NOTES

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Studies on Reactions of Isoprenoids. VIII.[1] Reactions of Sulfur Dichloride with Certain Cyclic-Acyclic 1,5-Dienes

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Although the reactions of sulfur dichloride (SD) with various olefins have been well investigated,[2-7] there seems to have been no study on the reactions of SD with cyclic-acyclic polyolefins. This paper deals with the reactions of SD with 1,5-cyclic-acyclic dienes I-III.[8]

The product from 4-cyano-1-(4-methyl-3-pentenyl)-1,4-cyclohexadiene (I) and SD is a viscous oil, the structure of which was assigned as 3-(1-*p*-cyanophenyl-4-methylene)pentyl sulfide IV on the basis of analytical and spectral data: IV gave a negative Beilstein- and a positive sulfur test[9] and analysis showed a composition of $C_{26}H_{28}N_2S$. IR spectrum (liquid film) exhibited strong bands at 2265 ($C{\equiv}N$), 1605 and 830 (1,4-disubstituted phenyl), and 1650 and 895 ($C{=}CH_2$) cm^{-1}. UV spectrum had a $\lambda_{\max}^{\mathrm{MeOH}}$ 231 mμ (log ε 4.37) which is very similar to that of *p*-tolunitrile, $\lambda_{\max}^{\mathrm{H_2O}}$ 234 mμ (log ε 4.2),[10] suggesting the presence of a *p*-alkylcyanobenzene moiety. NMR spectrum had signals at τ 2.38 and 2.68 (*ca.* 8 H, AB-q, $J=9.0$ Hz, phenyl protons), 4.92 and 5.03 (*ca.* 4H, each broad s, $C{=}CH_2$), 6.80—8.25 (6H, broad complex m allylic methylene protons and S–CH), and 8.33 and 8.49 (*ca.* 10H, each s, allylic methyl- and saturated methylene protons). In the mass spectrum at 70 eV, shown in Fig. la, the molecular ion peak could not be observed, as was also the case in the spectrum at 15 eV. However, appearance of ion peaks at *m/e* 269 (0.1%, $C_{17}H_{20}NS^+$) and 268 (0.08%, $C_{17}H_{19}NS^+$) excluded the possibility of a monomeric cyclic sulfide structure in accordance with analytical data. These ions could be formed by the characteristic α-cleavage of a dialkyl sulfide molecule.[11] The dimeric unsaturated sulfide structure was supported by ion peaks at *m/e* 154 (10%, $CH_2{=}C(CH_3){-}CH(\dot{C}H_2){-}\overset{+}{S}{=}CH{-}C(CH_3){=}CH_2$), 153 (8.5%, $CH_2{=}C(CH_3){-}C({=}CH_2){-}\overset{+}{S}{=}CH{-}C(CH_3){=}CH_2$), and 141 (10.5%, $CH_2{=}C(CH_3){-}CH_2{-}\overset{+}{S}{=}CH{-}C(CH_3){=}CH_2$). The other main fragmentation resulted from the cleavage of a sulfur-carbon bond to give ion peaks at *m/e* 217 (10%, $C_{13}H_{15}N\overset{+\cdot}{S}$), 215 (12%, $C_{13}H_{13}N\overset{+\cdot}{S}$), 213 (24%, $C_{13}H_{11}N\overset{+\cdot}{S}$), 186 (14%, $C_{13}H_{16}N^+$), 185 (48%, $C_{13}H_{15}N^{+\cdot}$). Sulfur-carbon bond rupture after isomerization of the side-chain double bond and loss of methyl and isopropyl group afforded ion peaks at *m/e* 200 (14%), 168 (22%), 174 (13%), 172 (24%), 142 (10%), and 140 (12%).[12] Appearance of ion peaks at *m/e* 117 (100%) and 116 (43%) in abundance supported structure IV involving a benzene ring but not a cyclic sulfide structure, since these fragmentations are typical for alkyl-

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[1] Part VII of this series: T. Sasaki, S. Eguchi, and T. Ishii, *J. Org. Chme.*, **45**, 249 (1970), in press.

[2] a) J. R. Nooi and G. J. Huijben, *J. Appl. Chem.*, **18**, 84 (1968); b) R. A. Grimm, *J. Amer. Oil Chem. Soc.*, **44**, 567 (1967).

[3] H. J. Backer and J. Strating, *Rec. Trav. Chim. Paya Bas*, **54**, 52 (1935).

[4] F. Lautenschlaeger, *J. Org. Chem.*, **33**, 2620 (1968).

[5] F. Lautenschlaeger, *ibid.*, **33**, 2627(1968) and references cited therein.

[6] F. Lautenschlaeger, *ibid.*, **31**, 1679 (1966).

[7] E. J. Corey and E. Block, *ibid.*, **31**, 1663 (1966).

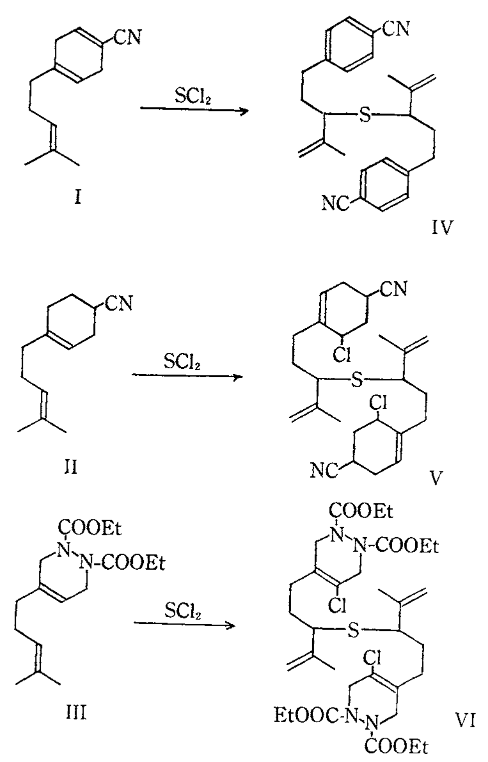
[8] T. Sasaki, S. Eguchi and T. Ishii, *ibid.*, **34**, 3749 (1969).

[9] R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley & Sons, Inc., New York (1956), pp. 57—62.

[10] L. Doub and J. M. Vandenbelt, *J. Amer. Chem. Soc.*, **69**, 2715 (1947).

[11] a) H. Budzikiewicz, C. Djerassi and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco (1967), pp. 276—296; b) J. H. Beynon, R. A. Saunders and A. E. Williams "The Mass Spectra of Organic Molecules," Elsevier Publishing Co., New York, N. Y. (1968), pp. 252—373

[12] For isomerizations before ruptures of terpene molecules in mass spectra, see D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966).



benzene derivatives.[13] All these analytical and spectral data led us to conclude that the product has the unsaturated symmetrical dialkyl sulfide sturcture IV.

The product from 4-cyano-1-(4-methyl-3-pentenyl)cyclohexene II and SD was also an oil, and its structure was assigned as 3-[1-(6'-chloro-4'-cyanocyclohex-1'-enyl)-4-methylene]pentyl sulfide (V) from analytical and spectral data. V had a composition of $C_{26}H_{34}N_2SCl_2$ from analysis and gave a positive Beilstein- and sulfur test.[9] IR spectrum (liquid film) exhibited strong bands at 2275 (saturated alkyl nitrile), 1645 (C=C), and 892 (C=CH$_2$) cm^{-1}. NMR spectrum showed signals at τ 4.55 (2 H, broad s, cyclohexenyl vinyl proton),[14] 5.08 (4H, broad s, C=CH$_2$), 5.45—7.10 (*ca.* 4H, broad complex m, -CHCl- and -CH-S-), 7.30—8.50 (*ca.* 24H, complex m, allylic methyl-, methylene- and methine protons). The mass spectrum at 70 eV is shown in Fig. 1b. The ion peak at *m/e* 255 ($C_{13}H_{17}\overset{+\cdot}{N}SCl$) corresponds to a fragmentation involving a sulfur-carbon bond fission, followed by a hydrogen abstraction.[11] In the other fragmentations, the most characteristic feature is the loss of hydrogen chloride to give ion peaks at *m/e* 219 (18%, $C_{13}H_{16}\overset{+\cdot}{NS}$) and 218 (100%, $C_{13}H_{15}\overset{+}{NS}$). Appearance of ion peaks at *m/e* 154 (2%), 153 (6%), 141 (2%), as well as at 117 (62.5%, $C_7H_7\overset{+\cdot}{N}$) as in the spectrum of IV, supported the unsaturated symmetrical dialkyl sulfide structure V. The spectrum at 15 eV was very simple, having ion peaks originating from a sulfur-carbon bond fission, at *m/e* 219, 218, 204, 186 and 185.

The reaction of 1,2-diethoxycarbonyl-4-(4-methyl-3-pentenyl)-3,6-dihydropyridazine III with SD also gave dimeric sulfide VI. A composition of $C_{32}H_{48}N_4O_8SCl_2$ was indicated by analysis, and by the positive Beilstein and sulfur tests.[9] IR spectrum (liquid film) showed bands at 1710 (C=O), 1650 (C=C) and 898 (C=CH$_2$) cm^{-1}, and NMR spectrum showed signals at τ 5.08

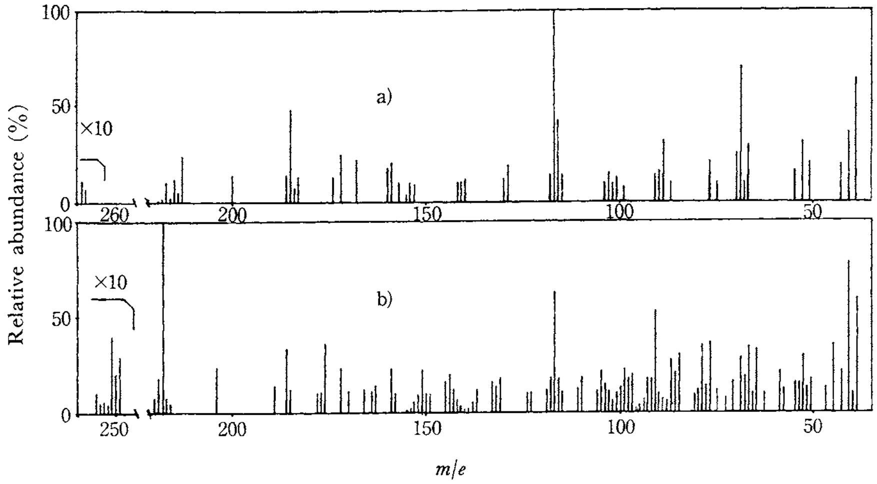


Fig. 1. Mass spectra of IV (a) and V (b) at 70 eV.

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[13] For example, see Ref. 11b, pp. 122—131.

[14] This chemical shift is very similar to that of a cyclohexenyl vinyl proton of II: see Ref. 8.

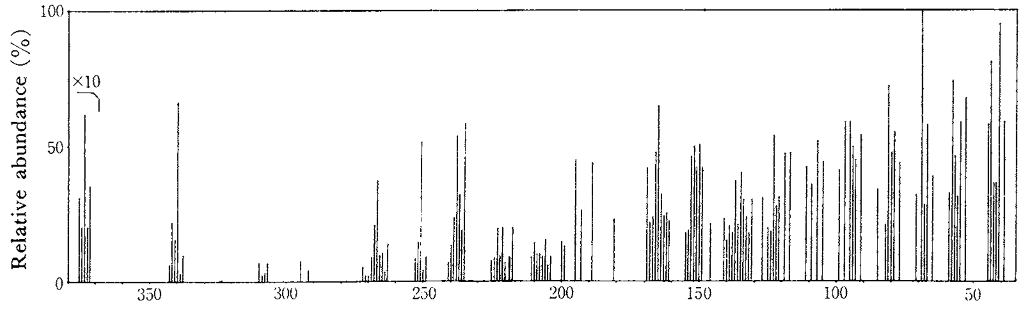

Fig. 2. Mass spectrum of VI at 70 eV.

(4H, broad and unsymmetrical s, C=CH$_2$), 5.50—7.20 (*ca.* 18H, m, N–CH$_2$–C=C, –CH–S–, and COOCH$_2$C$\underline{H}_3$*1), 7.45—8.45 (14H, m, allylic methylene-, methyl- and methylene protons of the side-chain), and 8.70 (12H, t, J=6.5 Hz, COOCH$_2$C$\underline{H}_3$). The mass spectrum (Fig. 2) showed an ion peak at m/e 376 (3.1%, $C_{16}H_{25}N_2{\cdot}\overset{+}{S}Cl$) which originated in a sulfur-carbon bond rupture.[11] The spectrum in the lower *m/e* regions was very complex compared to those of IV and V. Loss of hydrogen chloride from the ion peak at *m/e* 376 affords an abundant ion peak at *m/e* 340 ($C_{16}H_{24}N_2{\cdot}\overset{+}{S}$). Further loss of an ethoxylcarbonyl group from this ion yields an ion peak at *m/e* 267 ($C_{13}H_{19}N_2{\cdot}\overset{+}{S}$), whichcan afford an ion peak at *m/e* 193 ($C_7H_5N_2\overset{+}{S}$) by the loss of another ethoxycarbonyl group. Cleavage of carbon-carbon bond of the side-chain between the positions α and β to a pyridazine ring and the loss of hydrogen chloride afford an ion peak at *m/e* 239 ($C_{11}H_{15}N_2^+$), which can give rise to ion peaks at *m/e* 166, 165, 95, and 93 on the loss of an ethoxycarbonyl group. The base ion peak appeared at *m/e* 69 ($C_5H_9^+$), apparently arising from the side-chain. Ion peaks at *m/e* 154, 153 and 141 *etc.* were observed, supporting the dimeric sulfide structure VI.

All the reactions of SD with I-III occurred between two molecules of the dienes at their side-chain double bond and one molecule of SD to give IV-VI respectively,[15] though these reactions were carried out at high dilutions (2—4 wt% of olefins and 1.5 wt% of SD). The formation of these products can be explained by a facile attack of SD on a side-chain double bond and by chlorinations of cyclohexenyl or cyclohexadienyl moieties with SD.[16]

Experimental[17]

Addition Reaction of SD with I. To a mixture of 1.87 g (0.01 mol) of I[8] and 50 m*l* of reagent-grade dichloromethane at *ca.* −50°C under a nitrogen atmosphere in a 200-m*l* three-necked flask fitted with stirrer, addition funnel and nitrogen inlet-outlet, was added with stirring a solution of 0.64 m*l* (0.01 mol) of SD in 50 m*l* of reagent-grade dichloromethane.[7] Addition was carried out for 1 hr and the resulting red solution was allowed to stand at *ca.* 15°C for 5 hr, shaken several times with cold brine and dried over sodium sulfate. After removal of the solvent, the residue was distilled *in vacuo* to give 0.86 g (43%) of IV: bp 117—119°C/0.1 mmHg, $n_D^{22.5}$ 1.5550. Found: C, 77.79; H, 7.50; N, 6.96%. Calcd for $C_{26}H_{28}N_2S$: C, 77.97; H, 7.05; N, 7.00%.

Addition Reaction of SD with II. Similarly 1.89 g (0.01 mol) of II[8] was treated with 0.64 m*l* (0.01 mol) of SD as above, and the product obtained was distilled to give 1.26 g (53%) of V: bp 145—149°C/0.5 mmHg, $n_D^{22.5}$ 1.5544. Found: C, 65.73; H, 7.34; N, 5.63%. Calcd for $C_{26}H_{34}N_2SCl_2$: C, 65.38; H, 7.14; N, 5.87%.

Addition Reaction of SD with III. Similarly 3.10 g (0.01 mol) of III[8] was treated with 0.64 m*l* (0.01 mol) of SD as above. The work-up and distillation afforded 0.97 g (27%) of VI: bp 165—175°C/0.5 mmHg, $n_D^{22.5}$ 1.5227. Found: C, 53.61; H, 7.31; N, 8.33%. Calcd for $C_{32}H_{48}N_4O_8SCl_2$: C, 53.41; H, 6.81; N, 7.79%.

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*1 The methylene protons of the ethoxycarbonyl group appeared at τ 5.75 in a q, J=6.5 Hz in these overlapped signals.

15) The products seem to be diastereoisomeric mixture since these compounds have two or more asymmetric carbons.

16) a) Ref. 3: b) Chevron Res. Co., Brit. 1084670; *Chem. Abstr.*, **68**, 21528x (1968).

17) Microanalyses were carried out using a Yanagimoto C.H.N. Corder, Model MT-1. IR spectra were recorded on a JASCO Model IR-S IR spectrophotometer and UV spectra, on a JASCO Model ORD/UV-5 spectrophotometer. NMR spectra were obtained with a Hitachi H-60 spectrometer in deuterochloroform and are reported in τ values relative to TMS as an internal standard. Mass spectra were determined with a JEOL Model JMS-O1SG mass spectrometer at 70 and 15 eV of electron energy.