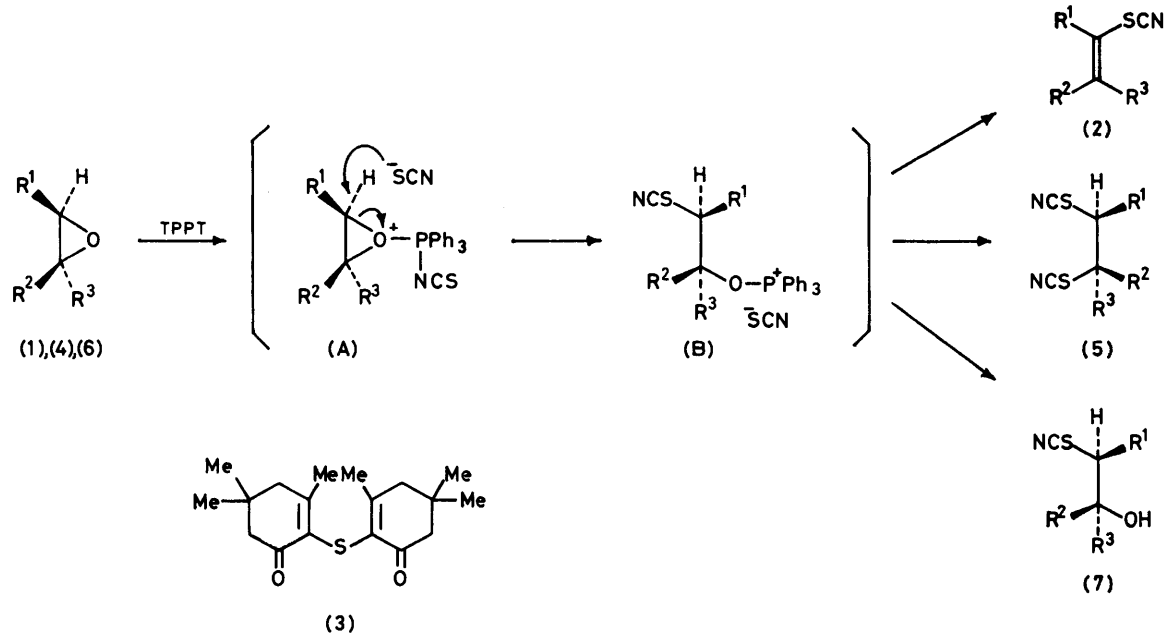
Reaction of Epoxides with Triphenylphosphine–Thiocyanogen (TPPT): Preparation of α-Thiocyanatovinyl Ketones, *vic*-Dithiocyanates, and *vic*-Dithiocyanatohydrins

By **Yasumitsu Tamura,* Tomomi Kawasaki, Hitoshi Yasuda, Noriko Gohda,** and **Yasuyuki Kita,** Faculty of Pharmaceutical Sciences, Osaka University, 133–1, Yamada-kami, Suita, Osaka, Japan

A number of epoxides smoothly react with TPPT under mild conditions to give α-thiocyanatovinyl ketones, *vic*-dithiocyanates, or *vic*-thiocyanatohydrins, depending on the structures of the epoxides used. The reactions proceed site- and stereo-specifically, to give α-thiocyanatovinyl ketones from αβ-epoxyketones, *threo*-dithiocyanate from *trans*-epoxide, *erythro*-dithiocyanate from *cis*-epoxide, and *vic*-thiocyanatohydrins from 1,1-disubstituted or fused epoxides, respectively. A possible mechanism for these reactions is put forward.

In a preceding communication,[1] we showed that the ring-opening thiocyanation of αβ-epoxyketones (1) using the combined reagent triphenylphosphine–thiocyanogen (TPPT) [2] was a useful method for the synthesis of α-thiocyanatovinyl ketones (2). We have now found that the treatment of various epoxides [(4) and (6)] with TPPT causes a novel ring-opening reaction to give *vic*-dithiocyanates (5) or *vic*-thiocyanatohydrins (7) depending on the structures of the epoxides used. This paper describes these interesting reactions of epoxides with TPPT, the stereochemistry of the products, and the reaction mechanism, including a full account of the work mentioned in the previous communication.[1]



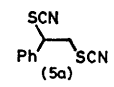
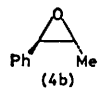
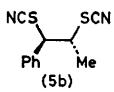
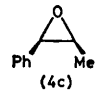
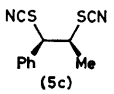
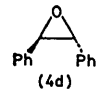
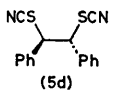
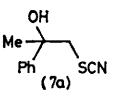
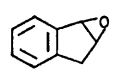
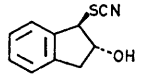
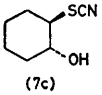
RESULTS

Treatment of the αβ-epoxyketones (1a—f) with TPPT in dry methylene chloride under argon at −40 °C for several hours gave good yields of the α-thiocyanatovinyl ketones (2a—f). An alternative preparation of (2) by the reaction of (1) with KSCN or NH_4SCN was examined, since α-substituted αβ-unsaturated ketones are generally prepared by the reaction of (1) with the corresponding nucleophilic substrates.[3] This route, however, is not a good one for the synthesis of (2). For example, the reaction of KSCN with 2,3-epoxy-3,5,5-trimethylcyclohexanone (1c) in methanol–water gave a 53% yield of bis-(2,4,4-trimethyl-6-oxocyclohex-1-enyl) sulphide (3), instead of the α-thiocyanatovinyl ketone (2c), and that of NH_4SCN gave a low yield of (2c) together with several unidentified products. The importance of (2) as a synthetic intermediate has already been demonstrated briefly in the previous communication.[1]

In the case of monosubstituted or 1,2-disubstituted epoxides (4a—d), the reaction proceeds through a site-specific thiocyanation followed by substitution with the SCN^- anion to give the corresponding *vic*-dithiocyanates (5a—d) in moderate yields (runs 1—4). As can be seen in the Table, stereospecific formation of *threo*-(5b) from *trans*-(4b) and *erythro*-(5c) from *cis*-(4c) was observed. Guy *et al.* have prepared [4] a mixture of (5b) and (5c) by the addition of thiocyanogen to 1-phenylprop-1-ene, and assigned their stereochemistry without separation of the isomers, considering the ^1H n.m.r. data of the related compounds. The n.m.r. data of both (5b) and (5c) are in good accordance with

TABLE

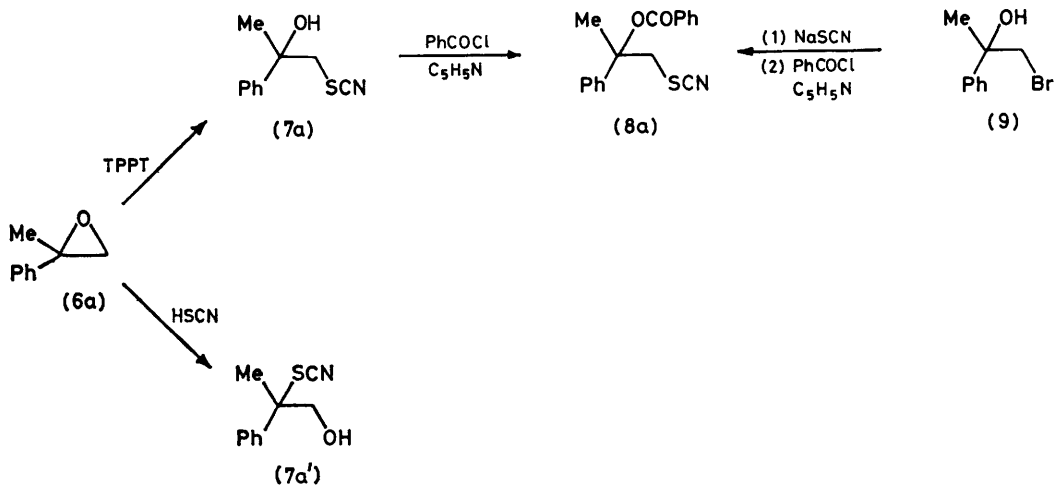
Results of thiocyanation reactions with TPPT

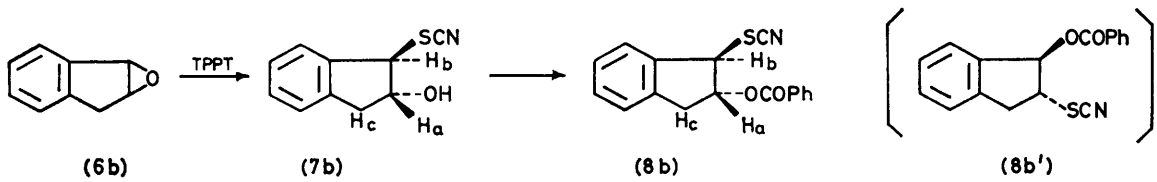
Run	Starting compound	Product	Yield * (%)	M.p. (°C) (solvent) [b.p. (°C) (mmHg)]	Lit. m.p. or b.p. (°C)	$\nu_{max.}$/cm^{-1} ($CHCl_3$)	δ (in $CDCl_3$) (J/Hz)
1	 (4a)	 (5a)	50	101.5—102.5 (C_6H_6–ether)	101—102 [4]	2 170	7.5—7.1 (5 H, m, aromatic); J 9, 10, H-1; 3.78 (1 H, dd, J 9, 10, H-2); 3.62 (1 H, dd, J 10, 14, H-2)
2	 (4b)	 (5b)	21	63.5—64.5 (n-hexane)		2 160	7.40 (5 H, s, aromatic); 4.57 (1 H, d, J 9, H-2); 4.1—3.6 (1 H, m, H-1); 1.53 (3 H, d, J 6.7, Me)
3	 (4c)	 (5c)	32	103—104 (n-hexane–pentane)		2 160	7.40 (5 H, s, aromatic); 4.41 (1 H, d, J 9.5, H-2); 4.1—3.6 (1 H, m, H-1); 1.88 (3 H, d, J 6.6, Me)
4	 (4d)	 (5d)	34	159.5—161 ($CHCl_3$)		2 170	7.6—6.9 (10 H, m, aromatic); 4.95 (2 H, s, H-1 and H-2)
5	 (6a)	 (7a)	42	84—90		3 420; 2 150	8.6—8.2 (1 H, br s, OH); 7.34 (5 H, s, aromatic); 4.60 (2 H, s, H-2); 1.81 (3 H, s, Me)
6	 (6b)	 (7b)	69	Oil		3 450; 2 160	7.45—7.1 (4 H, m, aromatic); 4.8—4.45 (2 H, m, H-2 and H-3); 3.8—3.3 (1 H, br s, OH); 3.34 (1 H, dd, J 6.4, 16.6, H-1); 2.85 (1 H, dd, J 3.8, 16.6, H-1)
7	 (6c)	 (7c)	43	[113—118 (0.18)]	148—152(7) [8]	3 570; 2 140	3.8—3.4 (1 H, m, H-1); 3.1—2.6 (2 H, m, H-2 and OH); 2.5—1.1 (8 H, m, H-3, H-6)

* Chromatographed or distilled yields are given.

the values reported by Guy *et al.*[5] The stereochemistry of (5) closely resembles that of *vic*-dihalides obtained by the reaction of epoxides and triphenylphosphine dihalides.[6]

We next examined the reaction of the 1,1-disubstituted and fused epoxides (6a—c). Treatment of these epoxides with TPPT under the same conditions as mentioned for the reaction of (1) or (4) with TPPT, gave *trans-vic*-thiocyanatohydrins (7a—c) (runs 5—7) without formation of the *vic*-dithiocyanates (5). The structure of the thiocyanatohydrin obtained from (6a) was tentatively assigned as (7a)



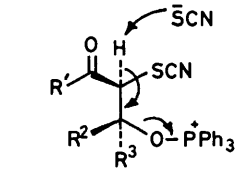


[not as (7a')] on the basis of the spectral evidence, and finally confirmed by the direct comparison of the benzoate (8a) with an authentic specimen prepared alternatively from the known bromohydrin (9) as shown.[7] The SCN^- anion of TPPT attacks the less hindered site of (6a) to give the anti-Markownikoff product (7a), in marked contrast with the behaviour in the reaction of (6a) and thiocyanic acid, which affords the Markownikoff product (7a').[8]

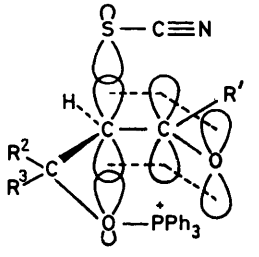
The introduction of the thiocyanato-group to the benzyl position of (6b) was confirmed by the comparison of the n.m.r. data of (7b) with those of its benzoate (8b). Thus the absorption of H_a to the hydroxy-group shifted to lower field (from δ 4.8—4.45 to 5.87—5.7) on benzoylation, and appears as a multiplet due to vicinal coupling with H_b and H_c, and H_b of the thiocyanato-group (shifting from δ 4.8—4.45 to 4.88 on benzoylation) appears as a doublet due to the vicinal coupling with H_a. If the benzoate had the isomeric structure (8b'), the α-proton of the hydroxy-group would appear as a doublet and that of the thiocyanato-group as a multiplet.

DISCUSSION

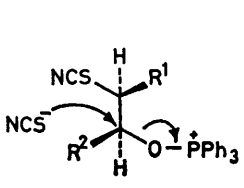
For the mechanism of the above reactions it is suggested that the epoxide oxygen combines with the electrophilic phosphorus atom of TPPT to give an intermediate (A), which undergoes a nucleophilic ring-opening reaction by thiocyanato-anion to give the β-thiocyanatoalkoxyphosphonium salt intermediate (B) by analogy with the mechanism [9] proposed in the reaction of epoxide with trimethylsilyl trifluoromethanesulphonate or halogenodimethylsulphonium halide in the presence of the base. A similar phosphonium salt intermediate (B) has already been proposed in the reaction of TPPT with some nucleophiles, *e.g.* alcohols,[10] carboxylic acids,[11] and organomethallic compounds.[12]



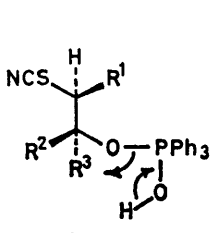
(i)



(ii)



(iii)



(iv)

The intermediate (B) derived from αβ-epoxyketones (1) undergoes a facile α-proton abstraction adjacent to the carbonyl group with the SCN^- anion followed by a spontaneous elimination of $Ph_3P{=}O$ to give the α-thiocyanatovinyl ketones (2) (i). The site-specific attack of the SCN^- anion on the α-site of (A) is explained by the stabilisation of the adjacent carbonyl group. Thus, the orbitals composed of the SCN^- anion, the epoxide oxygen as the leaving group, and the α-carbon, overlap with the π-bond of the carbonyl as shown in (ii). The intermediate (B), obtained by the site-specific attack of the SCN^- anion on the less hindered site of the intermediate (A), derived from monosubstituted or 1,2-disubstituted epoxides (4), causes nucleophilic substitution of the SCN^- anion on the carbon adjacent to the oxygen atom of the $-O-\overset{+}{P}Ph_3$ group with the elimination of $Ph_3P{=}O$ (Arbzov-type reaction [10,11,13]), giving *vic*-dithiocyanates (5) (iii). When the substitution of SCN^- anion is retarded by steric hindrance, as observed in the intermediate (B) derived from 1,1-disubstituted or fused epoxides (6), the hydrolysed product (7) of the P–O bond is produced (iv).

The S_N2 mechanism is proposed for the formation of (B) from (A) by consideration of the above results, since both the α-site attack of nucleophiles on the αβ-epoxyketones [3] and a less-hindered-site attack of the nucleophiles on the epoxides [14] are well documented in the S_N2 ring-opening reactions of epoxides.

EXPERIMENTAL

I.r. absorption spectra were recorded on a Shimazu-IR-27G spectrophotometer, and n.m.r. spectra on a Hitachi R-20A spectrometer. Chemical shifts are reported in p.p.m. (δ) relative to $SiMe_4$. Mass spectra were obtained with a Hitachi RMU-6M instrument with a direct-inlet system operating at 70 eV. Column chromatography was carried out on Merck silica gel 60.

General Procedures for the Preparation of αβ-Epoxyketones (1a—f).—The following procedure is typical. To a stirred solution of the αβ-unsaturated ketone (10 mmol) in methanol (50 ml) containing 30% aqueous H_2O_2 (1.2 equiv.) at −10 to 0 °C, sodium hydroxide (6N, 4 ml) was added dropwise and the reaction mixture was monitored by t.l.c. Stirring was continued at the same temperature until the starting material was consumed (several hours); in some cases the temperature was allowed to rise to 20 °C. The mixture was then poured into cold water and extracted with $CHCl_3$ (2 × 10 ml). The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to give the residue, which was distilled or recrystallised from an adequate solvent to give the αβ-epoxyketones (1a—f).

2,3-*Epoxycyclohexanone* (1a).—This was prepared from cyclohex-2-enone, b.p. 78—80 °C at 10 mmHg (lit., 75—78 °C at 10 mmHg [15] and 76—78 °C at 15 mmHg [16]).

2,3-*Epoxy*-3-*methylcyclohexanone* (1b).—This was prepared from 3-methylcyclohex-2-enone, b.p. 71—73 °C at 9 mmHg (lit., 85 °C at 15 mmHg [17] and 80—82 °C at 12.4 mmHg [18]).

2,3-*Epoxy*-3,5,5-*trimethylcyclohexanone* (1c).—This was prepared from 3,5,5-trimethylcyclohex-2-enone, b.p. 75—80 °C at 8 mmHg (lit., 70—73 °C at 5 mmHg [19] and 80—84 °C at 10 mmHg [20]).

2,3-*Epoxycyclopentanone* (1d).—This was prepared from cyclopent-2-enone, b.p. 71 °C at 17 mmHg (lit.,[21] b.p. is not reported).

4,5-*Epoxy*-17β-*acetoxyandrostan*-3-*one* (1e).—This was

prepared from 17β-acetoxyandrost-4-en-3-one, m.p. 132—133 °C (from methanol), *m/e* 345 (M^+). Although this product may have been a mixture of *cis*-(1e) and *trans*-(1e) from a comparison of the reported m.p.s [lit.,[22] *cis*-(1e), 169.5—171.5 °C and *trans*-(1e), 160.5—161.5 °C], it was used for the next reaction without separation of the isomers.

3,4-*Epoxypentan*-2-*one* (1f).—This was prepared from pent-3-en-2-one, b.p. 36—37 °C at 10 mmHg; $\nu_{max.}$ ($CHCl_3$) 1 700 cm^{-1}; *m/e* 100 (M^+).

Genral Procedures for the Preparation of Epoxides (4a—d) *and* (6a—c).—The following two procedures [methods (*A*) and (*B*)] are typical. (*A*) The olefin (10 mmol) was added to a stirred and ice-cooled solution of 85% *m*-chloroperbenzoic acid (12 mmol) in CH_2Cl_2 (50 ml). The mixture was allowed to stand at room temperature for 4 h. The solution was washed with 5% NaOH (20 ml) and saturated aqueous NaCl (30 ml), dried over $MgSO_4$, and concentrated under reduced pressure to give the corresponding epoxide.

(*B*) [7,23] A suspension of olefin (10 mmol), *N*-bromosuccinimide (NBS) (10 mmol), and water (30 ml) (in some cases, dioxan or dimethyl sulphoxide was added) was stirred vigorously at room temperature until the solid NBS disappeared (*ca.* 30 min). The corresponding bromohydrin layer was separated and the aqueous layer was extracted with $CHCl_3$. The combined extract was concentrated under reduced pressure to give the crude bromohydrin, which was treated with potassium hydroxide (13N, 1.5 ml). Extraction with ether, concentration, and distillation under reduced pressure gave the corresponding epoxide.

1,2-*Epoxy*-1-*phenylethane* (4a).—This compound is commercially available, b.p. 88 °C at 15 mmHg.

trans-1,2-*Epoxy*-1-*phenylpropane* (4b).—This was prepared by a modification of the Guss method [method (*B*)],[7] b.p. 95—100 °C at 30 mmHg (lit.,[24] 82 °C at 10 mmHg).

cis-1,2-*Epoxy*-1-*phenylpropane* (4c).—This was prepared by a modification of the Kano method [method (*B*)],[24] and also prepared by another method,[25] b.p. 80—82 °C at 10 mmHg (lit.,[25] 80 °C at 10 mmHg).

trans-1,2-*Epoxy*-1,2-*diphenylethane* (4d).—This was prepared by method (*A*), m.p. 69—70 °C (from n-hexane) (lit.,[26] 69 °C).

1,2-*Epoxy*-2-*phenylpropane* (6a).—This was prepared by a modification of the Guss method [method *B*],[7] b.p. 40—45 °C at 0.1 mmHg (lit.,[27] 62 °C at 2.3 mmHg).

1,2-*Epoxyindane* (6b).—This was prepared by a modification of the Guss method [method (*B*)],[7] b.p. 150 °C at 13 mmHg (bath temperature) (lit. 105—108 °C at 8 mmHg [28] and 66—67 °C at 25 mmHg [29]).

1,2-*Epoxycyclohexane* (6c).—This compound is commercially available, b.p. 132 °C.

Reaction of 2,3-*Epoxy*-3,5,5-*trimethylcyclohexanone* (1c) *with* KSCN.—A solution of (1c) (2 mmol) and KSCN (3 mmol) in MeOH–H_2O (1 : 1, 2 ml) was allowed to stand at room temperature for 1 day. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using chloroform as a solvent to give the sulphide (3) (163 mg, 53%). Recrystallisation from ether–light petroleum gave an analytical sample, m.p. 90—91 °C (Found: C, 70.4; H, 8.55. Calc. for $C_{18}H_{26}O_2S$: C, 70.55; H, 8.55%); $\nu_{max.}$ ($CHCl_3$) 1 665 and 1 590 cm^{-1}; δ ($CDCl_3$) 2.35 (4 H, s, C-4 or C-6), 2.31 (6 H, s, 3-Me), 2.23 (4 H, s, C-4 or C-6), and 1.00 (12 H, s, 5-Me_2); *m/e* 306 (M^+).

General Procedure for Thiocyanation of Epoxides (1a—f), (4a—d), *and* (6a—c).—The following procedure is typical. A solution of the epoxide (1), (4), or (6) (1 mmol) in dry CH_2Cl_2 (6 ml) was added dropwise to a stirred solution of freshly prepared TPPT (*ca.* 1.2 mmol) in dry CH_2Cl_2 (10 ml) at −40 °C under argon. The mixture was stirred for the requisite period (*ca.* 3—4 h) under the same conditions, allowed to warm slowly to room temperature, stirred overnight, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using chloroform as eluant to give the vinyl thiocyanate (2), *vic*-dithiocyanate (5), or *vic*-thiocyanatohydrin (7) depending on the epoxide used. The yields, i.r., n.m.r. and mass spectral data of the products (2a—f) were given in the previous communication [1] and those of the products (5a—d) and (7a—c) are listed in the Table.

2-*Thiocyanatocyclohex*-2-*enone* (2a).—This was prepared from 2,3-epoxycyclohexenone (1a) and TPPT (Found: C, 54.9; H, 4.55; N, 9.3. Calc. for C_7H_7NOS: C, 54.90; H, 4.61; N, 9.15%).

Spectroscopic data of the compounds (2b—f) were fully consistent with the proposed structures, while satisfactory analytical data could not be obtained because of their instability upon recrystallisation or distillation. Compounds (5a) and (7c) were identical with the authentic specimen, as determined by comparison of their melting or boiling points and spectral data.

threo-1,2-*Dithiocyanato*-1-*phenylpropene* (5b).—This was prepared from *trans*-1,2-epoxy-1-phenylpropane (4b) and TPPT (Found: C, 56.4; H, 4.2; N, 11.85. Calc. for $C_{11}H_{10}N_2S_2$: C, 56.40; H, 4.27; N, 11.96%).

erythro-1,2-*Dithiocyanato*-1-*phenylpropane* (5c).—This was prepared from *cis*-1,2-epoxy-1-phenylpropane (4c) and TPPT (Found: C, 56.3; H, 4.1; N, 11.9. Calc. for $C_{11}H_{10}N_2S_2$: C, 56.40; H, 4.27; N, 11.96%).

1,2-*Diphenyl*-1,2-*dithiocyanatoethane* (5d).—This was prepared from *trans*-1,2-epoxy-1,2-diphenylethane (4d) and TPPT (Found: C, 64.6; H, 4.05; N, 9.45. Calc. for $C_{16}H_{12}N_2S_2$: C, 64.83; H, 4.08; N, 9.45%).

The unknown compounds (7a) and (7b) were confirmed by the conversion into the benzoates (8a) and (8b).

Benzoylation of (7a).—A solution of 2-hyroxy-2-phenyl-1-thiocyanatopropane (7a) (1.5 mmol) in dry CH_2Cl_2 (6 ml) was added to an ice-cooled solution of benzoyl chloride (1.5 mmol) and triethylamine (1.5 mmol) in dry CH_2Cl_2 (6 ml). The mixture was allowed to stand at room temperature for 3 h, diluted with $CHCl_3$ (30 ml), and washed with dilute HCl, saturated aqueous $NaHCO_3$ (10 ml), and saturated aqueous NaCl (5 ml). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2 as eluant to give the benzoate (8a) (67%). Recrystallisation from methanol gave an analytical sample, m.p. 125.5—126 °C (Found: C, 68.45; H, 4.9; N, 4.8. Calc. for $C_{17}H_{15}NO_2S$: C, 68.69; H, 5.01; N, 4.71%); $\nu_{max.}$ ($CHCl_3$) 2 150 and 1 695 cm^{-1}; δ ($CDCl_3$) 7.8—6.9 (10 H, m, aromatic), 4.60 (1 H, d, *J* 11 Hz, 3-H), 4.50 (1 H, d, *J* 11 Hz, 3-H), and 2.10 (3 H, s, Me). This compound was identical with a sample prepared by the thiocyanation of the known bromohydrin (9) with NaSCN followed by benzoylation.

Benzoylation of (7b).—The benzoate (8b) (73%) was similarly prepared from 2-hydroxy-1-thiocyanatoindane (7b) (1.2 mmol), benzoyl chloride (1.7 mmol), and triethylamine (1.5 mmol) in dry CH_2Cl_2 (10 ml). Recrystallisation from $CHCl_3$–light petroleum gave an analytical sample, m.p. 50—51 °C (Found: C, 69.1; H, 4.35; N, 4.75. Calc. for $C_{16}H_{13}NO_2S$: C, 69.12; H, 4.45; N, 4.74%); $\nu_{max.}$

($CHCl_3$) 2 140 and 1 715 cm^{-1}; δ ($CDCl_3$) 8.5—7.5 (2 H, m, aromatic), 7.7—7.25 (7 H, m, aromatic), 5.87—5.7 (1 H, m, 2-H), 4.88 (1 H, d, *J* 2.6 Hz, 3-H), 3.73 (1 H, dd, *J* 7, 16.6 Hz, 1-H), and 3.16 (1 H, dd, *J* 2.6, 16.6 Hz, 1-H).

[0/1209 *Received*, 31*st July*, 1980]

REFERENCES

[1] Y. Tamura, T. Kawasaki, N. Gohda, and Y. Kita, *Tetrahedron Lett.*, 1979, 1129.

[2] Y. Tamura, M. Adachi, T. Kawasaki, H. Yasuda, and Y. Kita, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1132.

[3] Some nucleophiles such as RO^-, RS^-, R_2N^-, X^-, and CN^- have been reported: M. A. Tobias, J. C. Strong, and R. P. Napier, *J. Org. Chem.*, 1970, **35**, 1709; A. G. Schults, R. D. Lucci, W. Y. Fu, M. H. Berger, J. Erhardt, and W. K. Hagemann, *J. Am. Chem. Soc.*, 1978, **100**, 2150; L. D. Markley, *J. Org. Chem.*, 1973, **38**, 3417; A. G. Schultz and D. S. Kashdan, *ibid.*, 1973, **38**, 3814; M. Tomoeda, M. Inuzuka, T. Furuta, M. Shinozuka, and T. Takahashi, *Tetrahedron*, 1968, **24**, 959; A. G. Schultz, *J. Org. Chem.*, 1974, **39**, 3185; S. Kurozumi, T. Toru, T. Tanaka, M. Kobayashi, S. Miura, and S. Ishimoto, *Tetrahedron Lett.*, 1976, 4091; S. Kurozumi, T. Toru, M. Kobayashi, and Y. Hashimoto, *Synth. Commun.*, 1977, **7**, 169; A. G. Schultz, W. Y. Fu, R. D. Lucci, B. G. Kurr, K. M. Lo, and M. Boxer, *J. Am. Chem. Soc.*; 1978, **100**, 2140; V. N. Kovaleva, M. S. Mindel, N. P. Eley'yanov, and N. S. Kozlov, *Dokl. Adad. Nauk B. SSR*, 1970, 626 [*Chem. Abstr.*, 1970, **73**, 76720n]; V. N. Kovaleva, N. P. Elel'yanov, and N. S. Kozlov, *ibid.*, 1971, 617 [*Chem. Abstr.*, 1971, **75**, 118009m]; I. G. Tishchenko and G. I. Polozov, *Vestn. Beloruss. Un-ta., ser.* 2, 1975, 21 [*Chem. Abstr.*, 1976, **84**, 4537n]; K. Ponsold and G. Schubert, *Z. Chem.*, 1976, **16**, 438 [*Chem. Abstr.*, 1977, **86**, 106871a]; E. Campaigne and R. A. Forsch, *J. Org. Chem.*, 1978, **43**, 1044.

[4] R. G. Guy, 'The Chemistry of Cyanates and their Thio Derivatives,' Part 2, Chapter 18, ed. S. Patai, John Wiley and Son, New York, 1979, p. 859; R. Bonnet, R. G. Guy, and D. Lanigan, *Tetrahedron*, 1976, **32**, 2439; R. J. Maxwell, L. S. Silbert, and J. R. Russel, *J. Org. Chem.*, 1977, **42**, 1510; R. G. Guy and J. J. Thompson, *Tetrahedron*, 1978, **34**, 541.

[5] We thank Professor R. G. Guy for his kind information on the ^1H n.m.r. assignment of a mixture of (5b) and (5c).

[6] P. E. Sonnet and J. E. Oliver, *J. Org. Chem.*, 1979, **41**, 3279; A. G. Anderson, jun., and F. J. Freenor, *ibid.*, 1972, **37**, 626.

[7] C. O. Guss and R. Rosenthal, *J. Am. Chem. Soc.*, 1955, **77**, 2549.

[8] E. F. Van Tamelen, *J. Am. Chem. Soc.*, 1951, **73**, 3444; K. Takeda and T. Kaneko, *Chem. Pharm. Bull.*, 1960, **8**, 468.

[9] Conversion of epoxides into α-halogenoketones with halogenodimethylsulphonium halides in the presence of triethylamine; G. A. Olah, Y. D. Vanker, and M. Arvanaghi, *Tetrahedron Lett.*, 1979, 3653. Conversion of epoxides into allylic alcohols with trimethylsilyl trifluoromethanesulphonate and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU); S. Murata, M. Suzuki, and R. Noyori, *J. Am. Chem. Soc.*, 1979, **101**, 2738.

[10] Y. Tamura, T. Kawasaki, M. Adachi, M. Tanio, and Y. Kita, *Tetrahedron Lett.*, 1977, 4417.

[11] Y. Tamura, T. Kawasaki, M. Tanio, and Y. Kita, *Chem. Ind. (London)*, 1978, 806.

[12] Y. Tamura, T. Kawasaki, M. Adachi, and Y. Kita, *Synthesis*, 1979, 887.

[13] J. Burski, J. Kieszkowski, J. M. Michalski, M. Pakulski, and A. Skowronska, *J. Chem. Soc., Chem. Commun.*, 1978, 940.

[14] E. S. Gould, 'Mechanism and Structure in Organic Chemistry,' Holt, Reinhart, and Winston, New York, 1959, p. 284.

[15] H. O. House and R. L. Wasson, *J. Am. Chem. Soc.*, 1957, **79**, 1488.

[16] N. C. Yang and R. A. Finnegan, *J. Am. Chem. Soc.*, 1958, **80**, 5845.

[17] G. Magnusson and S. Thoren, *J. Org. Chem.*, 1973, **38**, 1380.

[18] E. Campaigne and R. A. Forsch, *J. Org. Chem.*, 1978, **43**, 1044.

[19] R. L. Wasson and H. O. House, *Org. Synth.*, 1957, **37**, 58; M. T. Langin-Lanteri and J. Huet, *Synthesis*, 1976, 541.

[20] G. A. MacAlpine and J. Warkentin, *Can. J. Chem.*, 1978, **56**, 308.

[21] G. A. Markos and W. Reusch, *J. Am. Chem. Soc.*, 1967, **89**, 3363; H. O. House and R. L. Wasson, *J. Am. Chem. Soc.*, 1957, **79**, 1488.

[22] T. Koda and S. Kawashima, *Chem. Pharm. Bull.*, 1972, **20**, 21.

[23] D. Van Ende and A. Krief, *Tetrahedron Lett.*, 1975, 2709.

[24] S. Kano, T. Yokomatsu, and S. Shibuya, *J. Chem. Soc., Chem. Commun.*, 1978, 785.

[25] F. Fischer, *Chem. Ber.*, 1961, **94**, 893.

[26] B. M. Lynch and K. H. Pausacher, *J. Chem. Soc.*, 1955, 1525.

[27] E. L. Elliel and M. N. Rerick, *J. Am. Chem. Soc.*, 1960, **82**, 1362.

[28] J. Sam and T. C. Snapp, *J. Pharm. Sci.*, 1965, **54**, 756 [*Chem. Abstr.*, 1965, **63**, 6937f].

[29] H. E. Audier, J. F. Dupin, and J. Jullien, *Bull. Soc. Chim. Fr.*, 1968, 3850.