Tetrahedron. Vol. 25, pp. 5267 to 5274. Pergamon Press 1969. Printed in Great Britain

ALICYCLIC COMPOUNDS—I

ACTION OF BASE ON BICYCLIC δ-KETOTOSYLATES—STUDIES RELATING TO THE SYNTHESIS OF CYCLODECENONES

P. C. MUKHARJI and A. N. GANGULY*
Department of Chemistry, Presidency College, Calcutta-12, India

(*Received in the UK* 18 *December* 1968; *Accepted for publication* 15 *July* 1969)

Abstract—The action of KOBu^t on *cis*- and *trans*-10-(2-oxo-decalyl)carbinyl tosylate was examined since the former might suffer fragmentation. Both the isomers, however, furnished saturated tricyclic ketones through intramolecular displacement. The structures of the two ketones have been unambiguously confirmed.†

THE sesquiterpenes, caryophyllene, humulene, germacrone, zerumbone, cembrene[1] etc are noted for their preparative inaccessibility and a tendency to transannualar reactions.[2] The presence of multiple unsaturation provided the impetus for developing new and efficient stereoselective methods for their synthesis.

We examined the action of base on bicyclic δ-ketotosylates,[3] in the hope that the carbanion derived from such a system (Fig. 1) can either be involved in (a) an intramolecular displacement to furnish a cyclobutyl ketone (Path A) or (b) a fragmentation to furnish an alkene and an αβ-unsaturated ketone (Path B).

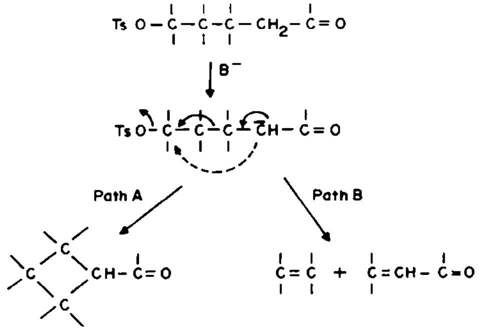


FIG. 1

An appositely constituted bicyclic ketotosylate, if it reacts according to Path B involving the bond common to the two rings, would therefore lead to a cycloalkadienone providing thus an easy entry to this class of compounds.

---

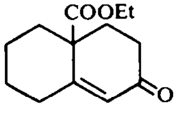
* Abstracted from the thesis submitted by A.N.G. for the D.Phil(Sc.) Degree, April 1967 of the University of Calcutta.

† Presented at the annual convention of the Chemical Research Committee of the Council of Scientific and Industrial Research, India and the Indian Chemical Society at the University of Aligarh, December, 1965.

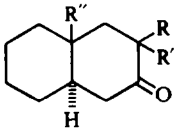
The well-known base catalysed fragmentation of monotosyl ester of cyclic-1: 3-glycols[4] provided examples which encouraged us to anticipate fragmentation (Path B) in the above systems.

Wharton[5] has achieved the synthesis of 6-methyl-cyclodec-5-ene-1-one by alkoxide catalysed fragmentation of 1-mesyloxy-9-methyl-decal-10-ol, a method which was exploited by Corey[6] in the synthesis of Caryophyllene and has since been applied to other bycyclic diol[7] and steroidal systems.[8] More recently other methods for the synthesis of Humulene[9] and Muscone[10] have been reported.

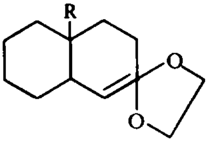
In 1960[3] we investigated the action of alkoxide on the decalone tosylates (IIc and VIb) in the hope that the *cis*-isomer (VIb) would suffer fragmentation to the cyclodecenone with an exocyclic methylene group (VII). However, both isomers furnished cyclobutyl ketones through intramolecular displacement.*



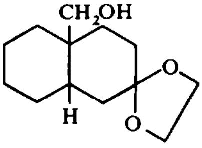
I



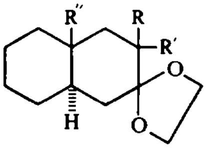
II a: R = R′ = H; R″ = COOEt
b: R = R′ = H; R″ = CH_2OH
c: R = R′ = H; R″ = CH_2OTs
d: R = Me; R′ = H; R″ = COOEt
e: R = Me; R′ = H; R″ = COOH
f: R = Me; R′ = H; R″ = COOMe
g: R = Me; R′ = H; R″ = CH_2OTs
h: R = R′ = Me; R″ = COOMe
i: R = R′ = Me; R″ = CH_2OTs



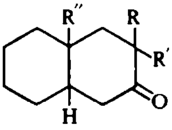
III a: R = COOEt
b: R = CH_2OH



IV



V a: R = R′ = H; R″ = COOEt
b: R = R′ = H; R″ = CH_2OH
c: R = Me; R′ = H; R″ = COOEt
d: R = Me; R′ = H; R″ = CH_2OH
e: R = Me; R′ = H; R″ = CH_2OTs
f: R = R′ = Me; R″ = COOMe
g: R = R′ = Me; R″ = CH_2OH



VI a: R = R′ = H; R″ = CH_2OH
b: R = R′ = H; R″ = CH_2OTs
c: R = R′ = Me; R″ = CH_2OH

The *trans*-hydroxymethyl decalone (IIb) was prepared from the octalone ester (I).[11] The *trans*-tosylate (IIc) reacted with KOBu^t to furnish in 90% yield a saturated tricyclic ketone through intramolecular displacement. Of the two possible structures (VIIIa and IX) VIIIa is more reasonable in consideration of the direction of preferred enolization of a *trans*-2-decalone.[12] This was confirmed through the following experiments.

---

* The fragmentation of a bicyclic δ-ketotosylate has been realised in another series culminating in the synthesis of a trimethyl cyclodecadienone [T. K. Das Gupta, D.Phil. thesis, Calcutta University, 1967; P. C. Mukharji and T. K. Das Gupta—Part II of this series.]

Oxidation of the ketone[13] followed by saponification, esterification and oxidation[14] furnished the cyclobutanone ester (X), which on oxidation afforded *trans*-cyclohexane-1-carboxy-1, 2-diacetic acid (XI) identified by direct comparison with an authentic specimen of the *trans*-acid prepared from the *trans*-decalone ester (IIa).

Bromination of VIIIa afforded the crystalline bromoketone (XII), which upon dehydrohalogenation gave in poor yield the unsaturated ketone (XIII; λ_{max} 5·95 μ; λ_{max}258 mμ, ε, 3200). The abnormal UV maxima is due to the intense strain associated with the 1:1:3 bicycloheptenone system. Such abnormal bathochromic shifts have been reported for the terpenoids Verbenone,[15a] [λ_{max} 253 mμ (6840)] and Muskatone[15b] [λ_{max} 255 mμ (5700)] where a similar chromophore is present.

The *cis*-tosylate (VIb) was prepared from the octalone (I).[11] It reacted with KOBu^t to furnish in 80% yield a saturated ketone (XIV) which upon oxidative degradation afforded the cyclobutanone ester (XV). The non-identity of this ketone with VIIIa further confirms the assigned structure (XIV). If the intramolecular alkylation in the *cis*-isomer involved the alternative position, the tricyclic ketone (VIIIa) would have been formed.

Formation of the tricyclic ketone (XIV) from the *cis*-isomer involves the formation of a highly strained *trans*- [0.2.4]bicyclo octane system in preference to the expected fragmentation.

Of the two possible conformations (XVI and XVII) for the *cis*-ketotosylate (VIb) only the non-steroid conformation where the angular tosyloxymethyl group is axial to the ring bearing the CO group can undergo the intramolecular displacement to furnish XIV. In the steroid conformation the tosyloxymethyl group is equatorial to the ring bearing the CO group and an intramolecular ring closure of this type is not sterically possible. Due to the conformational flexibility of a *cis*-decalone it may react in either of the two conformations which are readily interconvertible. Since the ketone (XIV) is the exclusive product of this reaction and is formed in high yield, it appears that the *cis*-ketotosylate (VIb) reacts only in the non-steroid conformation (XVII), presumably due to lower energy of the transition state for an intramolecular displacement in this conformation *vis-a-vis* the alternative path in the steroid conformation.

The tosylate of the *trans*-methyl decalone (IIg) similarly furnished the tricyclic ketone (VIIIb).

We wanted to examine the dimethyl decalones (IIi and VIc) under identical conditions in order to see if the presence of the intense 1:3 diaxial interaction would in any way effect the course of reaction. The *trans*-dimethylketoester (IIh) could be prepared by C-methylation of IId.[16] Attempted reduction of the corresponding ethylene ketal (Vf) with LAH however led to recovery of the unreacted ester.

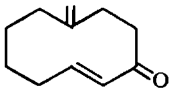
Results of studies in systems where the *cis*-decalone moiety has the steroid conformation will be reported in subsequent papers.

EXPERIMENTAL

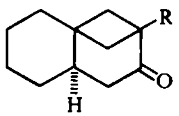
All m.ps and b.ps are uncorrected. Pet. ether refers to the fraction b.p. 40–60°. All solvent extracts were dried over Na_2SO_4. Alumina used for chromatography was E. Merck aluminium oxide standardised

---

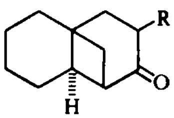
[*] The initial oxidation product has a highly strained *trans*-fused ring junction which probably inverts during preparation of carbonyl derivatives. The 2,4-dinitrophenylhydrazone initially separated as an oil and only solidified in contact with MeOH after several days.



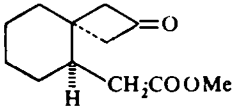
VII



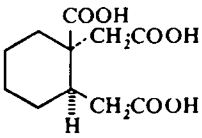
VIII a, R = H
b, R = Me



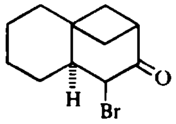
IX R = H



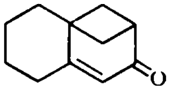
X



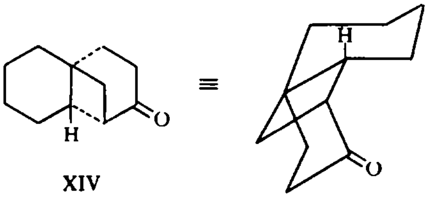
XI



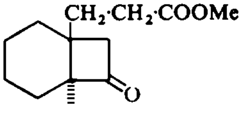
XII



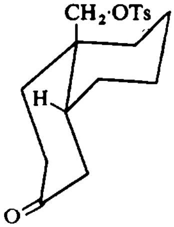
XIII



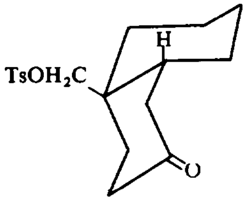
XIV



XV



XVI



XVII

according to Brockmann The UV spectra were taken on a Unicam spectrophotometer SP 500 in 95% EtOH unless otherwise stated. The IR spectra were taken in thin films unless otherwise stated on a Perkin–Elmer Infrachord model 137 E or model 237.

*10-Hydroxymethyl-2-oxo-*trans*-decalin* (IIb)

The *trans*-IIa (31 g) in dry benzene (300 ml) was refluxed with ethanediol (9·5 g) and a trace of PTSA using a Dean–Stark apparatus to afford Va (35 g), b.p. 145°/3 mm. This was reduced with LAH (4 g) in dry ether (200 ml) to yield Vb (27 g), b.p. 158°/0·9 mm, which solidified on standing, and after crystallization from ether-pet. ether had m.p. 73° (Lit:[11c] 73–74°).

A mixture of Vb (27 g), 65% MeOH aq (300 ml) and HCl (18 ml) was heated under reflux for 1 hr. After usual work up the residue was distilled to give three fractions: (i) b.p. 95–115°/0·5 mm (5·2 g); (ii) b.p. 130–145°/0·5 mm (7·2 g); (iii) b.p. 190–210°/0·5 mm, (6 g), which solidified and after crystallization from pet. ether had m.p. 118°. Redistillation of the above middle fraction afforded IIb (7 g) b.p. 140°/0·5 mm (Lit:[11c] 135°/1 mm) as a viscous oil. 2,4-*Dinitrophenylhydrazone* had m.p., 106° (Lit:[11c] 105–107°).

The structure of the products obtained in fraction (i) and (iii) above which have not been described[11d] will be reported in a subsequent communication.

10-*Hydroxymethyl-2-oxo-*trans*-decalin tosylate* (IIc)

A soln of *p*-toluenesulphonyl chloride (8 g) in anhyd pyridine (12 ml) was treated with an ice-cold soln of IIb (7 g) in anhyd pyridine and left at 5° for 48 hr. The mixture was poured into a slurry of ice and HCl and extracted with $CHCl_3$. The neutral $CHCl_3$ extract on concentration furnished IIc (12 g) which after trituration with pet. ether had m.p. 148–150°. This product was sufficiently pure for the next step.

4-*Oxo-tricyclo*[4.4,1^{1-3}.0]*undecane* (VIIIa)

A soln of IIc (10 g) in Bu^tOH (300 ml) was added dropwise with stirring under N_2 to warm $KOBu^t$ (from 1·25 g K and 400 ml $KOBu^t$) on a steam-bath. Stirring under reflux was continued for 6 hr more. Bu^tOH was then removed under diminished press, the residue was diluted with brine and extracted with pet. ether. Usual work up gave VIIIa (4·5 g) b.p. 114°/7 mm, λ_{max}273 mμ (ε, 42), λ_{max}5·86 μ. (Found: C, 80·13; H, 9·42. $C_{11}H_{16}O$ requires: C, 80·48; H, 9·75%).

2,4-*Dinitrophenylhydrazone* was crystallized from EtOH-$CHCl_3$; yellow; m.p. 169°. (Found: C, 59·22; H, 5·84; N, 16·23. $C_{17}H_{20}N_4O_4$ requires: C, 59·30; H, 5·81; N, 16·27%). *Semicarbazone* crystallized from MeOHaq had m.p. 218° d, λ_{max}225 mμ (ε, 13,600). (Found: C, 64·96; H, 8·54. $C_{12}H_{19}N_3O$ requires: C, 65·16; H, 8·59%).

4-*Methoxycarbonylmethyl-2-oxo-spiro*[5.3]*nonane* (X)

A soln of VIIIa (2 g) in dry $CHCl_3$ (20 ml) was treated at 0° with perbenzoic acid (1·9 g) in dry $CHCl_3$ containing a trace of PTSA and the mixture left at 5° for 15 days. It was then washed acid free, dried and concentrated to furnish the crude lactone which was saponified with 0·5 N methanolic KOH soln (60 ml). The acid isolated in the usual manner was esterified with diazomethane to furnish the hydroxyester, b.p. 145° (bath)/0·4 mm.

This hydroxyester (1·4 g) in anhyd pyridine (16 ml) was oxidized overnight by pyridine-chromic acid complex prepared from CrO_3 (2 g) and anhyd pyridine (20 ml) at room temp. Usual work up afforded X (0·45 g), b.p. 130–135° (bath/0·5 mm, λ_{max}5·62 and 5·78 μ.

Semicarbazone crystallized from MeOHaq had m.p. 155°. (Found: C, 58·22; H, 7·89. $C_{13}H_{21}N_3O_3$ requires: C, 58·42; H, 7·86%). 2,4-*Dinitrophenylhydrazone* was crystallized from MeOH; yellow; m.p. 118°. (Found: C, 55·85; H, 6·01. $C_{18}H_{22}N_4O_4$ requires: C, 55·38; H, 5·64%).

trans-1-*Carboxy cyclohexane-1,2-diacetic acid* (XI)

(a) To warm HNO_3 (5 ml) the above X (1 g) was slowly added. After the initial exothermic reaction, the mixture was again warmed on a steam-bath for a couple of min. It was extracted with $CHCl_3$ to afford a gummy acid which was esterified with diazomethane to yield the triester (0·5 g). Hydrolysis with HCl (12 ml) afforded XI, which after crystallization from conc HCl had m.p. 158°. (Found: C, 53·94; H, 6·48. $C_{11}H_{16}O_6$ requires: C, 54·42; H, 6·55%).

(b) The *trans*- IIa (3 g) was similarly oxidized with warm HNO_3 (14 ml) to afford XI* m.p. 158–160°. Admixture with acid obtained from the oxidation of X showed no depression in m.p.

4-*Oxo-tricyclo*[4.4.1^{1-3}.0)*undec-5-ene* (XIII)

Br_2 (2·0 g) was added dropwise to a cold soln of VIIIa (2 g) in dry ether (20 ml). The mixture was washed acid free, dried and concentrated to yield XII (2·5 g) which after crystallization from pet. ether had m.p. 96°, λ^{KBr}_{max} 5·82 μ. (Found: C, 53·88; H, 5·89. $C_{11}H_{15}OBr$ requires: C, 54·53; H, 6·22%).

The bromoketone XII (1 g) was heated under reflux with 2,4,6-collidine (1·8 ml) under N_2 for 1 hr, and then decomposed with iced-HCl and extracted with ether. Usual work up afforded XIII (0·275 g) b.p. 100–110° (bath)/0·4 mm, λ_{max}258 mμ (ε, 3200), λ_{max}5·95 μ.

2,4-*Dinitrophenylhydrazone* was purified by first passing through a short column of alumina and then crystallizing from EtOH-EtOAc: red flakes, m.p. 216°, $\lambda^{CHCl_3}_{max}$ 378 mμ (ε, 20, 400). This gradually blackened on storage. Satisfactory analysis could not be obtained.

10-*Hydroxymethyl-2-oxo-*cos*-decalin* (VIa)

A mixture of I (51 g), ethanediol (17·9 g), and PTSA (0·15 g) in dry benzene (300 ml) was refluxed for 4 hr using a Dean-Stark apparatus to afford IIIa (55 g) b.p. 128°/0·3 mm, which was reduced with LAH (5·7 g) in dry ether (350 ml) to give IIIb (36 g), b.p. 135°/0·5 mm; m.p. 90° on crystallization from ether–pet. ether (Lit.[11f] 91–92°).

---

* Kronenthal and Baker failed to oxidise the decalone ester (IIa) to the *trans*-acid (XI).

The ketalalcohol IIIb (15 g) in EtOH (30 ml) over 10% Pd on C catalyst absorbed 1 mole equiv H_2 at room temp and atm press during 5 hr. Usual work up furnished IV (13 g) b.p. 128°/0·3 mm which was deketalized with 65% MeOH aq (150 ml) and HCl (7 ml) to give VIa (5 g), b.p. 125–130°/0·3 mm; λ_{max} 2·95 and 5·87 μ.

2,4-*Dinitrophenylhydrazone* had m.p. 118–122° (Lit,[11d] 122–124°).

10-*Hydroxymethyl-2-oxo*-cis-*decalintosylate* (VIb)

A soln of *p*-toluene-sulphonyl chloride (17·1 g) in anhyd pyridine (25 ml) was added to a soln of VIa (14·7 g) in anhyd pyridine (25 ml) at 5°. After 48 hr at 5° it yielded VIb (26 g), m.p. 72–75°.

4-*Oxo-tricyclo*[4.4.1^{1-5}.0]*undecane* (XIV)

The tosylate VIb (19 g) in Bu·OH (400 ml) was added with stirring under N_2 to warm KOBu^t (from 2·45 g K and 800 ml Bu·OH) on a steam-bath. Stirring under reflux was continued for 5 hr. Usual work up afforded pure XIV (6·75 g), b.p. 125°/10 mm, λ_{max} 5·87 μ.

2,4-*Dinitrophenylhydrazone* was crystallized from MeOH; yellow; m.p. 134°. (Found: C, 59·32; H, 5·77. $C_{17}H_{20}N_4O_4$ requires: C, 59·30; H, 5·81%). *Semicarbazone* crystallized from MeOH aq. had m.p. 202°, λ_{max} 225 mμ (ε, 14,930). (Found: C, 65·11; H, 8·61. $C_{12}H_{19}N_3O$ requires: C, 65·16; H, 8·59%).

1-*Methoxycarbonyl-3-oxo*-bicyclo[4.2.0]*octane* (XV)

The ketone XIV (1·5 g) in anhyd $CHCl_3$ (15 ml) was left at 5° with a soln of perbenzoic acid (1·5 g) in anhyd $CHCl_3$ (15 ml) containing a trace of PTSA. After 15 days it was worked up in the usual manner to furnish the lactone which was saponified with 0·5 N methanolic KOH, then esterified with diazomethane and the hydroxyester oxidized with pyridine-CrO_3 complex. Usual work up gave XV (0·45 g), b.p. 133° (bath)/0·3 mm, λ_{max} 5·62 and 5·78 μ.

2,4-*Dinitrophenylhydrazone* which separated as an oil gradually solidified in contact with MeOH at 0° for several days. After crystallization from MeOH it had m.p. 104–106°. (Found: C, 55·39; H, 6·22. $C_{18}H_{22}N_4O_6$ requires: C, 55·38; H, 5·64%).

10-*Ethoxycarbonyl-3-methyl-2-oxo*-trans-*decalin* (IId)

The formyl derivative was prepared from IIa (20 g), ethylformate (26·34 g) and finely powdered MeOH-free NaOMe (9·6 g) in benzene (200 ml).[17] A mixture of this ketone (20 g), anhyd K_2CO_3 (10 g), and MeI (11·5 ml) in anhyd acetone (115 ml) was refluxed with stirring for 15 hr. The crude mixture of O-Me and C-Me derivatives (15 g) was hydrolysed at room temp, with a mixture of MeOH (75 ml), HCl (0·7 ml) and water (15 ml). The product in ether was washed with 4% NaOH aq to give the C-Me derivative (10 g) which was deformylated by heating under reflux for 2 hr with 10% KOH aq. Compound 11d (5·2 g), b.p. 110°/0·2 mm, was obtained as a low-melting solid, which on crystallization from pet. ether had m.p. 56°. (Found: C, 70·13; H, 8·92. $C_{14}H_{22}O_3$ requires: C, 70·59; H, 9·24%).

2,4-*Dinitrophenylhydrazone* was crystallized from MeOH-$CHCl_3$; m.p. 185°. (Found: C, 57·41; H, 5·89. $C_{20}H_{26}N_4O_4$ requires: C, 57·41; H, 6·22%). *Semicarbazone* crystallized from MeOH, m.p. 216°. (Found: N, 13·85. $C_{15}H_{25}N_3O_3$ requires: N, 14·23%).

3-*Methyl-2-oxo*-trans-*decalin*-10-*carboxylic acid* (IIe)

Saponification of IId with 10% methanolic KOH soln (7 ml) under reflux led to recovery of unreacted ester. Prolonged hydrolysis with boiling HCl gave IIe in 46% yield. Crystallization from pet. ether afforded a pure specimen, m.p. 120°. (Found: C, 68·32; H, 8·50. $C_{12}H_{18}O_3$ requires: C, 68·57; H, 8·57%).

Esterification of IIe with diazomethane gave the IIf which on crystallization from pet. ether had m.p. 80°. (Found: C, 70·09; H, 9·31. $C_{13}H_{20}O_3$ requires: C, 69·64; H, 8·92%).

2,4-*Dinitrophenylhydrazone* was crystallized from MeOH-$CHCl_3$; m.p. 189°. (Found: C, 56·0; H, 5·96. $C_{19}H_{21}N_4O_6$ requires: C, 56·43; H, 5·94%). *Semicarbazone* crystallized from MeOH had m.p. 230°. (Found: N, 14·94. $C_{14}H_{23}N_3O_3$ requires: N, 14·94%).

10-*Hydroxymethyl-3-methyl-2-oxo*-trans-*decalin tosylate* (IIg)

The ketoester IId (15·5 g), ethane diol (4·03 g) in dry benzene (100 ml) and a trace of PTSA were heated under reflux for 3 hr using a Dean–Stark apparatus to furnish Vc (16·1 g) b.p. 126°/0·5 mm, which was reduced with LAH (1·5 g) to give Vd (12·5 g), b.p. 145°/0·4 mm.

3,5-*Dinitrobenzoate* crystallized from pet. ether had m.p. 188°. (Found: C, 58·37; H, 6·15. $C_{21}H_{26}N_2O_8$ requires: C, 58·06; H, 5·99%).

The ketalalcohol Vd (6g) in anhyd pyridine (10 ml) was treated with *p*-toluene-sulpholyl chloride (5·25 g) in anhyd pyridine (10 ml) and left at 5° for 48 hr. The crude tosylate (10 g) was heated under reflux for 15 min with MeOH (45 ml) and HCl (15 ml)[18] to afford IIg (5·5 g), which on crystallization from pet. ether had m.p. 158°, λ_{max} 226 mμ (ε, 15,400). (Found: C, 64·84; H, 7·64. $C_{19}H_{26}SO_4$ requires: C, 65·13; H, 7·43%).

4-*Oxo*-3-*methyl-tricyclio*[4,4,1^{1-3},0]*undecane* (VIIIb)

The ketosylate IIg (5·2 g) in Bu^{t}OH (150 ml) was added dropwise with stirring under N_2 to warm KOBu^t (from 0·5 g K and 200 ml Bu^{t}OH) on a steam-bath and refluxed for 5 hr. Usual work up furnished VIIIb (1·7 g), b.p. 110–120° (bath/1·0 mm, λ_{max} 5·85 μ.

2,4-*Dinitrophenylhydrazone* was crystallized from EtOH-$CHCl_3$; orange; m.p. 138°, $\lambda_{max}^{CHCl_3}$ 372 mμ (ε, 25,000). (Found: C, 59·95; H, 6·16; N, 15·48. $C_{18}H_{22}N_4O_4$ requires: C, 60·30; H, 6·14; N, 15·68%). *Semicarbazone* after crystallization from MeOH had m.p. 206° d, λ_{max} 228 mμ (ε, 14,700). (Found: N, 17·53. $C_{13}H_{21}N_3O$ requires: N, 17·86%).

10-*Methoxycarbonyl*-3,3-*dimethyl*-2-*oxo*-trans-*decalin* (IIh)

The formyl derivative (4·4 g) was prepared as before from IId (5 g) ethyl formate (4·66 g) and MeOH-free NaOMe (2·25 g) in dry benzene (170 ml). The formyl ketone (3·7 g) in dry benzene (55 ml) was heated under reflux for 8 hr with n-butyl-mercaptan (3·78 g) and a trace of PTSA under N_2.[16] Usual work up furnished the thiomethylene derivatives (5·2 g), b.p. 195°/1·5 mm, which gave a negative $FeCl_3$ test.

A soln of the thiomethylene compound (5·2 g) in Bu^{t}OH (7 ml) was slowly added with stirring under N_2 to a soln of KOBu^t (from 3·6 g K and 80 ml Bu^{t}OH). To this MeI (13 ml) was added during 1 hr with gentle reflux and the reaction mixture left overnight. Excess of alkali was neutralised with glacial AcOH (0·5 ml), and Bu^{t}OH partly removed. The residue after usual work up was hydrolysed with ethanediol (45 ml), KOH (5·4 g) and water (12·5 ml) for 20 hr under N_2. It was then diluted with water and extracted once with ether; the aq. layer was acidified and extracted with ether to give the crude acid (2·5 g) which was esterified (diazomethane) to give IIh (1·2 g) as a mobile liquid, b.p. 125°/0·5 mm.

2,4-*Dinitrophenylhydrazone* was crystallized from MeOH-$CHCl_3$; yellow; m.p. 208–209°. (Found: C, 57·62; H, 6·25. $C_{20}H_{26}N_2O_6$ requires: C, 57·41; H, 6·25%). *Semicarbazone* crystallized from MeOH had m.p. 242–243°. (Found: N, 13·94. $C_{15}H_{25}N_3O_3$ requires: N, 14·23%).

The m.p. of the semicarbazone and 2,4-dinitrophenylhydrazone of this product were depressed on admixture with the corresponding derivatives of IIf.

Attempted preparation of 10-*hydroxymethyl*-3,3-*dimethyl*-2-*oxo*-trans-*decalin* (Vg)

The ethylene ketal Vf (5 g), b.p. 128°/0·3 mm, was prepared from IIh (5 g), ethanediol (1·5 g) and a trace of PTSA in dry benzene (50 ml) in the usual manner. The ester Vf (5 g) was stirred under reflux for 20 hr with LAH (0·5 g) in ether (200 ml) and then worked up in the usual way. The IR spectrum revealed only a weak band at 2·9 μ and a strong band at 5·78 μ. The tertiary ester apparently survived reduction under the above condition.

Acknowledgements—Some of the preliminary experiments were carried out by Dr. G. S. Sambamurti[3] and Mrs. Maya Mukherjee. The authors are grateful to Dr. S. C. Bhattacharyya, formerly of the National Chemical Laboratory, Poona, Prof. J. N. Chatterjee of the Patna University, Patna, Dr. M. M. Dhar of Central Drug Research Laboratory, Lucknow and Dr. N. K. Chaudhuri of the Worcester Foundation for Experimental Medicine, Shrewsbury, Mass., U.S.A. for the IR spectra and to the Council of Scientific and Industrial Research, India, for grants and Research Fellowship (A.N.G. and M.M.) and to the Ministry of Education, Government of India, for a Research Training Scholarship (G.S.S.).

REFERENCES

[1] F. Sorm, *Medium ring terpenes* in *Fortschritte der Chemie Organischer Naturstoffe* p. 11. Wien, Springer-Verlag (1961); T. G. Halsall and D. W. Theobold, *Quart Rev.* **16**, 101 (1962).

[2] A. C. Cope, M. M. Martin and M. A. McKervey, *Ibid.* **20**, 119 (1966).

[3] P. C. Mukharji, G. S. Sambamurti, Unpublished work; G. S. Sambamurti, D. Phil. thesis, Calcutta (1964).

[4] A. Eschenmoser and A. Frey, *Helv. Chim. Acta* **35**, 1660 (1962); R. B. Clayton, H. B. Henbest and N. Smith, *J. Chem. Soc.* 1983 (1957).

[5] P. S. Wharton, *J. Org. Chem.* **26**, 4781 (1961).

[6] E. J. Corey, R. B. Mitra and H. Uda, *J. Am. Chem. Soc* **86**, 485 (1964).

[7] [a] J. A. Marshall and C. J. V. Scanio, *J. Org. Chem.* **30**, 3019 (1965); J. A. Marshall, C. J. V. Scanio and W. J. Iburg, *Ibid.* **32**, 3750 (1967);
[b] J. A. Marshall and G. H. Bundy, *J. Am. Chem. Soc.* **88**, 4291 (1966).

[8] M. Tanabe and D. F. Crowe, *J. Org. Chem.* **30**, 2776 (1965).

[9] E. J. Corey and E. Hamanaka, *J. Am. Chem. Soc.* **89**, 2758 (1967).

[10] A. Eschenmoser, Dorothee Fliex and G. Ohloff, *Helv. Chim. Acta* **80**, 708 (1967).

[11] [a] A. S. Hussey, H. P. Liao and R. H. Baker, *J. Am. Chem. Soc.* **75**, 4727 (1953);
[b] W. G. Dauben, R. C. Tweit and R. L. McLean, *Ibid.* **77**, 48 (1955);
[c] A. S. Dreiding and A. J. Tomasewski, *Ibid.* **77**, 411 (1955);
[d] L. S. Minickler, A. S. Hussey and R. H. Baker, *Ibid.* **78**, 1009 (1956);
[e] R. L. Kronenthal and E. I. Baker, *Ibid.* **79**, 1095 (1957);
[f] W. G. Dauben and J. B. Rogan, *Ibid.* **79**, 5009 (1957);
[g] M. Idelson and E. I. Baker, *Ibid.* **80**, 908 (1958).

[12] R. B. Turner, W. B. Meader and R. E. Winkler, *Ibid.* **79**, 4122 (1957).

[13] J. Vrkoc, V. Herout and E. Sorm, *Coll. Czech. Comm.* **28**, 1084 (1963); M. Soucek and P. Vlad, *Ibid.* **28**, 1211 (1963).

[14] G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Am. Chem. Soc.* **75**, 422 (1953).

[15] [a] R. N. Moore and G. S. Fisher, *Ibid.* **78**, 4362 (1956);
[b] V. H. Kapadia, B. A. Nagasampagi, V. G. Naik and Sukh Dev, *Tetrahedron* **21**, 607 (1967).

[16] P. E. Ireland and J. A. Marshall, *J. Am. Chem. Soc.* **81**, 6336 (1959); *J. Org. Chem.* **27**, 1615 (1962).

[17] J. W. Cornforth and R. Robinson, *J. Chem. Soc.* 1855 (1949).

[18] G. Stork, P. Rosen, N. Goldman, R. V. Coombs and J. Tsuji, *J. Am. Chem. Soc.* **87**, 275 (1965).