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A Novel Method for Angular Functionalized Methylation *via* Ring Opening of Bromocyclopropane*,[1a,b,2]

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An angular dibromomethyl group was introduced into 1,1-dimethyl-1,2,3,4-tetrahydrophenanthren-9-ol (I) by the abnormal Reimer-Tiemann reaction using bromoform. I was converted into bromocyclopropane ketone (III), which had a very high reactivity toward various nucleophiles to give the ring-opened products, having angular formyl group IX, XIX, XX and XXVII, cyanomethyl group XII, sulfonylmethyl group XIII, nitromethyl group XIV, thiomethyl group XVII, and iminomethyl group XVIII. These results suggest that this reaction may be a useful method by angular functionalized methylation for the synthesis of natural products.

The abnormal Reimer-Triemann reaction[4] for alicyclic phenols has been utilized for the reaction introducing an angular dihalogenomethyl group which may be converted into a methyl group.[5] We wish to report that an angular dibromomethyl group, which was introduced into 1,1-dimethyl-1,2,3,4-tetrahydrophenanthren-9-ol (I) by the abnormal Reimer-Tiemann reaction,[6] can be converted into an angular formyl, cyanomethyl, nitromethyl, thiomethyl, sulfonylmethyl, and iminomethyl group in a regiospecific and stereospecific manner.

The dropwise addition of bromoform to a solution of I in 15% aqueous sodium hydroxide at about 80° gave 4a-dibromomethyl-1,1-dimethyl-1,2,3,4,4a,9-hexahydro-9-oxophenanthrene (II). The catalytic reduction of II over 10% palladium-carbon in ethanol at room temperature gave the bromocyclopropane ketone[7] (III) in 70% yield. The following data are entirely consistent with the presence of a cyclopropane ring in III. Reduction of III with sodium borohydride in methanol produced the alcohol (IV) in a good yield. Hydrogenolysis of the bromine atom on the cyclopropane ring of IV with sodium in boiling propanol gave the cyclopropane-alcohol (V), whose nuclear magnetic resonance (NMR) spectrum showed a pair of doublets centered at 9.32 and 9.06 τ (J=3.5 Hz), which were assigned to the characteristic geminal cyclopropyl protons. The treatment of IV with ethanolic hydrogen chloride afforded quantitatively the bromocyclopropane olefin (VI). This olefin (VI) was catalytically hydrogenated and subsequently treated with sodium in boiling propanol to give an oily cyclopropane derivative (VII), whose NMR spectrum showed a couple of doublets centered at 9.23 and 9.08 τ (J=5 and 5 Hz) assigned to signals for the geminal cyclopropyl protons.

In order to convert the bromocyclopropane derivative (VI) into an angular aldehyde group, a successful route would be the solvolytic nucleophilic displacement of the bromine

* Dedicated to the memory of Prof. Eiji Ochiai.

1) *a*) H. Yamaguchi, T. Maeda, and T. Okamoto, *Chem. Pharm. Bull.* (Tokyo), **16**, 1145 (1968); *b*) H. Yamaguchi and T. Okamoto, *Chem. Pharm. Bull.* (Tokyo), **17**, 214 (1969).

2) This paper constitutes part II of a series entitled "Chemical Studies on Diterpenoids." Part I: M. Somei and T. Okamoto, *Yakugaku Zasshi*, **92**, 397 (1972).

3) Location: *Hongo, 7-3-1, Bunkyo-ku, Tokyo, 113, Japan.*

4) K. Auwers and G. Heil, *Chem. Ber.*, **35**, 4207 (1902).

5) R.B. Woodward, *J. Am. Chem. Soc.*, **62**, 1208 (1940).

6) M.S. Gibson, *J. Chem. Soc.*, **1961**, 2251.

7) The stereochemical structure will be discussed in the succeeding paper: H. Yamaguchi, K. Suematsu, and T. Okamoto, *Chem. Pharm. Bull.* (Tokyo), in press.

atom on the cyclopropane ring and a regiospecific ring opening. Acetolysis of VI with silver acetate in acetic acid gave the acetoxy-cyclopropane olefin (VIII) in an excellent yield. By the treatment of VIII with potassium hydroxide in methanol, the aldehyde (IX) was obtained in a quantitative yield.[8] The structure of the aldehyde (IX) was determined as follows: Catalytic reduction of IX over platinum oxide in glacial acetic acid with warming gave only A/B-*trans*-fused saturated aldehyde (X), which was reduced by the Wolf-Kischner method to A/B-*trans*-fused podocarpatriene (XI), which was identical to a sample synthesized by Fetizon[9] by comparing their NMR spectra.

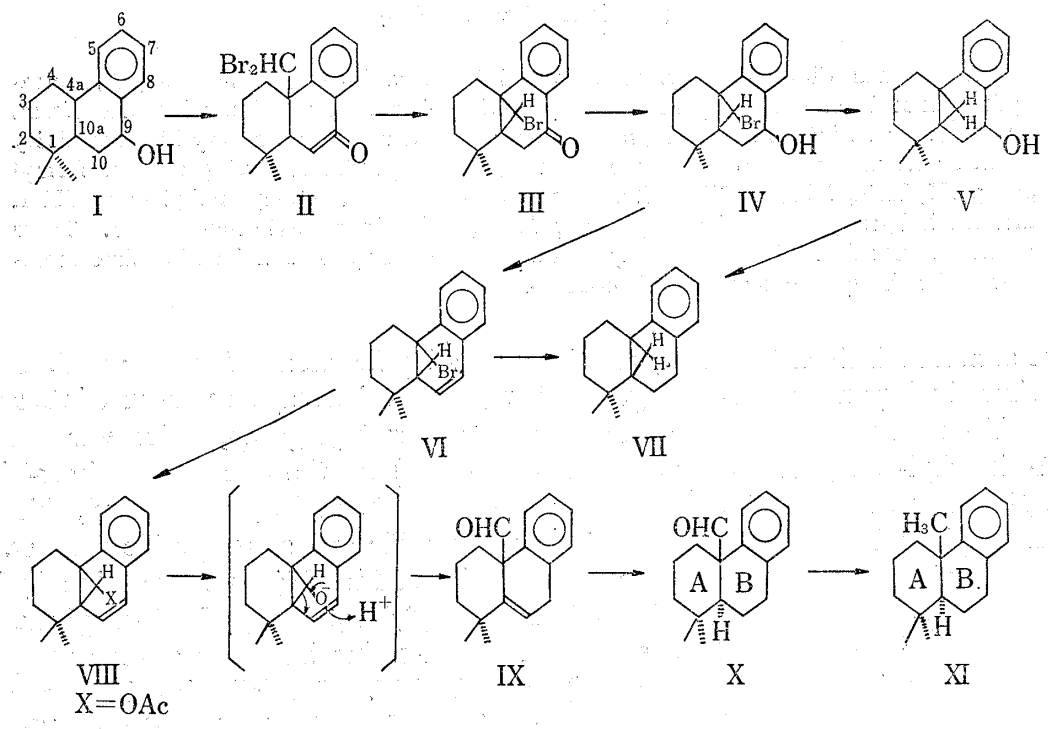


Chart 1

Bromocyclopropane ketone (III) was more reactive toward various nucleophiles than bromocyclopropane olefin (VI). Angular functionalized methylation was achieved by nucleophilic displacement of bromine atom with various reagents and by regiospecific ring opening of the cyclopropane ring.

Treatment of bromocyclopropane ketone (III) with potassium cyanide in dimethyl sulfoxide at 60° gave upward ring-opened (fission from the bond A) product (XII), which had an angular cyanomethyl group at C-4a. The reaction yield was high (70%) and no downward ring-opened (fission from the bond B) product was detected. Bromocyclopropane ketone (III) reacted with sodium *p*-toluenesulfinate in dimethyl sulfoxide at about 60° to give upward ring-opened product (XIII) in 88% yield. No other product was isolated. Reaction of III with sodium nitrite proceeded smoothly at about 50° in dimethyl sulfoxide to yield upward ring-opened product (XIV) in 50% yield. Reaction of III with those reagents mentioned above might involve the substituted cyclopropane derivatives (XV) as reaction intermediates, which might convert spontaneously into upward ring-opened products (XII, XIII, and XIV) under these reaction conditions. This kind of intermediate (XV) was isolated in the reaction of III with sodium benzylthiolate in dimethyl sulfoxide at room temperature. The reaction product was benzylthiocyclopropane derivative (XVI) and the yield was quantitative. Treat-

8) C.H. Depuy, *Acc. Chem. Res.*, **1**, 33 (1968).
9) M. Fetizon and G.M. Moream, *Bull. Soc. Chim. Fr.* **1965**, 3431.

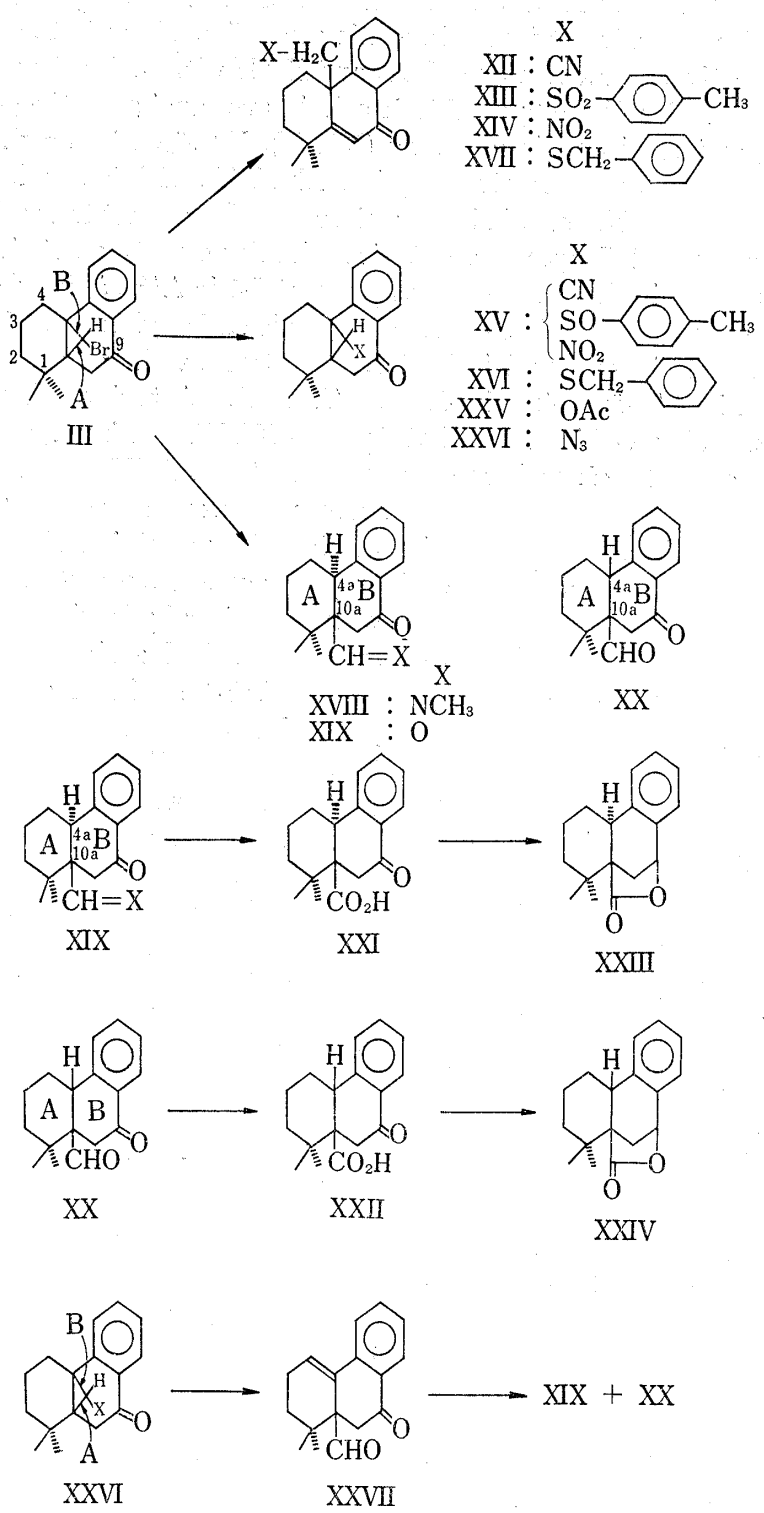
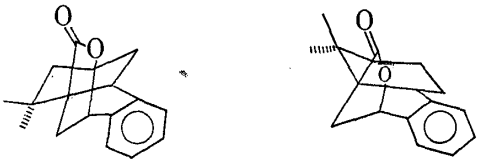


Chart 2

ment of XVI with sodium hydroxide in methanol at reflux led to upward ring-opened product (XVII) in 80% yield. No downward ring-opened product was detected.

In contrast to the upward ring-opening with the reagents mentioned above, an exclusive downward ring-opening was observed. When bromocyclopropane ketone (III) was reacted with methylamine in ethanol at 190° in a sealed tube, affording iminomethyl ketone (XVIII) as a major product and two isomeric aldehyde ketones (XIX and XX) in 60% and poor yield, respectively. The iminomethyl ketone (XVIII) gave aldehyde ketone (XIX) by acid hydroly-

sis. The structures of XIX and XX was confirmed from the following evidences. Oxidation of XIX and XX with chromium trioxide in acetic acid afforded the keto acid (XXI) and its isomer (XXII), respectively. Reduction of XXI and XXII with sodium borohydride in boiling ethanol and treatment with dilute hydrochloric acid in methanol gave the γ-lactone (XXIII), IR ν_{max}^{KBr} 1775 cm^{-1}, and the isomeric γ-lactone (XXIV), IR ν_{max}^{KBr} 1780 cm^{-1}. The formation of γ-lactone indicates that the aldehyde group in both XIX and XX should attach to carbon at C-10a, and that XIX and XX should be stereoisomers with respect to the A/B ring junction. From the studies of their NMR spectra and their molecular models, a definite structure of the two γ-lactones was determined. The β-methyl group at C-1 in A/B-*cis*-fused γ-lactone (XXIV) (Fig. 1) may be in the paramagnetic cone of the lactonic carbonyl group. Thus, some extent of downfield shift should be expected in its NMR spectrum, while no such anisotropic effect whould be expected in A/B-*trans*-fused γ-lactone (XXIII). Actually, a large downfield shift of about 0.4 ppm was observed in the methyl signal of XXIV. This means that the A/B ring juncture of XXIV could be *cis* and, consequently, that of XXIII would be *trans*.



XXIII XXIV

Fig. 1

Bromocyclopropane ketone (III) was reacted with acetic acid containing silver acetate to give cyclopropane acetoxyketone (XXV), which was treated with potassium hydroxide in methanol at room temperature to afford a single product, downward ring-opened A/B-*trans*-fused aldehyde (XIX) in a high yield Bromocyclopropane ketone (III) reacted with sodium azide in dimethyl sulfoxide at about 50° to form cyclopropyl azide (XXVI) in 80% yield, which was treated with a mixture of hydrochloric acid and acetic acid to give the downward ring-opened aldehyde (XXVII) and phenanthren-9-ol (I) in 25% and 60% yield, respectively. Reduction of the aldehyde (XXVII) with hydrogen over platinum oxide in ethanol gave A/B-*trans*-fused aldehyde (XIX) as a major product (90%) and its stereoisomer (XX) in a very small yield.

Our present results suggest that the regiospecific and stereospecific ring-opening of bromocyclopropane derivatives accompanied by substitution with various nucleophiles may provide a useful method of angular functionalized methylations for the synthesis of some natural products. Application of this method to the synthesis of morphine derivatives will be reported in a succeeding paper.[10]

Experimental

Melting points were uncorrected and NMR spectra were measured in deuteriochloroform.

4a-Dibromomethyl-1,1-dimethyl-1,2,3,4,4a,9-hexahydro-9-oxophenanthrene (II)——To a solution of 2.0 g of phenol[6] (I) in 15% aq. NaOH, 10 ml of $CHBr_3$ was added slowly at 70—80° with vigorous stirring. The mixture was stirred for 6 hr at the temperature. The reaction mixture was extracted with $CHCl_3$. The organic phase was washed and dried. Evaporation of the solvent left an oil which was chromatographed over Al_2O_3 with a mixture of hexane and $CHCl_3$ to produce 800 mg of the compound (II) as yellow prisms (from cyclohexane), mp 146—148°. IR ν_{max}^{KBr} cm^{-1}: 1665; UV λ_{max}^{EtOH} nm (ε): 236 (899), 256 (4910). NMR: 3.29 (1H, s), 3.50 (1H, s). *Anal.* Calcd. for $C_{17}H_{18}OBr_2$: C, 51.28; H, 4.55. Found: C, 51.10; H, 4.57.

Bromocyclopropane Ketone (III)——A solution of 800 mg of II in EtOH was hydrogenated over 10% Pd/C at room temperature at atmospheric pressure. The catalyst was filtered off and washed with EtOH. The solvent was evaporated from the filtrate *in vacuo* to leave an oil, which was purified by chromatography over silica gel to give 500 mg of bromocyclopropane ketone (III) as needles (hexane), mp 128—130°. IR ν_{max}^{KBr} cm^{-1}: 1672. NMR τ 6.32 (1H, s), 7.17 (2H, s). *Anal.* Calcd. for $C_{17}H_{19}OBr$: C, 63.96; H, 6.00. Found: C, 64.11; H, 5.99.

Bromocyclopropane Alcohol (IV)——To a solution of 70 mg of III in MeOH 90 mg of sodium borohydride was added at 0° with stirring and then the mixture was stirred at room temperature for 3 hr. To the mixture was added water and the solvent was evaporated. Its $CHCl_3$ extract was washed, dried, and the solvent was evaporated to leave an oil, which was chromatographed over silica gel with a mixture of hexane and $CHCl_3$

10) T. Okamoto and K. Kawada, *Chem. Pharm. Bull.* (Tokyo),

to afford the alcohol (IV) as colorless needles, mp 134°. IR ν_{max}^{KBr} cm^{-1}: 3400. NMR τ: 6.14 (1H, s). *Anal.* Calcd. for $C_{17}H_{21}OBr$: C, 63.55; H, 6.59. Found: C, 62.76; H, 6.55.

Reduction of Bromocyclopropane Alcohol (IV) to V and VII——To a boiling solution of 100 mg of IV in PrOH 1.0 g of sodium metal was added in small portions. The mixture was refluxed for 1 hr. The solvent was removed, and water was added to the residue, $CHCl_3$ extract was washed, dried, and evaporated to leave a residue, which was chromatographed over silica gel with a mixture of hexane-$CHCl_3$.

From the 1st fraction, 15 mg of VII was obtained as an oil, NMR τ: 9.23, 9.08 (1H, 1H, d, d, J=5, 5 Hz). The 2nd eluate gave 40 mg of V as an oil, IR ν_{max}^{film} cm^{-1}: 3400, NMR: 9.32, 9.06 (1H, 1H, d, d, J=3.5, 3.5 Hz).

Bromocyclopropane Olefine (VI)——A solution of 350 mg of IV in EtOH-HCl was heated at 70—75° for 2 hr in a sealed tube, the solvent was evaporated *in vacuo* and the residual oil was chromatographed over silica gel with hexane, affording 275 mg of VI as neadles (MeOH), mp 83—83.5°, NMR τ: 6.37 (1H, s), 4.00 (1H, d, J=13 Hz), 3.29 (1H, d, J=13 Hz). *Anal* Calcd. for $C_{17}H_{19}Br$: C, 67.31; H, 6.32. Found: C, 67.88; H, 6.30.

Catalytic Reduction of VI to VII——A solution of 30 mg of VI in EtOH was hydrogenated over 10% Pd/C at atomospheric pressure for 1.5 hr. Removal of the catalyst and evaporation of the solvent gave an oil, which was dissolved in PrOH, and added with 600 mg of sodium metal. Usual work-up and chromatography over silica gel with hexane gave 15 mg of an oil, which was identical with VII described above.

Acetoxy-cyclopropane Olefin (VIII)——A mixture of 100 mg of VI and 100 mg of AgOAc in AcOH was heated at 100° for 3 hr. Removal of the solvent gave a residue, which was treated with $CHCl_3$. Evaporation of the solvent and purification by chromatography over silica gel with a mixture of hexane and CH_2Cl_2 gave 65 mg of VIII as prisms (hexane), mp 87.5—89.0. IR ν_{max}^{KBr} cm^{-1}: 1738. NMR τ: 8.35 (3H, s), 5.72 (1H, s), 4.20 (1H, d, J=11 Hz), 3.12 (1H, d, J=11 Hz). *Anal.* Calcd. for $C_{19}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.16, H, 8.06.

Hydrolysis of Acetoxy-cyclopropane Olefin (VIII) to Aldehyde (IX)——A mixture of 1.00 g of VIII and 630 mg of KOH in MeOH was stirred at room temperature overnight. The mixture was made neutral with 2N HCl and then extracted with CH_2Cl_2. The extract was washed, dried, and evaporated to leave a residue, which was crystallized from hexane to 645 mg of IX as needles (hexane), mp 90.5—91.5°. IR ν_{max}^{KBr} cm^{-1}: 2800, 2700, 1725, 1670. NMR τ: 6.48 (2H, d, J=4.5 Hz), 3.83 (1H, t, J=4.5), 0.72 (1H, long-ranged coupled d, J 1<Hz). *Anal.* Calcd. for $C_{17}H_{20}O$: C; 84.95, H; 8.39. Found: C; 84.21, H; 8.13.

Hydrogenation of the Aldehyde (IX) to X——A solution of 15 mg of IX was hydrogenated over PtO_2 in EtOH at atmospheric pressure at 70°. Removal of the catalyst and evaporation of the solvent from the filtrate gave an oil, which was chromatographed over silica gel with a mixture of hexane and $CHCl_3$. Recrystallization from hexane gave 4 mg of the aldehyde (X) as needles, mp 100—103°. IR ν_{max}^{KBr} cm^{-1}: 2840, 2740, 1705. Mass Spectrum m/e: 242 (M^+).

Wolf-Kischner Reduction of the Aldehyde (X) to Podocarpatriene (XI)——A mixture of 50 mg of X, 1.0 g of KOH, and 1.5 ml of hydrazine in 5 ml of diethylene glycol was distilled gradually at 105—180° and then the residual mixture was heated at 220. The extract of the reaction mixture and the distillate with hexane was washed and dried. Removal of the solvent and chromatography of the residue on Al_2O_3 gave an oil, which was identical with an authentic sample (XI) obtained by Fetizon by comparing their NMR spectra. Mass Spectrum m/e: 228 (M^+).

The Reaction of III with KCN to XII——A mixture of 150 mg of III and 150 mg KCN in 20 ml of Me_2SO was warmed at 60—80° for 6 hr, $CHCl_3$ was added and the mixture was washed with water and then dried. Removal of the solvent and chromatography of the residue over silica gel with a mixture of $CHCl_3$ and EtOAc afforded 60 mg of XII as needles (hexane-$CHCl_3$ mixture), mp 204.5—205.5°. IR ν_{max}^{KBr} cm^{-1}: 2240, 1650. NMR τ: 7.16, 6.92 (1H, 1H, d, d, J=16 Hz), 3.40 (1H, s). *Anal.* Calcd. for $C_{18}H_{19}OH$: C, 81.47: H, 7.22. Found: C, 80.62; H, 7.01.

Reaction of III with Sodium *p*-Toluenesulfinate to XIII——A mixture of 130 mg of III and 250 mg of sodium *p*-toluenesulfinate in 40 ml Me_2SO was stirred at 55—80° for 6 hr. Work-up as mentioned above and chromatography gave 120 mg of XIII as needles (CH_2Cl_2 and hexane), mp 234—235°. IR ν_{max}^{KBr} cm^{-1}: 1650. NMR τ: 6.32, 5.78 (1H, 1H, d, d, J=15 Hz), 3.32 (1H, s). *Anal.* Calcd. for $C_{24}H_{24}O_3S$: C, 73.06; H, 6.64. Found: C, 72.73; H, 7.37. The starting material (III) was recovered in 20 mg.

Reaction of III with $NaNO_2$ to XIV——A mixture of 300 mg of III and 300 mg of $NaNO_2$ in 20 ml of Me_2SO was stirred at 40—60° for 5 hr. Work-up as mentioned above and chromatography over silica gel gave 160 mg of recovered starting material (III) and 67 mg of XIV as needles (hexane-CH_2Cl_2), mp 174—175°. IR ν_{max}^{KBr} cm^{-1}: 1650, 1545. NMR τ: 5.17, 5.03 (1H, 1H, d, d, J=17 Hz), 3.32 (1H, s). *Anal.* Calcd. for $C_{17}H_{17}O_3N$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.66; H, 6.69; N, 5.04.

Benzylthiocyclopropane Derivatives (XVI)——A solution of 100 mg of III and 60 mg of sodium benzylthiolate in 2 ml of Me_2SO was stirred at room temperature overnight. Work-up as mentioned above and chromatography over silica gel afforded 65 mg of XVI as needles (hexane-CH_2Cl_2), mp 81.0—81.5°. IR ν_{max}^{KBr} cm^{-1}: 1658, 1455. NMR τ: 7.57 (1H, s), 7.55, 7.35 (1H, 1H, d, d, J=16.5 Hz), 7.00 (2H, s). *Anal.* Calcd. for $C_{24}H_{26}OS$: C, 79.35; H, 7.02. Found: 78.80; H, 7.47.

Reaction of III with methylamine to the Iminomethyl Ketone (XVIII), A/B-*trans*-fused Aldehyde (XIX), and A/B-*cis*-fused Aldehyde (XX)——A mixture of III and 33% $MeNH_2$ in EtOH was heated at 190° for 6 hr

in a sealed tube. The solvent was removed *in vacuo* and the residue was chromatographed over silica gel with a mixture of hexane and $CHCl_3$ to give 5 mg of the A/B-*cis*-fused aldehyde (XX), 20 mg of the A/B-*trans*-fused aldehyde (XIX), and 80 mg of the imino ketone (XVIII). A/B-*cis*-fused aldehyde (XX), mp 127—129° (cyclohexane). IR ν_{max}^{KBr} cm^{-1}: 2860, 2710, 1715, 1675; NMR τ: 7.35, 6.90 (2H, A/B-*trans* fused aldehyde (XIX), mp 163—165° (hexane), IR ν_{max}^{KBr} cm^{-1}: 2890, 2770, 1715, 1680. NMR τ: 7.72, 6.86 (2H, AB-q, $J=16$ Hz), 0.1 (1H, s). Mass Spectrum *m/e*: 256 (M^+). Iminomethyl ketone (XVIII), mp 137.5—139.5° (petr. ether). IR ν_{max}^{KBr} cm^{-1}: 1670, 1655. NMR τ: 7.82, 6.66 (2H, AB-q, $J=16$ Hz), 6.95 (3H); *Anal.* Calcd. for $C_{18}H_{23}ON$: C, 80.25; H, 8.61; N, 5.20. Found: C, 80.58; H, 8.23; N, 5.00.

Hydrolysis of XVIII to A/B-*trans*-fused Aldehyde (XIX)——A mixture of 40 mg of XVIII in 30 ml of 2N/3 HCl was heated at 100° for 3 hr. The reaction mixture was extracted with ether, the organic layer was washed and dried, and the solvent was evaporated to leave an oil, which was chromatographed over silica gel with hexane, to afford 15 mg of a compound, which was identical with XIX

A/B-*trans*-fused Keto Acid (XXI)——To a solution of 110 mg of XIX in 4 ml of AcOH, a mixture of 130 mg of CrO_3 in AcOH was added at 0° with stirring, and the resulting mixture was stirred at 0° for 4 hr, and then the temperature allowed to rise up to room temperature. To it was added MeOH at 0° and mixture was extracted with CH_2Cl_2. The organic phase was washed, dried, and the solvent was evaporated to leave a residue, which was chromatographed over silica gel with a mixture of $CHCl_3$ and AcOEt to afford 60 mg of the keto acid (XXI), mp 233—235°. IR ν_{max}^{KBr} cm^{-1}: 3400—2400, 1715, 1655. NMR τ: 7.67, 6.90 (2H, q).

A/B-*cis*-fused Keto Acid (XXII)——Oxidation of 130 mg of XX with CrO_3 in AcOH was carried out as for XIX, and 60 mg of the *cis*-keto acid (XXII), mp 228° was obtained. IR ν_{max}^{KBr} cm^{-1}: 3200—3800, 1725, 1665. NMR τ: 7.22, 6.83 (2H, A/B-q).

A/B-*trans*-fused γ-Lactone (XXIII)——To a solution of 60 mg of XXI in MeOH 150 mg of NaH was added and the mixture was refluxed for 6 hr. To the reaction mixture was added 2N HCl to make it acidic. The mixture was extracted with AcOEt, which was washed, dried, and evaporated to leave a residue, which was chromatographed over silica gel with a mixture of AcOEt and $CHCl_3$ to provide 10 mg of XXIII as needles (petr. ether), mp 121—122°. IR ν_{max}^{KBr} cm^{-1}: 1780, 1255. NMR τ: 8.95 (6H, s), 8.00, 7.30 (2H, AB-q), 4.90 (1H, q). Mass Spectrum *m/e*: 256 (M^+).

***cis*-γ-Lactone (XXIV)**——Reduction and γ-lactonization of XXII were performed as for XXI to give the *cis*-γ-lactone (XXIV) as needles, mp 144—145°. IR ν_{max}^{KBr} cm^{-1}: 1775, 1250. NMR τ: 9.00 (3H, s), 8.58 (3H, s), 7.56, 7.40 (2H, AB-q) 4.92 (1H, q). Mass Spectrum *m/e*: 256 (M^+).

Acetolysis of III to Acetoxy Cyclopropane Ketone (XXV)——A mixture of 105 mg of III and 65 mg of AcONa in 4 ml of AcOH was stirred at 30° for 2 days. The solvent was evaporated to leave a residue, which was extracted with CH_2Cl_2. The extract was dried and evaporated to leave an oil, which was chromatographed over silica gel with $CHCl_3$ to provide 8 mg of XXV as an oil. IR ν_{max}^{film} cm^{-1}: 1750, 1685. NMR τ: 8.42 (3H, s), 7.32, 7.03 (1H, 1H, d, d, $J=17$ Hz), 5.30 (1H, s).

Hydrolysis of Acetoxy Cyclopropane Ketone (XXV) to A/B-*trans*-fused Aldehyde (XIX)——To a solution of 10 ml of 10% EtOH–EtONa, 6 mg of XIX was added and hydrolysed to give 5 mg of a compound, which was identical with the A/B-*trans*-fused aldehyde (XIX).

Reaction of III with Sodium Azide to the Cyclopropyl Azide (XXVI)——A mixture of 150 mg of III and 150 mg of NaN_3 in Me_2SO was stirred at 45—60° for 6 hr. Worked up as described before and chromatographed over silica gel with a mixture of CH_2Cl_2 and hexane to give 112 mg of XXVI as needles (MeOH), mp 102—103°. IR ν_{max}^{KBr} cm^{-1}: 2090, 1670. NMR τ: 7.40, 7.14 (1H, 1H, d, d, $J=17$ Hz), 6.67 (1H, s). *Anal.* Calcd. for $C_{17}H_{19}ON_3$: C, 72.57; H, 6.81; N, 14.94. Found: C, 73.95; H, 6.69; N, 14.60.

Decomposition of Cyclopropyl Azide (XXVI) with Acid to Aldehyde (XXVII)——To a solution of 10 mg of XXVI in 4 ml of AcOH a solution of 2 ml of AcOH containing HCl (10%) was added with stirring at room temperature. The mixture was kept stirred for 3 hr, to it water was added and extracted with CH_2Cl_2. The organic phase was washed and dried, and the solvent was evaporated to leave a residue, which was chromatographed over silica gel with a mixture of hexane and $CHCl_3$ to provide 25 mg of the aldehyde (XXVII) as needles (hexane), mp 146—147°. IR ν_{max}^{KBr} cm^{-1}: 2820, 2700, 1715, 1695. NMR τ: 7.52, 6.94 (1H, 1H, d, d, $J=15$ Hz), 3.02 (1H, t, $J=3$ Hz), 0.30 (1H, s). *Anal.* Calcd. for $C_{17}H_{18}O_2$: C, 80.21; H, 7.13. Found: C, 79.49; H, 7.06. The other product isolated was the phenol (I) (60 mg).

Catalytic Reduction of the Aldehyde (XXVII) to A/B-*trans*-fused Aldehyde (XIX) and A/B-*cis*-fused Aldehyde (XX)——A solution of 10 mg of XXVII in EtOH was hydrogenated over 5 mg of PtO_2 at atmospheric pressure for 1 hr. The catalyst was filtered off and washed with EtOH. The solvent was removed from the filtrate to leave an oil, which was chromatographed over silica gel with CH_2Cl_2 and 1 mg of A/B-*cis*-fused aldehyde (XX) and 7 mg of A/B-*trans*-fused aldehyde (XIX) were obtained.