Tetrahedron. Vol. 25, pp. 5287 to 5294. Pergamon Press 1969. Printed in Great Britain

ALICYCLIC COMPOUNDS—IV
ACTION OF BASE ON SOME BICYCLIC AND MONOCYCLIC KETOTOSYLATES

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(*Received in the UK 20 December* 1968; *Accepted for publication* 14 *July* 1969)

Abstract—The tricyclic cyclopropyl ketones (VIA, B) could not be isomerized by base to the cycloalkadienone. The monocyclic tosylates (XXIX and XXII) did not react in the manner of their decalone and octalone analogues (I and XX).

WE reported[1] that the decalone tosylates (I and II) gave the tricyclic ketones (III and IV) instead of undergoing fragmentation to a cycloalkadienone in presence of KOBu^t. Consequently, we examined bicyclic ketotosylates of the type V in the expectation that the cyclopropylketones (VI) derived through primary cyclization[2] may rearrange to the cycloalkadienone (VII) in presence of strong base as depicted in Fig. 1. The rearrangement appeared reasonable since the mechanistic character of the process bears a formal resemblance to the transformation of carenone (VIII) type intermediates to cycloheptadienones.[3,4]

We examined the action of different bases on the two bicyclic ketotosylates (VA and VB) which afforded the tricyclic cyclopropyl ketones (VIA and VIB). But we failed to bring about the anticipated rearrangement of the compounds (VIA and VIB).

Syntheses of the required ketotosylates (V) were achieved from the monocyclic ketoesters (XA and XB) as outlined in Fig. 2. The *cis*-ring junction in these ketoesters (XIVA and XIVB) follows from their genesis, since hydrocyanation of the unsaturated esters (XI) would involve addition from the least hindered side.

Attempts to prepare the ketoester (XIVA) from the diketoester (XVIIA) through base catalysed cyclodehydration to XVIIIA proved abortive, though a successful synthesis of this type is on record.[5] However the homologue (XVIIIB) could be prepared by cyclodehydration of XVIIB.[6] Catalytic hydrogenation of XVIIIB gave XIVB identical with specimen prepared by the other route.

The tosylate (VB) was converted to the cyclopropyl ketone (VIB) when treated with base under reflux. No evidence of further rearrangement to an unsaturated ketone was observed. On boiling with acid the ketone (VIB) was isomerized to the unsaturated ketone (XIXB).

The tosylate (VA) behaved in an analogous manner to give the cyclopropyl ketone (VIA), which with acid was isomerized to the conjugated ketone (XIXA). The tricyclic ketones (VIA and VIB) resisted rearrangement under mild basic conditions. Vigorous

* Abstracted in part from the thesis submitted by G.S.S. for the D.Phil(Sc.) degree of the University of Calcutta, November 1964.

treatment with excess strong base gave resinous tar. The facile cyclopropane ring fission observed in carenone (VIII) could not be duplicated in these compounds.

Acid cleavage of the cyclopropyl ketone (VIA and VIB) gave the unsaturated ketones (XIXA and XIXB). Fission of the cyclopropane ring in the above ketone can theoretically involve either the bond *a* or bond *b* to give in each case a tertiary carbonium ion. Formation of cyclopentenones clearly, therefore, involves fission of the bond *a* of the cyclopropane ring which is the bond between the least and most substituted C atoms. In the rigid skeleton of VIA and VIB it is orbitals of bond *a* which are nearly parallel to and more effectively overlap with the π-electron of the CO group and acid catalysed cleavage involves this bond. It has recently been demonstrated by Norin and Dauben[7] that reductive opening of conjugated cyclopropyl ketones by Lithium in liquid ammonia also involves that bond of the cyclopropane ring which better overlaps the π-bonds of the adjacent unsaturated centre.

As described[8] the octalone tosylate (XX) rearranged to the tricyclic ketone (XXI) presumably through solvolytic rearrangement of the homoallylic system. Since the reaction appeared to provide an easy entry to the [3.2.0]bicycloheptenone skeleton, which is otherwise accessible mainly through photochemical transformation of cycloheptadienones,[9] we investigated the action of base on the cyclohexenone tosylate (XXII).

The enol ether of the diketoester (XXIII) on LAH reduction and acid hydrolysis gave the required unsaturated ketocarbinol (XXIV). The structure was confirmed by catalytic reduction to the ketocarbinol (XXV) which was identical with a specimen prepared from the known keto ester[10] (XXVI).

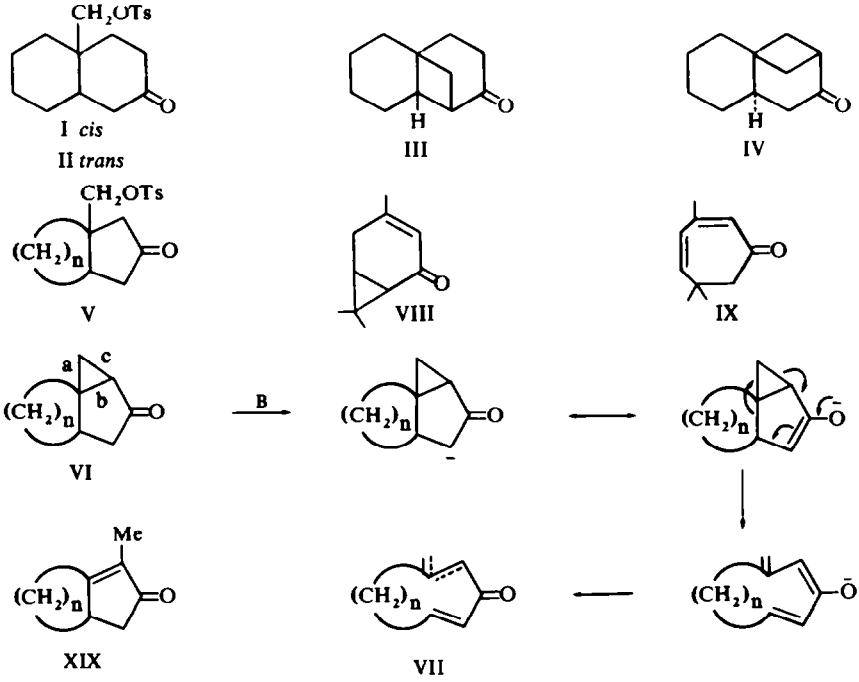

FIG. 1

In presence of just one equivalent of KOBu^t in hot Bu^{t}OH this tosylate (XXII) gave a product which was extremely prone to polymerization. The crude material exhibited UV absorption at 225 mμ (6,000), 262 mμ (600) and 274 mμ (450). The mobile oil obtained gradually turned viscous on keeping at 5° overnight and completely resinified on attempted distillation. Solvolytic rearrangement of the type previously encountered[8] to give the bicyclic ketone (XXVII) did not therefore occur in this case. Bicycloheptenones of this type are known to be quite stable under conditions in which this product polymerized. Considering these properties it appears that the monocyclic tosylate suffers fragmentation to the trienone (XXVIII) which then rapidly polymerizes.

The different course of reaction for the two homoallylic systems (XX and XXII) could possibly be ascribed to the conformation of the carbinyl tosylate group. In the *trans*-octalone tosylate (XX), the carbinyl tosylate is in the axial conformation and the π-bond of the adjacent unsaturated centre is in proper geometric disposition to assist during solvolysis, the ionization and the stabilization the resultant neopentyl carbonium ion through the cyclobutanoium ion.[8] In the monocyclic tosylate (XXII) the bulkier carbinyl tosylate group would prefer to remain in the ψ-equatorial conformation where participation of the adjacent π-bond will be geometrically prohibited. Presumably due to this subtle conformational factor the reaction in the monocyclic compound takes a completely different course.*

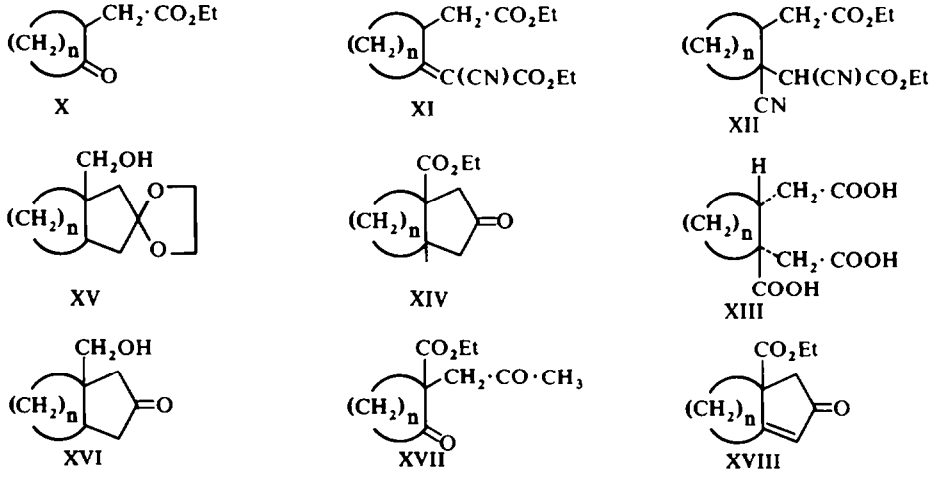

FIG. 2

The bicyclic ketone (XXX) could not be obtained from the cyclohexanone carbinyl tosylate (XXIX) under conditions in which the decalone tosylates (I and II) were converted to the ketones (III and IV). The reaction furnished an oil exhibiting UV absorption at 228 mμ which completely polymerized during attempted distillation.

* Solvolytic rearrangement involving Wagner type migration of the CH_3 or CH_2-group in the tosylate (XXII) would seem less likely, as such a change would create a carbonium ion in the vinylogous α-position of a carbonyl group. This unfavourable electronic situation would make such migrations prohibitive. Wagner type migration of the adjacent vinyl carbon also appears unlikely from electronic considerations. None of the products, however, that could arise from such a migration would exhibit the degree of instability shown by reaction product.

Presumbly the conformation of the carbinyl tosylate also controls the course of the reaction in this compound.

The isomeric ketotosylate (XXXI) has been reported[11] to yield equal amounts of the two isomeric ketones (XXXII and XXXIII) on treatment with KOBu^t in hot Bu^{t}OH. Wiberg[11] has suggested a mechanism which involves solvolytic ring expansion to the intermediate (XXXIV) which then collapses to the bicyclic ketone (XXXIII). It seems that a better mechanistic pathway, which can explain the formation of equal amounts of the two ketones, would be an intermediate of the type XXXV or its equivalent in which migration of the cyclopropane bond *a* would give the ketone XXXII and of the bond *b* the ketone XXXIII. Solvolysis of the carbinyl tosylate (XXXI) would indeed derive considerable assistance from the enol or its equivalent which constitute essentially a homoallylic system and the formation of the two isomeric ketones (XXXII and XXXIII) can then be visualised as arising through the rearrangement of the intermediate cyclopropyl carbinyl carbonium ion (XXXV).

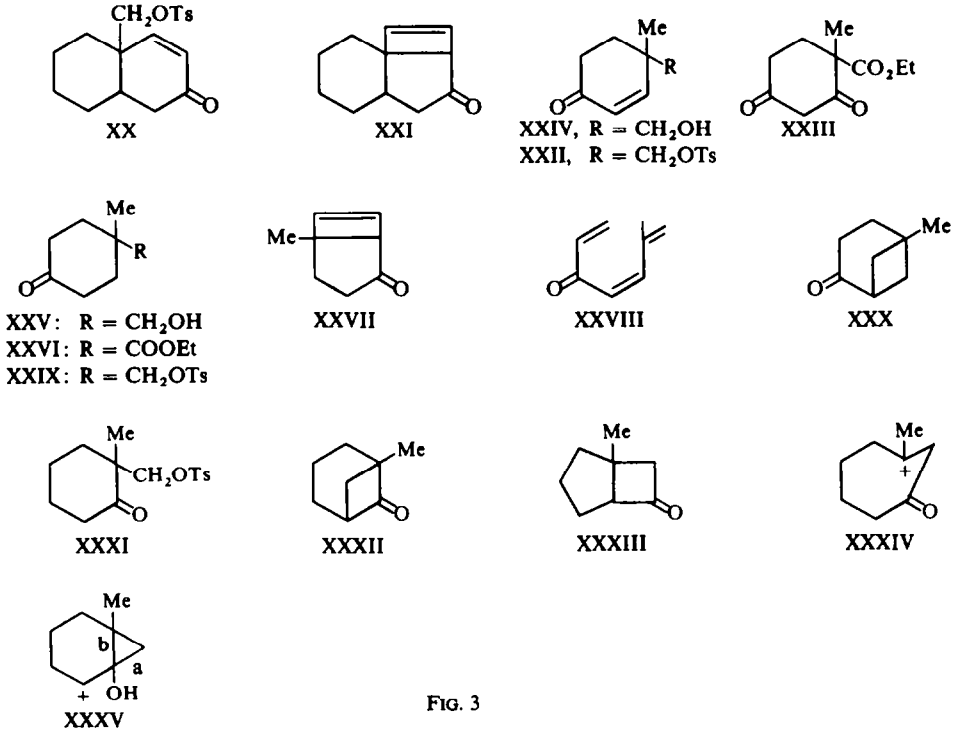

FIG. 3

EXPERIMENTAL

The m.ps and b.ps are uncorrected. Solvent extracts were dried over Na_2SO_4. Alumina used for chromatography was E. Merck aluminium oxide standardised according to Brockmann. Pet. ether indicates the fraction, b.p. 40–60°. The UV spectra were taken in 95% EtOH on Unicum Spectrophotometer Model Sp 500 unless stated to the contrary. The IR spectra were taken in thin films unless otherwise state in Perkin-Elmer "Infrachord" Recording Spectrophotometer.

Ethyl cyclohexanone-2-acetate (XB) *and ethyl cyclopentanone-2-acetate* (XA)

The keto esters were prepared both by (i) Stork's[12] enamine alkylation method as well as by (ii) alkylation

of the sodio derivative of the appropriate β-ketoesters with ethyl bromoacetate followed by hydrolysis and esterification. The keto ester XB had b.p. 125°/7 mm, yellow *2,4-dinitrophenylhydrazone* m.p. 128° (Lit:[13] 126°), and (XA), b.p. 115°/8 mm.

cis-*Cyclohexan*-1-*carboxy*-1,2-*diacetic acid* (XIIIB) *and* cis-*cyclopentan*-1-*carboxy*-1,2-*diacetic acid* (XIIIA)

The tribasic acids were prepared from the ketoesters (XB and XA) according to the following general procedure: The ketoester (0·5 mole), ethyl cyanoacetate (0·52 mole), gl. AcOH (0·5 mole), ammonium acetate (0·15 mole) in benzene (500 ml) were refluxed under a Dean–Stark apparatus until no more water separated.[14a] After usual work up, XIA and XIB were isolated by distillation and used for the next step.

Compounds XIA or XIB (0·25 mole) in EtOH (300 ml) were treated with KCN (0·50 mole) in water (200 ml) during 30 min. The mixture was then cooled in ice and partly neutralized with HCl (50 ml). After another 30 min the mixture was acidified with excess of HCl and the oil extracted with ether.[14b] Removal of ether left a brown viscous oil which on prolonged hydrolysis with conc HCl gave the corresponding tricarboxylic acids. The triethyl esters were prepared by alcohol-H_2SO_4 method. The acid XIIIB had m.p. 188°. (Found: C, 54·04; H, 6·59. $C_{11}H_{16}O_6$ requires: C, 54·10; H, 6·56%); *triethyl ester*, b.p. 155°/0·3 mm, (Found: C, 61·67; H, 8·16; $C_{17}H_{28}O_6$ requires: C, 62·19; H, 8·53%). The acid XIIIA had m.p. 148°. (Found: C, 51·87; H, 5·92. $C_{10}H_{14}O_6$ requires: C, 52·17; H, 6·08%); *triethyl ester* b.p. 175°/1 mm, (Found: C, 60·72; H, 7·81. $C_{16}H_{26}O_6$ requires: C, 61·14; H, 8·27%).

1-*Ethoxycarbonyl*-8-*oxo*-cis-*bicyclo* [4.3.0] *nonane* (XIVB) *and* 1-*ethoxycarbonyl*-7-*oxo*-cis-*bicyclo* [3.3.0] *octane* (XIVA)

The ketoesters were prepared from the corresponding tribasic esters by Dieckmann reaction. The appropriate triester (0·1 mole) in anhyd benzene (100 ml) was heated under N_2 with Na dust (0·12 g atom) until the Na particles disappeared. Decomposition with cold dil acid and usual work up furnished the β-ketoester (positive $FeCl_3$ test) which was hydrolysed with 20% HCl (150 ml) for 12 hr to give the keto acids which were esterified by alcohol-H_2SO_4 method. The ester XIVB had b.p. 102°/0·3 mm, *semicarbazone*, m.p. 161°. (Found: N, 16·15. $C_{13}H_{21}N_3O_3$ requires: N, 15·73%); *thiosemicarbazone*, m.p. 151° (Lit:[6] 151°). The ester XIVA had b.p. 114°/1·0 mm, *semicarbazone*, m.p. 157°. (Found: N, 16·58. $C_{12}H_{19}N_3O_3$ requires: N, 16·60%).

1-*Hydroxymethyl*-8-*oxo*-cis-*bicyclo* [4.3.0] *nonane* (XVIB) *and* 1-*Hydroxymethyl*-7-*oxo*-cis-*bicyclo* [3.3.0] *octane* (XVIA)

The ketoester (0·1 mole) and ethylene glycol (0·12 mole) in anhyd benzene (200 ml) containing *p*-toluenesulphonic acid (0·15 g) were heated under reflux until the calculated amount of water had separated. Usual work up gave the ketal ester which was directly used for the next operation.

The ketal ester (0·1 mole) in anhyd ether (100 ml) was reduced with LAH (0·75 mole) suspended in anhyd ether (200 ml) under reflux for 12 hr. The ketalalcohols were isolated in the usual way. The ketalalcohol XVB had b.p. 125°/0·15 mm and λ_{max}^{film} 2·6 μ, 3,5-dinitrobenzoate had m.p. 110°. (Found: C, 56·38; H, 5·47. $C_{19}H_{22}N_2O_8$ requires: C, 56·40; H, 5·42%).

The ketalalcohol XVA had b.p. 135°/0·5 mm, λ_{max}^{film} 2·6 μ, *3,5-dinitrobenzoate*, m.p. 85°. (Found: C. 55·08; H, 5·12. $C_{18}H_{20}N_2O_8$ requires: C, 55·10; H, 5·10%).

The deketalization was best effected by heating under reflux the ketalalcohol (5·0 g) in MeOH (50 ml) with 5% HCl aq (50 ml) until the turbidity just disappeared (45 min). Usual work up followed by fractionation furnished the products in 90% yield.

The ketoalcohol XVIB had b.p. 118°/0·1 mm and λ_{max}^{film} 2·6 and 5·8 μ, *3,5-dinitrobenzoate*, m.p. 175°. (Found: C, 56·73; H, 4·79; $C_{17}H_{18}N_2O_7$ requires: C, 56·35; H, 5·01%); *2,4-dinitrophenylhydrazone*, m.p. 150°. (Found: C, 54·98; H, 5·72. $C_{16}H_{20}N_4O_5$ requires: C, 55·17; H, 5·75%). The ketoalcohol XVIA had b.p. 135°/1 mm and λ_{max}^{film} 2·6 and 5·8 μ, (*3,5-dinitrobenzoate*, m.p. 92°. (Found: C, 53·02; H, 4·78. $C_{16}H_{16}N_2O_7$ requires: V, 53·33; H, 4·76%).

Ethyl-2-(2′-*oxopropyl*)*cyclohexanone*-2-*carboxylate* (XVII)

Freshly distilled propargyl bromide (39·30 g) was added dropwise to the sodio derivative prepared from ethylcyclohexanone-2-carboxylate (51 g) and Na dust (7·5 g) in benzene (200 ml) with cooling. It was then refluxed (5 hr), cooled, washed with water, concentrated and distilled to give the product (56 g), b.p. 136°/9 mm. *Semicarbazone* crystallized from EtOH had m.p. 154° (Lit:[6] 152·7–153·5°). As reported by Dauben[6] the procedure of Raphael and Islam[15] gave an impure product consisting largely of the pimelate.

The above propargyl derivative (56 g) in MeOH (100 ml) was added dropwise (slight exothermic reaction)

to the catalyst prepared from red HgO (3·8 g), BF_3-etherate (3 ml) and trichloroacetic acid (0·2 g) in MeOH (15 ml). After 2 hr at room temp it was decomposed by pouring into dil H_2SO_4 and extracted with ether. Usual work up gave XVIIIB (45 g), b.p. 135°/1 mm. *Disemicarbazone* had m.p. 216°, insoluble in all common solvents (Lit:[15] 214°).

1-*Ethoxycarbonyl*-8-*oxo-bicyclo* [4.3.0] *non*-6-*ene* (XVIII)

The dikoester XVIIB (5·6 g) was added to cold KOBu^t prepared from K (1 g) and Bu^{t}OH (30 ml) and the mixture kept at 5° for 5 min. After acidification with dil AcOH it was extracted with ether. The crude residue left after removal of ether was dissolved in benzene (50 ml) and heated (2 hr) with *p*-toluenesulphonic acid (0·15 g).[5] After usual work up the residue on careful fractionation gave the unsaturated ketone (1 g), b.p. 135°/3 mm and λ_{max} 230 mμ (ε, 8400). *Semicarbazone* had m.p. 202° (Lit:[6] 202·6–202·8) (Found: N, 15·94. $C_{13}H_{19}N_3O_3$ requires: N, 15·85%). The procedure described by Dauben[6] however gave better results.

The above unsaturated ester (1 g) in EtOH (15 ml) over 10% Pd on C catalyst (0·1 g) absorbed one mole equiv H_2 at room temp and atom press during 40 min. Usual work up and distillation gave XVB.

Base treatment of the ketotosylates (VA *and* VB)

Formation of cyclopropyl ketones: 3-*oxo-tricyclo* [3.3.1$^{1-2}$:0] *nonane* (VIA) *and* 3-*oxo-tricyclo* [4.3.1$^{1-2}$:0] *decane* (VIB)

The ketotosylates were prepared by adding in one lot freshly distilled *p*-toluenesulphonyl chloride (0·052 mole) to a soln of the keto alchol (0·05 mole) in anhyd pyridine (20 ml) at 0° and letting the mixture stand for 48 hr at 5°. Usual work up gave the tosylate as viscous oil, which was directly used for all subsequent steps.

(i) The oily ketotosylate VB (6·4 g) in ether (200 ml) and 1·15% NaOH aq (90 ml) were stirred at room for 16 hr to give VIB (2 g), b.p. 110°/10 mm, λ_{max} 276 mμ (ε, 120) and λ_{max}^{film} 5·8 μ. (Found: C, 79·62; H, 9·11. $C_{10}H_{14}O$ requires: C, 80·00; H, 9·33%). *2,4-Dinitrophenylhydrazone* (prepared at 0°) was crystallized from FtOH-EtOAc: deep red, m.p. 152°, $\lambda_{max}^{CHCl_3}$ 373 mμ (ε, 27,000). (Found: C, 57·77; H, 5·56; N, 16·94. $C_{16}H_{18}N_4O_4$ requires: C, 58·19; H, 5·49; N, 16·96%). *Semicarbazone* was crystallized from MeOH aq; m.p. 165°, λ_{max} 232 mμ (ε, 13,700). (Found: C, 63·31; H, 8·07; N, 19·62. $C_{11}H_{17}N_3O$ requires: C, 63·73; H, 8·27; N, 20·27%).

The same ketone was obtained when VB was heated under reflux (6 hr) with an excess of methanolic NaOH or with methanolic NaOMe soln.

The tosylate VB (5·3 g) was heated under reflux with stirring (3 hr) with a slurry of KOBu^t, prepared from K (1·3 g) in anhyd benzene (200 ml). Usual work up and distillation gave VIB (1·5 g). When either VB or VIB was heated with excess of KOBu^t in refluxing toluene or with NaH in THF for about 10 hr, only intractable tars were obtained.

(ii) The tosylate VA on similar treatment yielded VIA, b.p. 80°/4 mm, λ_{max} 280 mμ (ε, 110) and λ_{max}^{film} 5·8 μ. (Found: C, 79·15; H, 8·62. $C_9H_{12}O$ requires: C, 79·41; H, 8·82%). *2,4-Dinitrophenylhydrazone* had m.p. 128° (from EtOH-EtOAc and 175° (from EtOH-$CHCl_3$); $\lambda_{max}^{CHCl_3}$ 370 mμ (ε, 26,700). (Found: C, 56·76; H, 5·04; N, 17·99. $C_{15}H_{16}N_4O_4$ requires; C, 56·96; H, 5·06; N, 17·71%). *Semicarbazone* was crystallized from MeOH aq. m.p. 156°, λ_{max} 232 mμ (ε, 11,600). (Found: C, 62·23; H, 7·35; N, 21·31. $C_{10}H_{15}N_3O$ requires: C, 62·17; H, 7·82; N, 21·75%).

Acid rearrangement of the cyclopropyl ketones (VIA and VIB)

(i) The ketone VIB (0·4 g) was heated under reflux for 3 hr under N_2 with a mixture of H_2SO_4 (3 ml), gl AcOH (6 ml) and water (6 ml). The product was isolated in the usual way and purified by sublimation at bath temp 150–155°/10 mm to give XIXB (0·2 g), λ_{max} 240 mμ (ε, 15,000) and λ_{max}^{film} 5·95 and 6·15 μ. *2,4-Dinitrophenylhydrazone* was crystallized from EtOH-EtOAc: red, m.p. 136°, $\lambda_{max}^{CHCl_3}$ 395 mμ (29,000)* (Found: C, 58·26; H, 5·60. $C_{16}H_{18}N_4O_4$ requires: C, 58·18; H, 5·45%).

(ii) The ketone VIB (0·5 g) in $CHCl_3$ (20 ml) at 0·5° was saturated with dry HCl gas (2·5 hr) and left overnight. Usual work up gave an oil (0·45 g), b.p. 140° (bath)/8 mm, which was found to contain Cl_2; λ_{max} 235 mμ (ε, 3,000) and 282 mμ (ε, 175); λ_{max} 5·75 μ (strong) and 5·95 μ (weak). *2,4-Dinitrophenylhydrazone* of this oil was also found to be a mixture of yellow and red crystals which could not be easily separated.

* This ketone as well as its 2,4-dinitrophenylhydrazone was found by direct comparison different from $\Delta^{1;9}$-2-octalone[12] (λ_{max} 239 mμ (ε, 12,700); 2,4-dinitrophenylhydrazone, m.p. 171°). The latter could arise if the cleavage, of the cyclopropane ring had involved the bond *b*.

(iii) The ketone VIA (0·35 g) was similarly treated with H_2SO_4 (3 ml), gl AcOH (6 ml) and water (6 ml) for 3 hr. Usual work up gave XIXA (0·15 g), λ_{max} 240 mμ (ε, 14,700); λ_{max}^{film} 5·95 μ. 2,4-*Dinitrophenylhydrazone* was crystallized from EtOH-EtOAc: red, m.p. 194°, $\lambda_{max}^{CHCl_3}$ 396 mμ (ε, 30,000). (Found: C, 57·13; H, 5·03. $C_{15}H_{16}N_4O_4$ requires: C, 56·96; H, 5·06%).

4-Methyl-4-ethoxycarbonyl-cyclohexan-1,3-dione (XXIII)

The methoiodide of 4-diethylaminobutanone-2- from the base (21·45 g) and MeI (25·65 g) in EtOH (15 ml) was added to the sodio derivative of diethylmethyl malonate prepared from the malonate (26 g) and Na (3·45 g) in EtOH (60 ml) at 0° with stirring. The mixture was stirred at this temp for 5 hr and then refluxed for 4 hr. Usual work up gave the condensation product (23 g), b.p. 123°/3 mm which was heated under reflux for 20 hr with NaOEt from Na (2·3 g) and EtOH (120 ml). EtOH was then removed under reduced press, the residue diluted with water and acidified and the liberated oil extracted with ether. Usual work up and distillation afforded the diketone as a viscous oil which solidified and after crystallization from benzene -pet. ether had m.p. 90°. (Found: C, 60·25; H, 7·17. $C_{10}H_{14}O_4$ requires: C, 60·60; H, 7·07%).

4-Methyl-4-hydroxymethyl-Δ^2-cyclohexenone (XXIV)

The diketone XXIII (17·5 g) and anhyd EtOH (26 g) in benzene (250 ml) containing *p*-toluenesulphonic acid (0·4 g) were heated under reflux (16 hr) using a Dean–stark apparatus. Usual work up gave the enol ether (13·3 g) b.p. 128–129°/0·7 mm.

The enol ether (13·3 g) in ether (20 ml) was reduced with LAH (4·4 g) in ether (150 ml) during 6 hr at room temp. Excess of LAH was then decomposed with EtOAc and the mixture poured into iced H_2SO_4. Usual work up gave the unsaturated keto alcohol (6 g), b.p. 113–114°/0·2 mm, λ_{max} 229 mμ (ε, 11,000) and λ_{max}^{film} 2·6 and 6·0 μ. 2,4-*Dinitrophenylhydrazone* crystallized from EtOH had m.p. 168°. (Found: C, 52·40; H, 5·03. $C_{14}H_{16}N_4O_5$ requires: C, 52·50; H, 5·00%).

4-Methyl-4-tosyloxymethyl-Δ^2-cyclohexenone (XXII)

The unsaturated ketoalcohol XXVIII (3 g) in pyridine (6 ml) was treated with *p*-toluenesulphonyl chloride (4·9 g) in pyridine (8 ml) at 0° and left at 5° for 48 hr. After usual work up and crystallization from ether-pet. ether it has m.p. 53–55°.

Base treatment of the tosylate (XXII)

The ketosylate (7·75 g) in Bu^{t}OH (50 ml) was added dropwise to a soln of KOBu^t in Bu^{t}OH prepared from K (1·1 g) and Bu^{t}OH (300 ml) at 70° under N_2. The initial deep red colour gradually started to fade as KOTs began to separate. After 3 hr at this temp the soln became almost neutral. It was worked up in the usual way with ether. Concentration of ether left a somewhat viscous liquid which was dissolved in pet. ether (15 ml) and left overnight at 5°. An insoluble viscous oil separated. The supernatant pet. ether was removed and concentrated to leave an oil which had λ_{max} 225 mμ (ε, 6,000)‖ 262 mμ (ε, 600) and 274 mμ (ε, 450). This gradually polymerized to a viscous gum on storage. Attempted distillation led to complete decomposition.

Identical results were also obtained when the base treatment was carried out at about 50° for 4 hr.

4-Methyl-4-hydroxymethyl-cyclohexanone (XXV)

(i) Compound XXVI was prepared according to published procedure.[10] The ketoester (10·0 g), ethylene glycol (5·2 g) in benzene (200 ml) and *p*-toluenesulphonic acid (0·1 g) were heated in the usual way. Conventional work up afforded the ketal (11 g), b.p. 142°/1·4 mm. The ketal (11 g) in ether (10 ml) was added to LAH (1·1 g) in ether (150 ml). After reflux (12 hr) the reaction mixture was worked up to afford the ketal-alcohol (8 g) b.p. 140°/1·3 mm.

The ketal alcohol (8 g) in MeOH (60 ml) was heated under reflux (45 min) with 5% HCl aq (60 ml). Usual work up afforded XXV (5·2 g), b.p. 131°/1 mm. 2,4-*Dinitrophenylhydrazone* was crystallized from EtOH: yellow, m.p. 161°. (Found: N, 17·13. $C_{14}H_{18}N_4O_5$ requires: N, 17·39%).

(ii) The unsaturated ketoalcohol XXIV (1 g) in EtOH (15 ml) over 10% Pd on C (0·1 g) absorbed one mole equivalent of H_2 at room temp and atm press. Usual work up furnished XXV. 2,4-*Dinitrophenylphydrazone* after crystallization from EtOH had m.p. 161°, undepressed on admixture with the above specimen. The crystalline XXIX, m.p. 58°, was prepared from the keto alcohol in the usual way.

Base treatment of the tosylate (XXIX)

(i) The keto tosylate (2·06 g) in Bu^{t}OH (20 ml) was added to warm KOBu^t in Bu^{t}OH from K (0·273 g) and Bu^{t}OH (75 ml) under N_2. Separation of KOTs commenced as soon as the soln started to reflux. After about 3 hr the mixture was almost neutral to litmus. After dilution with water, the soln was extracted with pet. ether and processed in the usual way to give an oil (0·8 g) which decomposed on attempted distillation under reduced press. The crude oil had λ_{max} 228 mμ (ε, 5,200).

(ii) A soln of KOBu^t in Bu^{t}OH from K (0·274 g) and Bu^{t}OH (45 ml) was added dropwise to the tosylate (2·08 g) in Bu^{t}OH (40 ml) at 78° under N_2. After 3 hr reflux the mixture was worked up in the usual way to give an oil (0·9 g) which had λ_{max} 228 mμ (ε, 5,100). This decomposed on attempted distillation. On keeping the material gradually turned to a thick viscous mass.

Acknowledgement—The authors are grateful to Prof. Dr. D. K. Banerjee of the Indian Institute of Science, Bangalore, Dr. S. C. Bhattacharyya formerly of National Chemical Laboratory, Poona, and to Dr. N. K. Chaudhuri of the Worcester Foundation for Experimental Biology, Shrewsbury, Mass. U.S.A., for the Infra Red Spectra and to the Council of Scientific and Industrial Research, New Delhi for grants and Research Fellowship (P.K.S.) and to the Ministry of Education, Government of India for a Research Training Scholarship (G.S.S.) during 1960–1963.

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