third to fifth eluates, crystallised from EtOH as colourless flakes, m.p. 100–101°.

The yellow TNB complex of the white solid recrystallised from MeOH in yellow needles, m.p. 159–60° (Found: C, 61.41; H, 3.49; N, 10.61. $C_{20}H_{13}N_3O_6$ requires: C, 61.38; H, 3.35; N, 10.74%).

The regenerated hydrocarbon crystallised from EtOH in flakes, m.p. 100–101°. It was identified as phenanthrene by m.m.ps of the solid and its TNB complex and by TLC, IR and UV.

The colourless oil with violet fluorescence from the subsequent eluates (6th and 7th) was converted into its TNB complex which recrystallised from MeOH in orange needles, m.p. 207–209° (lit.[16,17] 209.4–210.2°) (Found: C, 64.82; H, 3.69; N, 9.27. $C_{24}H_{17}N_3O_6$ requires: C, 65.01; H, 3.86; N, 9.47%).

The regenerated hydrocarbon showed UV absorption at 231 (4.63), 256 (3.85), 261 (4.4) nm characteristic of a pyrene derivative.

*αα-(2'-Propylcyclohexane)-β-(*p*-toluyl)-propionic acid* (**2**: R = Me). Powdered anhyd. $AlCl_3$ (50 g) was gradually added with stirring to an ice-cold soln of **1** (20 g) in dry toluene (80 ml). The mixture was kept at room temp. for 12 hr and warmed at 60–65° for 0.5 hr to complete the reaction. The product was decomposed with ice and HCl and excess toluene was removed by steam. The separated dark residue was purified as in the case of **2** (R = H). The keto acid (14 g) was collected at 225–229°/0.7 mm as a viscous mass which crystallised from benzene-petroleum (60–80°), m.p. 133–134°; IR (KBr) 1700 cm^{-1} (C=O of acid); UV (EtOH) 249 nm (Found: C, 75.1; H, 8.9. $C_{19}H_{26}O_3$ requires: C, 75.46; H, 8.67%).

The pyrylium derivative of **2** (R = Me) readily soluble in alkali, did not melt upto 290°.

*αα-(2'-Propylcyclohexane)-γ-(*p*-tolyl)-butyric acid* (**3**: R = Me). Compound **2** (R = Me; 10 g) was reduced on Pd–C (2.0 g, 10%) in glacial AcOH (50 ml) containing a few drops of $HClO_4$ at 50° and 3 atm of H_2. The usual work up gave a thick colourless oil (8 g) at 190–195°/0.6 mm. It crystallised from petroleum (60–80°) in fine needles, m.p. 111–13°; IR (KBr) 1690 cm^{-1} (CO, acid) (Found: C, 79.3; H, 9.63. $C_{19}H_{28}O_2$ requires: C, 79.12; H, 9.79%).

The methyl ester (from CH_2N_2) of **3** (R = Me) purified by chromatographic fractionation over alumina with hexane distilled at 123–124°/0.3 mm as a colourless oil; IR (film) 1750 (C=O of ester), 1225 1150 cm^{-1} (C–O of ester) (Found: C, 79.50; H, 10.02. $C_{20}H_{30}O_2$ requires: C, 79.42; H, 10.00%).

1-*Propyl*-3'-*methyl*-8,9-*benzo*-7-*ketospiro*[5,5]*undecane* (**4**: R = Me). The acid (**3**: R = Me; 6 g) was converted into the corresponding acid chloride by treating it with thionyl chloride following the usual procedure. Powdered anhyd. $AlCl_3$ (3.2 g) was gradually added with stirring to the acid chloride dissolved in dry petroleum (60–80°) (40 ml). The mixture was kept at room temp. for 3 hr and at 60–70° for 1 hr and worked up as usual and purified by chromatographic fractionation over alumina with hexane. The spiro ketone distilled as a light straw coloured oil (4 g) having a characteristic odour at 145–150°/0.3 mm; IR (film) 1680 cm^{-1} (C=O of keto) (Found: C, 84.29; H, 9.72. $C_{19}H_{26}O$ requires: C, 84.39; H, 9.69%).

1-*Propyl*-3'-*methyl*-8,9-*benzospiro*[5,5]*undecane*-7-*ol* (**5**: R–Me). A soln of **4** (R = Me; 2 g) in dry THF (20 ml) was gradually added to a suspension of LAH (2 g) in dry THF (20 ml) cooled in ice. It was refluxed for 2 hr and worked up as usual. The spiro-ol (1.8 g) distilled at 135–140°/0.5 mm as a thick oil; IR (film) 3400 cm^{-1} (OH).

Catalytic dehydrogenation of 1-*propyl*-3'-*methyl*-8,9-*benzospiro*[5,5]*undecane*-7-*ol* (**5**: R = Me). The spiro compound **5** (R = Me; 1.0 g) was heated with Pd–C (10%) catalyst (0.12 g) in a sealed tube at 360–380° for 24 hr. The product was worked up in the usual way and subjected to chromatographic fractionation over alumina with hexane which gave a colourless homogeneous (TLC) oil with blue fluorescene. The TNB complex of the oil was recrystallised from MeOH in orange needles, m.p. 153–54° (lit.[18] m.p. 155°) (Found: C, 62.25; H, 3.85; N, 10.33. $C_{21}H_{15}N_3O_6$ requires: C, 62.22; H, 3.73; N, 10.37%).

The regenerated hydrocarbon crystallised from EtOH melted at 62–63° (lit.[4,18–20] m.p. 62–63°); IR (film) 2910, 1600, 1500, 1450, 880, 835, 815, 745, 712 cm^{-1}; UV (EtOH) 249, 273, 297 nm.

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