

## Condensed Cyclic and Bridged-ring Systems. Part V.<sup>1</sup> Application of the Intramolecular Oxo-carbenoid Insertion Reaction to the Preparation of Two New Bridged-ring Ketones

By Usha R. Ghatak,\* Jayanta K. Ray, and Sephali Chakrabarty, Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India

Two new bridged-ring ketones, 5,6,7,8,10,11-hexahydro-8,12-dimethyl-5,8,11-ethan[1]yl[2]ylidenebenzocyclo-nonen-9-one (5) and 1,3,3a,4,9,9a-hexahydro-1,3a-dimethyl-1,4-ethanocyclopenta[*b*]naphthalen-2-one (6), have been synthesised by intramolecular oxo-carbenoid C-H insertion reactions in the copper-catalysed decomposition of the 8-diazoacetyl-5,6,7,8,9,10-hexahydro-8,11-dimethyl-5,9-methanobenzocyclo-octenes (3) and (4), epimeric at position 8.

REGIOSELECTIVE intramolecular C-H insertion in the copper-catalysed oxo-carbenoid decomposition of  $\alpha$ -diazomethyl ketones has been developed recently<sup>2,3</sup> as a route to bridged-ring ketones. To evaluate the effect of the steric environment of the diazomethyl group on the mode of the carbenoid decomposition, an investigation of the copper-catalysed decompositions of the rigid diastereoisomeric  $\alpha$ -diazomethyl ketones (3) and (4) was undertaken, which resulted in the synthesis of two new bridged-ring ketones (5)<sup>3</sup> and (6).

The diazo-ketones (3) and (4) were prepared from the easily accessible<sup>4</sup> acids (1) and (2), respectively, in the usual manner. Treatment of the diazoketone (3) with anhydrous copper(II) sulphate in refluxing dry tetrahydrofuran (method A) gave the bridged cyclopentanone (5) in 50–52% yield after chromatography on basic alumina. The product gave a single 2,4-dinitrophenylhydrazone. The homogeneity and structure of the ketone (5) were confirmed by its chromatographic and spectral properties. The i.r. spectrum showed a single carbonyl band at 1740 cm<sup>-1</sup>, typical of a five-membered

ring ketone. The n.m.r. spectrum (at 60 MHz in CCl<sub>4</sub>) consisted of a well defined methyl doublet at  $\delta$  0.93 (*J* 7 Hz), a methyl singlet at  $\delta$  1.12, methylene and methine proton (6 H) multiplets in the region  $\delta$  1.28–2.20, a partly resolved pair of doublets for CO·CH<sub>2</sub> centred at  $\delta$  2.68 (containing the C-5 benzylic proton signal under the peak at lower field at  $\delta$  2.78), the C-11 benzylic proton signal at  $\delta$  3.53 as the centre of four unsymmetrical multiplets, and finally the aromatic proton (4 H) multiplet at  $\delta$  7.1. The reason for deshielding of the benzylic proton situated at the strained C-11 is not clear. Repeating the decomposition of the diazo-ketone (3) in dry cyclohexane in the presence of anhydrous copper(I) oxide with irradiation by tungsten lamps (method B) gave the ketone (5) in 58% yield.

In contrast, in attempted decomposition of the epimeric diazo-ketone (4) in refluxing cyclohexane according to method A, even after 13 h the starting material was mostly unchanged. However, use of method B resulted in complete disappearance of the diazo-ketone (monitored by i.r.) after 6–7 h. Chromatography on neutral alumina gave only a single isolable crystalline ketone (6), in 20–23% yield. The i.r. spectrum showed a single carbonyl band at 1740

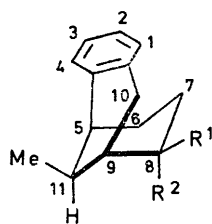
<sup>3</sup> Preliminary communication, U. R. Ghatak and S. Chakrabarty, *J. Amer. Chem. Soc.*, 1972, **94**, 4756.

<sup>4</sup> U. R. Ghatak, J. Chakravarty, R. Dasgupta, and P. C. Chakraborti, *J.C.S. Perkin I*, 1975, 2438.

<sup>1</sup> Part IV, U. R. Ghatak, Sk. K. Alam, P. C. Chakraborti, and B. C. Ranu, *J.C.S. Perkin I*, 1976, 1669.

<sup>2</sup> (a) D. Fărcasin, E. Wiskott, E. Osawa, W. Thielecke, E. M. Engler, J. Slutsky, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1974, **96**, 4669; (b) S. Chakrabarty, J. K. Ray, D. Mukherjee, and U. R. Ghatak, *Synth. Comm.*, 1975, **5**, 275, and references cited therein; (c) W. C. Agosta and S. Wolff, *J. Org. Chem.*, 1975, **40**, 1027.

$\text{cm}^{-1}$ . The n.m.r. spectrum (at 60 MHz in  $\text{CDCl}_3$ ) revealed two methyl singlets at  $\delta$  1.00 and 1.05, methylene and methine proton (5 H) multiplets between  $\delta$  1.26 and 1.90, inner lines of the *gem*-coupled  $\text{CO}\cdot\text{CH}_2$  protons at  $\delta$  2.20 and 2.33 (the outer lines were not discernible

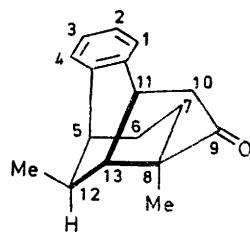


(1)  $\text{R}^1 = \text{CO}_2\text{H}$ ,  $\text{R}^2 = \text{Me}$

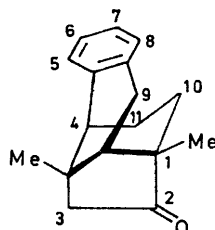
(2)  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{CO}_2\text{H}$

(3)  $\text{R}^1 = \text{CO}\cdot\text{CHN}_2$ ,  $\text{R}^2 = \text{Me}$

(4)  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{CO}\cdot\text{CHN}_2$



(5)



(6)

owing to overlapping with other signals), three benzylic proton multiplets centred at  $\delta$  2.65 and 2.96, and the aromatic proton (4 H) multiplet at  $\delta$  7.1.

#### EXPERIMENTAL

For general procedures see Part IV.<sup>1</sup>

*exo*-8-Diazoacetyl-5,6,7,8,9,10-hexahydro-8,exo-11-dimethyl-5,9-methanobenzocyclo-octene (3).—The acid (1) (0.6 g, 2.4 mmol) was neutralised with methanolic *ca.* 5% sodium methoxide (phenolphthalein as indicator). The solvent was evaporated off under reduced pressure. To the sodium salt, dry benzene ( $3 \times 15$  ml) was added and distilled off (3 times) to remove traces of methanol. To a rapidly stirred, ice-cold suspension of the sodium salt in dry benzene (50 ml) and pyridine (0.1 ml), oxalyl chloride (1 ml) was added dropwise. The mixture was stirred at room temperature for 30 min and finally warmed at *ca.* 60 °C for 1 h. The precipitate was filtered off and the filtrate concentrated under reduced pressure. The dark yellow liquid was dissolved in dry ether (50 ml) and added to a stirred solution of an excess of cold ethereal diazomethane [from *N*-methyl-*N*-nitrosourea (4 g) containing triethylamine (1 ml). Stirring in the cold was continued for another 2 h and the mixture was left overnight at room temperature, then filtered and evaporated. The resulting

yellow oil was dissolved in dry ether (50 ml) and filtered rapidly through a short column of neutral alumina to afford the diazo-ketone (3) as a pale yellow oil (0.6 g),  $\nu_{\text{max}}$  2 115  $\text{cm}^{-1}$ .

5,6,7,8,10,11-Hexahydro-8,12-dimethyl-5,8,11-ethan[1]yl-[2]ylidenebenzocycloocten-9-one (5).—*Method A.* The diazo-ketone (3) (0.6 g, 2.2 mmol) dissolved in dry tetrahydrofuran (100 ml) was added slowly to a stirred, refluxing suspension of anhydrous copper sulphate (1.5 g) in dry tetrahydrofuran (100 ml) during 3 h. The mixture was refluxed with stirring for another 5 h, filtered, and evaporated to afford a yellow liquid. This was dissolved in the minimum volume of light petroleum and chromatographed on alkaline alumina (30 g). Elution with petroleum-benzene (9:1) gave a liquid which was distilled [160–170 °C and 0.2 mmHg (bath temp.)] to yield the ketone (5) (0.3 g, 52.5%),  $\lambda_{\text{max}}$  252 (log  $\epsilon$  3.35) and 273 nm (3.10);  $\nu_{\text{max}}$  1 735 and 1 600  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CCl}_4$ ) 0.93 (3 H, d,  $J$  7 Hz), 1.12 (3 H, s), 1.28–2.20 (6 H, mm), 2.38 (2 H, partly resolved d,  $\text{CO}\cdot\text{CH}_2$ ), 2.78 (1 H, m, benzylic H), 3.53 (1 H, m), and 7.1 (4 H, m);  $M^+$  240. The 2,4-dinitrophenyl-hydrazone crystallized from ethyl acetate-methanol; m.p. 171° (Found: C, 65.6; H, 5.75.  $\text{C}_{23}\text{H}_{24}\text{N}_4\text{O}_4$  requires C, 65.7; H, 5.75%).

*Method B.* A solution of the diazo-ketone (3) (1 g, 3.7 mmol) in dry cyclohexane (100 ml) was added dropwise to a stirred, refluxing suspension of freshly prepared anhydrous copper(II) oxide (2 g) in cyclohexane (100 ml), which was irradiated with two 200 W tungsten lamps during 3 h. Refluxing was continued for another 3 h when the diazo-ketone i.r. band had disappeared. Filtration and evaporation afforded a yellow oil which was chromatographed to give the ketone (5) (0.52 g, 58%), identical (mixed t.l.c. and i.r.) with the sample described above.

*endo*-8-Diazoacetyl-5,6,7,8,9,10-hexahydro-8,exo-11-dimethyl-5,9-methanobenzocyclo-octene (4).—By the procedure described for the diazo-ketone (3), the acid (2) (200 mg) was converted into the semi-solid diazo-ketone (4) (190 mg), purified by chromatography on neutral alumina,  $\nu_{\text{max}}$  2 125  $\text{cm}^{-1}$ .

1,3,3a,4,9,9a-Hexahydro-1,3a-dimethyl-1,4-ethanocyclopenta[*b*]naphthalen-2-one (6).—A solution of the diazo-ketone (4) (0.2 g, 0.74 mmol) in dry cyclohexane (100 ml) was added during 3 h to a stirred refluxing suspension of anhydrous copper(II) oxide (0.8 g) in dry cyclohexane (150 ml) irradiated with two 200 W tungsten lamps (method B). After *ca.* 6 h the diazoketone i.r. band had disappeared. The product was chromatographed on neutral alumina (50 g) and eluted with benzene-petroleum (1:9) to afford the ketone (6) as a solid (40 mg, 23%), m.p. 104° (from light petroleum),  $\lambda_{\text{max}}$  261 (log  $\epsilon$  2.71), 266 (2.81), and 273 nm (2.85);  $\nu_{\text{max}}$  1 740 and 1 600  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ) 1.00 (3 H, s,  $\text{CH}_3$ ), 1.05 (3 H, s,  $\text{CH}_3$ ), 1.26–1.90 (5 H, mm), 2.20 and 2.33 (2 H, br, dd), 2.65–2.96 (3 H, mm), and 7.1 (4 H, m);  $M^+$  240 (Found: C, 84.75; H, 8.3.  $\text{C}_{17}\text{H}_{20}\text{O}$  requires C, 84.95; H, 8.4%).