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167. Shoji Takemura, Hiromi Terauchi, Yoshiko Ando, and Yoshio Ueno : Reaction of N-Halosulfonamide. III.*1 Reaction of N,N-Dibromobenzenesulfonamide with Cyclopentene.

(*Faculty of Pharmacy, Kinki University**2)

Reaction of N,N-dibromobenzenesulfonamide (I) with cyclopentene (II) was investigated and it was shown that N-(DL-*trans*-2-bromocyclopentyl)benzenesulfonamide (III), DL-*trans*-1,2-dibromocyclopentane (V), cyclopentadiene (VI) and benzenesulfonamide (VII) were formed on the reaction. Contrary to the case of reacting I with cyclohexene, DL-*cis* isomer of III could not be obtained in the present case.

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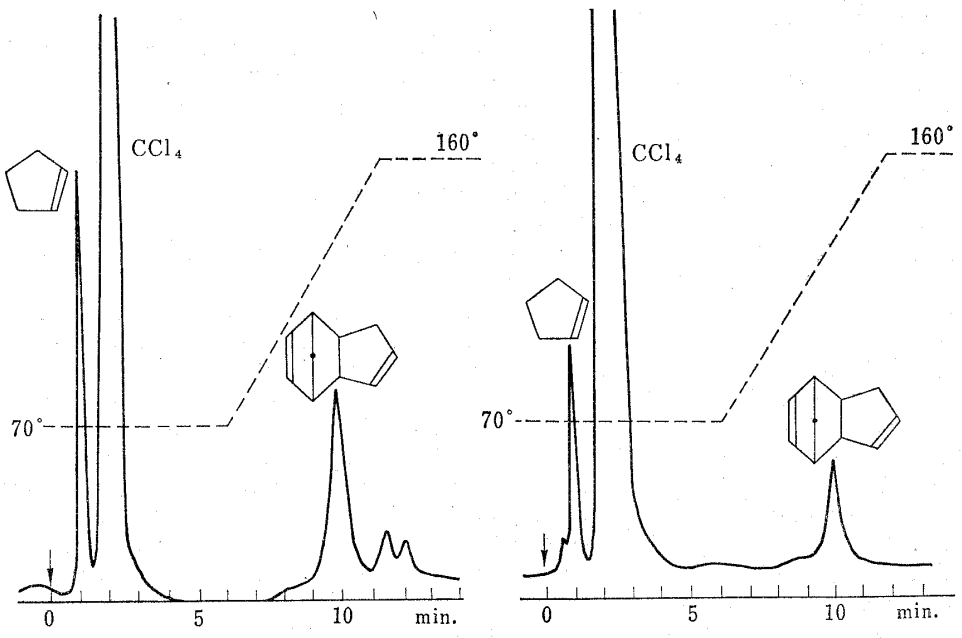
In our previous papers,*1 it was reported that N,N-dihalobenzenesulfonamide reacted with cyclohexene to afford unique addition products.

The present investigation was undertaken in order to apply this reaction for other cyclic olefins and we have taken up the reaction of N,N-dibromobenzenesulfonamide (I) with cyclopentene (II).



Fraction of b.p. 41~42°.

A mixture of cyclopentene, carbon tetrachloride, and dicyclopentadiene.

Fig. 1. Gas Chromatogram of the Fraction, b.p. 41~42° from the Reaction Mixture of N,N-Dibromobenzenesulfonamide and Cyclopentene

An exothermic reaction occurred by mixing I with an excess of II in carbon tetrachloride and the products isolated therefrom were N-(DL-*trans*-2-bromocyclopentyl)benzenesulfonamide (III), DL-*trans*-1,2-dibromocyclopentane (V), cyclopentadiene (VI), and a small amount of benzenesulfonamide (VII) (Fig. 1). DL-*cis* isomer (IV) of III could not be isolated in this case while considerable amount of the correspondig *cis* isomer was obtained in the reaction of I with cyclohexene.

*1 Part I : This Bulletin, **15**, 1193 (1967) ; Part II : *Ibid.*, **15**, 1198 (1967).

*2 Kowakae, Fuse, Osaka-fu (竹村庄司, 寺内弘実, 安藤佳子, 上農義雄).

The compound Ⅲ was obtained in good yield as colorless needles, m.p. 113~115°, $C_{11}H_{14}O_2NBrS$. The structure of this was confirmed by the identification with the authentic sample prepared from DL-*trans*-2-bromocyclopentylamine hydrobromide (Ⅸ) (a novel compound) and benzenesulfonyl chloride. The novel hydrobromide (Ⅸ) was obtained by the treatment of cyclopenteneimine (Ⅷ)[1] with hydrogen bromide in ether. It was shown by Tamelen and Wilson[2] that the treatment of *p*-nitrobenzoyl derivative of *trans*-2-chlorocyclopentylamine (XIII) with base gave 2-(*p*-nitrophenyl)-4,5-trimethylene-2-oxazoline (Ⅺ) while that of the corresponding *cis* isomer (XV) did not. Treatment of Ⅸ with *p*-nitrobenzoyl chloride in alkaline medium directly gave the oxazoline (Ⅺ) which was identified with the authentic sample.[3] Therefore Ⅲ and Ⅸ undoubtedly exhibit the *trans* configuration.

The mother liquor, after the removal of Ⅲ, was distilled to collect a fraction boiling at 41~42°. The distillate was subjected to gas chromatographic test and the peaks of excessive cyclopentene, carbon tetrachloride, dicyclopentadiene, and dimer of cyclopentadiene were detected.

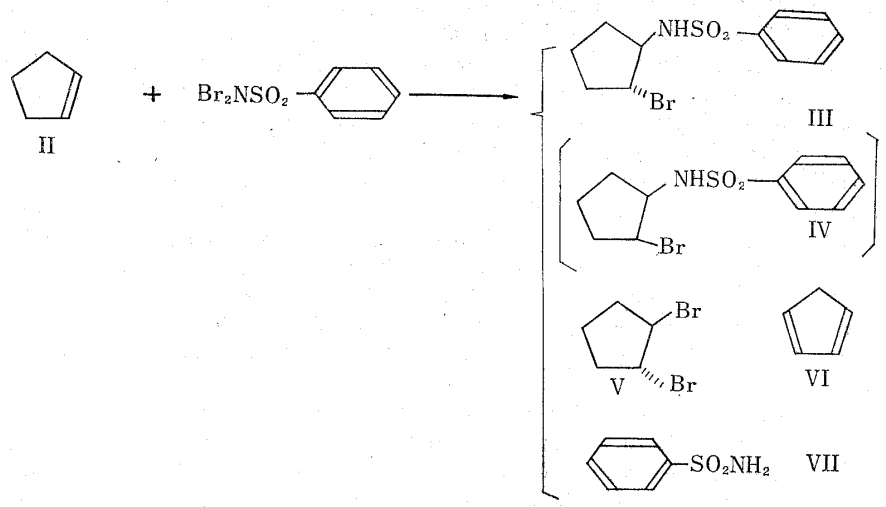


Chart 1.

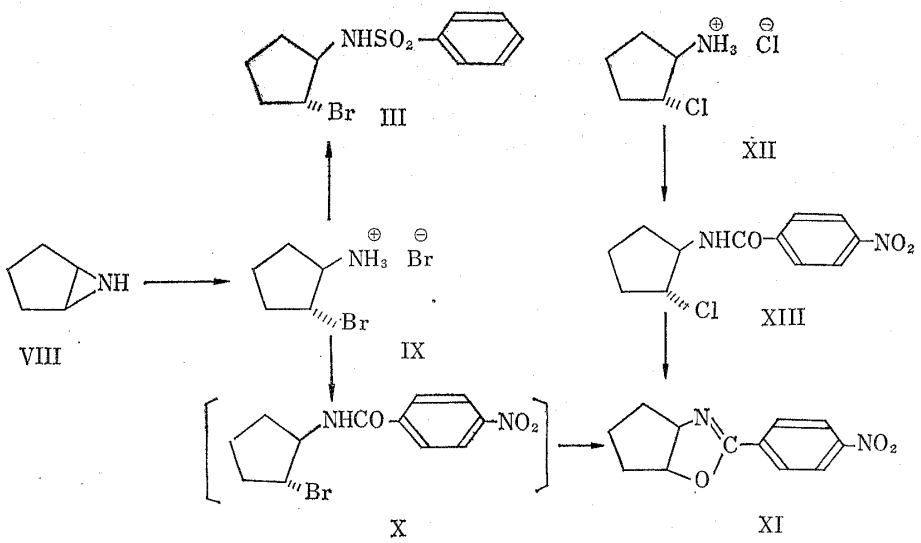


Chart 2.

1) P.E. Fanta : J. Chem. Soc., **1957**, 1441.
2) E.E. van Tamelen, R.S. Wilson : J. Am. Chem. Soc., **74**, 6299 (1952).
3) G.E. McCasland, D.A. Smith : *Ibid.*, **72**, 2190 (1950).

Column chromatography of the residual liquid after removal of the above low-boiling fraction afforded a slightly yellow oil, b.p_{15} 75~76°, $C_5H_8Br_2$, which was identified as DL-*trans*-1,2-dibromocyclopentane (V)[4] as well as additional crop of III and small amount of benzenesulfonamide (VII) as colorless needles.

Experimental

Reaction of N,N-Dibromobenzenesulfonamide (II) with Cyclopentene (I)——N,N-Dibromobenzenesulfonamide (II) (10 g.) was added in small portions to CCl_4 (5 ml.) containing cyclopentene (I) (9 g.) under ice-cooling and stirring. An exothermic reaction occurred and, when the reaction subsided, the mixture was allowed to reflux for 2 hrs.

1) N-(DL-*trans*-2-Bromocyclopentyl)benzenesulfonamide (III): The above reaction mixture was cooled, kept standing overnight, and filtered to give crystals which were recrystallized from ethanol to colorless needles (6.7 g., 85%), m.p. 113~115°. *Anal.* Calcd. for $C_{11}H_{14}O_2NBrS$: C, 43.43; H, 4.64; N, 4.60. Found: C, 43.74; H, 4.59; N, 4.40. IR ν_{max}^{Nujol} cm^{-1}: 3230 (ν_{N-H}), 1154, 1379 (ν_{SO_2N}). This compound was identical with the authentic N-(DL-*trans*-2-bromocyclopentyl)benzenesulfonamide (III) by mixed melting point determination and comparison of IR spectra.

2) Cyclopentadiene (VI): The filtrate after separation of III in the above step was distilled to collect a fraction boiling at 41~42° and the destillate was allowed to stand in a refrigerator for 2 days. Gas chromatography (Fig. 1) was carried out under the following condition: Sample, 15 μl.; Column, Polyethyleneglycol 6000 (30%), 1.5 m., 3 mm. ϕ, 70~160°; Carrier gas, He, 15 ml./min., 0.32 kg./cm^2; Detector, Thermal conductivity detector. Identical peaks with these of the authentic dicyclopentadiene, carbon tetrachloride, and cyclopentene were detected by comparison of retention times.

3) DL-*trans*-1,2-Dibromocyclopentane (V) and benzenesulfonamide (VII): The residual liquid freed from the fraction, b.p. 41~42°, was evaporated to dryness under reduced pressure, the resulting residue (7.2 g.) was chromatographed on a silica gel column, and eluted with *n*-hexane, $CHCl_3$, and MeOH in this order. Evaporation of the *n*-hexane eluate left light yellow oil (1.35 g., 18.49%), b.p_{15} 75~76°, which was identified by good agreement of its IR spectrum with that of authentic DL-*trans*-1,2-dibromocyclopentane.[4] Elution with $CHCl_3$ afforded additional crop of III (1.2 g., 12.33%) as a major product. From the final fraction eluted with MeOH were obtained colorless crystals, m.p. 154~156°(0.9 g.) which were identified with the authentic benzenesulfonamide (VII).

DL-*trans*-2-Bromocyclopentylamine Hydrobromide (IX) and 2-(*p*-Nitrophenyl)-4,5-*cis*-trimethylene-2-oxazoline (XI)——Dry hydrogen bromide gas was bubbled through a solution of cyclopenteneimine (VIII)[1] (1.5 g.) in ether (22 ml.). Since the precipitated IX was extremely hygroscopic, it was immediately allowed to react with *p*-nitrobenzoyl chloride by Schotten-Baumann procedure. The crude product taken out from the reaction mixture was recrystallized from abs. EtOH to colorless needles, m.p. 135~136°, IR ν_{max}^{Nujol} cm^{-1}: 1652, 1602, 1520, 1350, 1079, 860, which were identified with an authentic sample, m.p. 136~139°, prepared by the known method[3] by comparison of IR spectra and a mixed melting point determination.

N-(DL-*trans*-2-Bromocyclopentyl)benzenesulfonamide (III)——Crude *trans*-2-bromocyclopentylamine hydrobromide (IX) (0.3 g.) was dissolved in pyridine (5 ml.), benzenesulfonyl chloride (0.15 ml.) was dropwise added thereto under stirring, the whole was stirred for more 10 min., and the resulting precipitate was recrystallized from 95% EtOH to colorless crystals (20 mg.), m.p. 112~114°, which were identified with the sample of III, isolated from the reaction mixture of N,N-dibromobenzenesulfonamide (II) and cyclopentene (I) as disclosed previously.

4) N. D. Zelinsky, R. J. Lewina: Ber., **60**, 477 (1933).