v/v). The extracts were evaporated *in vacuo*, and the residue was again chromatographed on a preparative TLC plate [silica gel GF_{254}, ethanol–ethyl acetate (1: 6, v/v)], giving IV (4 mg), mp 233—236°. Identity was confirmed by means of mixed melting-point test, TLC, and IR spectrum.

In the reaction of Ia·H_2O[3] (2.59 g, 10 mmoles) with boiling 0.1N ethanolic sodium ethoxide (50 ml) for 10 hr, the formation of a minute amount of benzaldehyde was confirmed by the same procedure as described above.

Treatment of the monohydrate[3] (4.30 g, 10 mmoles) of IIb with boiling 0.1N aq. NaOH (300 ml) for 30 min also produced benzaldehyde in a very low yield.

Deoxygenation of 9-Benzyl-1-benzyloxyadenine Hydrobromide (IIb) in N,N-Dimethylacetamide (DMAC)——A stirred mixture of IIb·H_2O[3] (2.00 g, 4.65 mmoles) and DMAC (5 ml) was kept at 120° in a stream of nitrogen for 6 hr. After cooling, the mixture was diluted with H_2O (20 ml) and extracted with ether. The extracts were combined, washed with H_2O, dried over anhyd. Na_2SO_4, and evaporated to leave an oily residue. This oil was allowed to react with 2,4-dinitrophenylhydrazine—H_3PO_4 reagent,[13] and 240 mg (18%) of benzaldehyde 2,4-dinitrophenylhydrazone, mp 240—241°, was obtained.

In this reaction, replacement of the solvent by 90% or 50% aq. DMAC resulted in reduction in yield of the hydrazone derivative to 3 or 0.5%.

When a stirred mixture of 9-benzyladenine 1-oxide[3,11] (1.13 g, 4.68 mmoles), benzyl bromide (800 mg, 4.68 mmoles), and DMAC (5 ml) was heated at 120° for 6 hr, the formation of benzaldehyde in 20% yield was evidenced by isolating it as the corresponding 2,4-dinitrophenylhydrazone in a manner similar to that described above.

[Chem. Pharm. Bull. 20(8)1821—1823(1972)]

UDC 547.298.3.04 : 547.592.2.04

Reaction of N-Haloamide. XIV.[1] Reaction of N,N-Dichlorophenylacetamide with Cyclohexene

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(Received January 31, 1972)

It has been reported that the reactions of N,N-dihalobenzenesulfonamide and N,N-dichlorobenzamide with cyclohexene gave adducts, 2-halo-1-benzenesulfonamidocyclohexane and 2-chloro-1-benzamidocyclohexane, respectively.[3]

This report deals with the reaction of N,N-dichlorophenylacetamide (I) with cyclohexene (II) which gives adducts different from that expected from above reactions.

N-Chlorophenylacetamides were prepared by the modified procedure of the synthesis of N,N-dichlorourethane.[4] Passage of chlorine through a heterogeneous mixture of acetic acid-sodium acetate buffer solution and phenylacetamide in chloroform for one hour resulted in the formation of crystalline N-monochlorophenylacetamide (III), mp 126—127°. When the chlorine-passage was continued for three hours more, a yellow oil was obtained. It was likely N,N-dichlorophenylacetamide (I) on the basis of measurement of active chlorine (iodometry) and infrared spectrum.

The dichloroamide (I) was relatively unstable, decomposed on distillation, while monochloroamide (III) was very stable. No change was observed on refluxing of III with cyclohexene (II). Upon storage at 0°, dichloroamide (I) could be kept without decomposition for several weeks.

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3) Y. Ueno, S. Takemura, Y. Ando, and H. Terauchi, *Chem. Pharm. Bull.* (Tokyo), **15**, 1193 (1967); K. Otsuki, S. Takemura, K. Okamoto, and Y. Ueno, *ibid.*, **17**, 528 (1969).
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Addition of N,N-dichlorophenylacetamide (I) in carbon tetrachloride to a cooled solution of cyclohexene (II) resulted in the formation of crystals of III in a few minutes. After the removal of III from the reaction mixture, the solution was subjected to a silica gel column chromatography. Elution of the column gave following products; a colorless oil, bp_7 98—100° (IV) which was identified with authentic *trans*-2-chlorocyclohexyl phenylacetate, *trans*-1,2-dichlorocyclohexane (V), and a small amount of labile oil (VI). The establishment of the structure of the latter oil (VI) failed because of its lability on further purifications. The yields of III, IV, and V were 32, 40, and 7% respectively. No product expected from the reaction of N,N-dihalobenzenesulfonamide or N,N-dichlorobenzamide with cyclohexene could be detected in the reaction mixture.

A small amount of crystalline substance, $C_{14}H_{17}ONCl_2$ (VII), mp 82—84°, was obtained in a few runs. This showed positive KI-starch reaction and its infrared spectrum exhibits the bands at 1600 cm^{-1} ($\nu_{C=N}$), 1580 cm^{-1} ($\delta_{arom.}$) and no bands of N–H and C=O bonds. The nuclear magnetic resonance (NMR) spectrum of VII indicates the structure of imidochloride of IV; signals centered at 1.5 ppm corresponding to eight protons on cyclohexane ring, the broad signals at 3.75 ppm (one proton) and 4.25 ppm (one proton) are assignable to the protons attached to carbons bearing chlorine and oxygen atoms respectively, two protons of benzylic methylene appear at 3.95 ppm as a singlet and the signals of aromatic five protons are observed in the neighborhood of 7.25 ppm. The hydrolysis of VII with a mixture of ethanol and hydrochloric acid gave phenylacetic acid and *trans*-2-chlorocyclohexanol, while gentle hydrolysis of VII in dil. acetic acid produced IV. Above mentioned spectral and chemical evidence supports the structure of an imidochloride of *trans*-2-chlorocyclohexyl phenylacetate (IV). The poor yield and the difficulty to obtain VII are caused by its lability. A large portion of VII appeared to be decomposed to IV on chromatography on comparing the thin-layer chromatograms before and after the filtration of the reaction mixture through a short silica gel column.

On the basis of above results, it is concluded that two or more reactions, an addition reaction to form IV *via* VII and more complicate reactions to give III, V, and VI, occurred competitively in this reaction system.

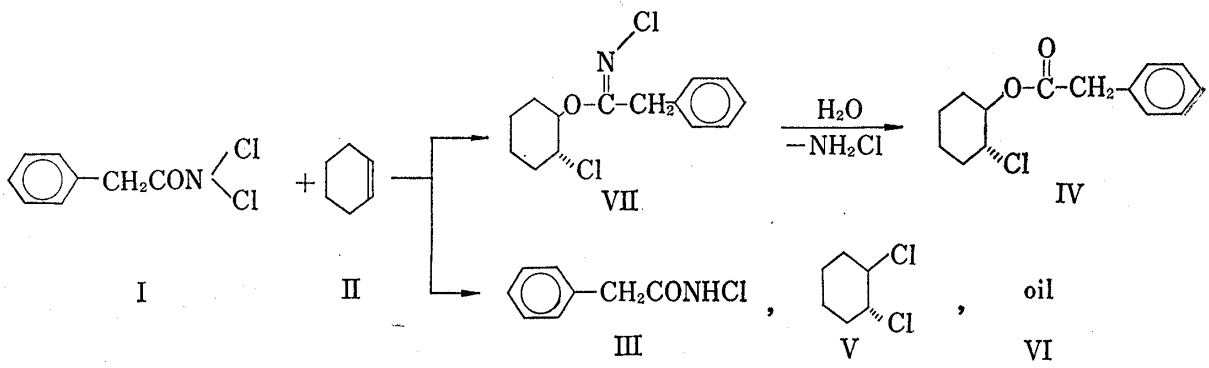

Chart 1

Experimental

N-Chlorophenylacetamide (III)——Chlorine was passed through a mixture of phenylacetamide (4.6 g), NaOAc (7 g), H_2O (30 ml), AcOH (0.7 ml), and $CHCl_3$ (25 ml) for 1 hr with stirring and chilling. The $CHCl_3$-layer was separated and the aqueous layer was extracted with $CHCl_3$. The combined $CHCl_3$ solution was washed with H_2O and dried over Na_2SO_4. Evaporation of $CHCl_3$ leaved a residue which was recrystallized from $CHCl_3$ to give colorless needles (4.5 g), mp 128°, IR_{max}^{Nujol} cm^{-1}: 3130 (ν_{N-H}), 1660 (ν_{NHCO}), 770, 730 (δ_{arom}). *Anal.* Calcd. for C_8H_8ONCl: C, 56.63; H, 4.76; N, 8.26; Cl, 20.91. Found: C, 56.40; H, 4.94; N, 8.20; Cl, 21.60. The value of active chlorine measured by iodometry was 86.5% of theoretical.

N,N-Dichlorophenylacetamide (I)——Chlorine was bubbled through the mixture of phenylacetamide (18.4 g), NaOAc (28 g), H_2O (120 ml), AcOH (2.8 ml), and $CHCl_3$ (100 ml) for 4 hr. The resulted yellow

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$CHCl_3$-layer was separated, washed with H_2O, and dried over Na_2SO_4. The solvent was evaporated to leave a yellow oil (34.5 g). $IR_{max}^{liq.}$ cm^{-1}: 1720 (ν_{CON}). Active chlorine measured by iodometry was 86% of theoretical. Reduction of this substance with aqueous $NaHSO_3$ solution gave quantitative amount of phenylacetamide. This compound is relatively unstable and could not be purified on distillation or chromatography.

Reaction of I with II, Isolation of III, IV, V, VI, and VII——To a mixture of cyclohexene (5.7 g, 0.07 mole) and CCl_4 (6 ml) (5°), a cooled solution of N,N-dichlorophenylacetamide (I) (15 g, 0.07 mole) in CCl_4 (40 ml) was dropwise added with stirring. After the colorless crystals appeared, the stirring was continued for another 30 min. The crystals were filtered (4 g, 32%) and recrystallized from $CHCl_3$, mp 126—127°. Identity of them with N-chlorophenylacetamide (III) was established by comparison of IR spectra and by admixed melting point determination.

After the removal of N-chlorophenylacetamide, the mother liquor was evaporated to dryness *in vacuo*. The residue was subjected to a silica gel column chromatography. Elution of the column with *n*-hexane gave *trans*-1,2-dichlorocyclohexane, bp_{22} 72° (0.7 g) in the first fraction. This was identified with authentic sample by the comparison of infrared (IR) spectra and the retention time in gas chromatogram. Subsequent elution gave a colorless oil (VI) (1.5 g). The oil was partially decomposed by allowing to stand for a day at room temperature or on distillation. From the third fraction *trans*-2-chlorocyclohexyl phenylacetate (IV), bp_7 98—100° (3.5 g) was obtained. It was identical with authentic sample by comparison of IR spectra and retention time in gas chromatogram. From the forth fraction eluted with a mixture of *n*-hexane containing $CHCl_3$, crystals, mp 82—84° (recrystallized from *n*-hexane) (VII, 0.5—1.0 g) were obtained in a few runs. IR_{max}^{Nujol} cm^{-1}: 1600 ($\nu_{C=N}$), 1580, 725 (δ_{arom}). NMR ($CDCl_3$) ppm: 1.5 (8H), 3.75 (1H, broad), 4.25 (1H, broad), 3.95 (2H, singlet, $-CH_2-C_6H_5$), 7.25 (5H, singlet, $-C_6H_5$). *Anal.* Calcd. for $C_{14}H_{17}ONCl_2$: C, 58.74; H, 5.94; N, 4.89; Cl, 24.82. Found: C, 58.51; H, 5.93; N, 4.82; Cl, 24.75. The crystals, VII, were refluxed for 1 hr with a mixture of conc. HCl and EtOH (1:2 volume). The hydrolyzate was extracted with $CHCl_3$, and the $CHCl_3$-phase was washed with H_2O, and dried over Na_2SO_4. After the removal of $CHCl_3$, the residue was subjected on a silica gel column to obtain *trans*-2-chlorocyclohexanol, and phenylacetic acid. Gentle hydrolysis of VII by warming with 10% AcOH for 1 hr on a water bath gave a homogeneous solution. The hydrolyzate was concentrated *in vacuo* to dryness. The residue was subjected to a silica gel column chromatography to give a homogeneous oil, bp_7 98—100° which was identified with IV by the comparison of IR spectra and the retention time in gas chromatography. After the elution of the forth fraction (VII), the said column was finally eluted with $CHCl_3$ to obtain a small amount of additional N-chlorophenylacetamide (III).

***trans*-2-Chlorocyclohexyl Phenylacetate (IV)**——*trans*-2-Chlorocyclohexanol[5] (1 g) was mixed with phenylacetic acid (1 g) and 2 drops of H_2SO_4. The mixture was warmed on a water bath for 1 hr. Upon cooling, the mixture was neutralized with aqueous $NaHCO_3$, and extracted with $CHCl_3$. The $CHCl_3$-extract was washed with H_2O and dried over Na_2SO_4 and the solvent was evaporated *in vacuo*. The residual oil (1 g) was purified by distillation, bp_7 98—100°. $IR_{max}^{liq.}$ cm^{-1}: 1735 (ν_{-OCO-}), 3030, 760, 740 (arom.). *Anal.* Calcd. for $C_{14}H_{17}O_2Cl$: C, 66.51; H, 6.78; Cl, 14.03. Found: C, 66.23; H, 6.81; Cl, 14.22.

5) G.H. Coleman, *Org. Synth. Coll.* Vol., 1, 158.

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