to a nitrogen atom. The infrared spectrum shows an OH peak at 3380 cm^{-1} and a broad absorption at 2500–3000 cm^{-1} characteristic of amine hydrochlorides.

Experimental Section

3,4-Di(4'-methylbenzoyl)furoxane[7] (1), mp 124°, 3,4-di(4'-chlorobenzoyl)furoxane[8] (2), mp 124°, and 3,4-di(4'-chlorobenzoyl)furazane[9] (5), mp 115°, were prepared according to procedures given in the literature.

3,4-Di(4'-methylphenyloxiranyl)furoxane (3).—To a solution of 1 g of **1** in 20 ml of dry chloroform was added ethereal diazomethane from 2 g of nitrosomethylurea and 0.5 ml of methanol. The mixture was left for 5 hr at room temperature. The solvents were distilled off under reduced pressure, and methanol (4 ml) was added to the residue. The product **3** crystallized and was purified by recrystallization from methanol. The yield was 0.65 g, 60%, mp 126°.

Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.65; H, 5.1; N, 8.0. Found: C, 68.5; H, 5.1; N, 7.8.

3,4-Di(4'-chlorophenyloxiranyl)furoxane (4).—The same procedure as above was used with 1 g of **2**. The product **4**, 0.7 g, yield 65%, melted at 128°.

Anal. Calcd for $C_{18}H_{12}Cl_2N_2O_4$: C, 55.3; H, 2.9; N, 7.2. Found: C, 55.4; H, 2.9; N, 7.1.

Reduction of 4 to 1-Amino-2-(*p*-chlorophenyl)-2-propanol Hydrochloride (6).—A solution of **4** (0.6 g) in anhydrous ether (20 ml) was added dropwise to lithium aluminum hydride (0.2 g) in anhydrous ether (20 ml) in a flask protected from atmospheric moisture. The reaction mixture boiled spontaneously, after which it was heated under reflux for *ca.* 15 min. Aqueous sodium hydroxide (2 ml of 10%) was added cautiously to the mixture; the precipitate was filtered off and the filtrate was dried over magnesium sulfate. The ether was distilled off and the residue was treated with ether saturated with HCl. A crystalline hydrochloride, **6**, resulted. It was recrystallized from an acetone–ethanol mixture. The yield was 0.4 g (63.5%), mp 190–193°.

Anal. Calcd for $C_9H_{13}Cl_2NO$: C, 48.7; H, 5.9; N, 6.3. Found: C, 49.0; H, 6.0; N, 6.3.

The nmr spectra were measured at 60 Mc/sec with a Varian HR-60 apparatus using 10% solutions in carbon tetrachloride of the substances **1** and **5** and with tetramethylsilane as standard. The product **6** was examined as a 10% solution in deuterium oxide with acetone as the standard.

The infrared spectra were measured with a Unicam SP-200 spectrometer.

Registry No.—**3**, 14002-09-6; **4**, 14002-10-9; **6**, 14002-11-0; diazomethane, 334-88-3.

Synthesis of 4H-3,1-Benzoxazin-4-ones from 2-Isocyanatobenzoyl Chloride and Aliphatic Amines

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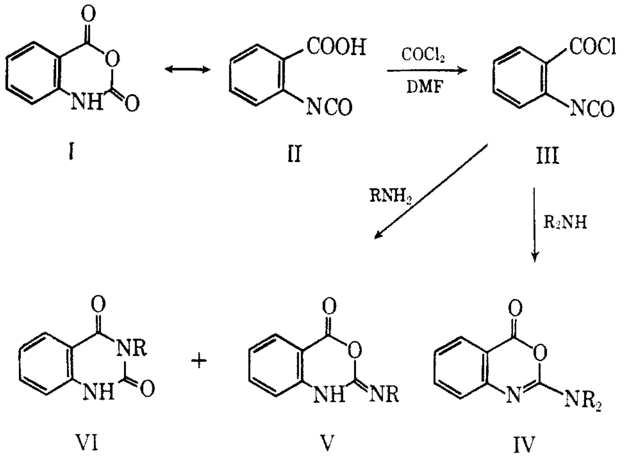
Whereas the reaction of 2-isocyanatobenzoyl chloride (III) with aromatic amines has been reported to afford ureidoamides,[1] we have found the reaction of III with primary and secondary aliphatic amines to give rise to the cyclic 4H-3,1-benzoxazin-4-ones V and IV, respectively (Scheme I). Compound IV was formed exclusively from the secondary amines, but an isomeric mixture of V and VI was obtained from the primary amines. The rearrangement of 1,2-dihydro-2-alkylimino-4H-3,1-benzoxazin-4-ones (V) to the 3-alkyl-2,4-quinazolinediones (VI) has been reported.[2,3]

Scheme I



The unequivocal synthesis of 4H-3,1-benzoxazin-4-ones (IV), having an endocyclic carbon–nitrogen double bond, verifies the hypothesis of Kurihara and Yoda,[4a] who predicted that the intensity of the C=N absorption band should be weaker than that of the C=O band in endocyclic C=N bond-containing 4H-3,1-benzoxazin-4-ones. Although the position of these absorptions in IV (C=N, 1667 cm^{-1}; C=O, 1761 cm^{-1}) are quite near to those of compound V (C=N, 1640–1690 cm^{-1}; C=O, 1730–1760 cm^{-1}),[3,4] for which the exocyclic structure has been postulated,[4a] the predicted order of intensity was verified in all cases.

The 2-isocyanatobenzoyl chloride (III) was prepared by the phosgenation of isatoic anhydride (I) in the presence of a catalytic[5] amount of N,N-dimethylformamide and the reaction proceeds most likely *via* 2-isocyanatobenzoic acid (II) as the intermediate. In the absence of catalyst no reaction took place.

The reaction of compound III with di-*n*-butylamine can be used as a quantitative analytical method. In the standard di-*n*-butylamine titration method for the determination of isocyanate equivalents,[6] for example, III consumes 2 equiv of the amine, thereby showing that the intermolecular reaction (which would require 3 equiv of amine) occurs at a much slower rate than does the intramolecular reaction.

Experimental Section[7]

2-Isocyanatobenzoyl Chloride (III).—To a suspension of isatoic anhydride (16.3 g, 0.1 mole) in chlorobenzene (165 ml) was added N,N-dimethylformamide (0.33 g, 2% by weight). Phosgene was passed through the mixture until a clear solution

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[1] Y. Iwakura, H. Uno, and S. Kang, *J. Org. Chem.*, **31**, 142 (1966). These authors obtained 3-phenylquinazoline-2,4-dione (VI, R = C_6H_5) by reacting 2-isocyanatobenzoyl chloride with aniline in the presence of tri-*n*-butylamine.

[2] H. Herlinger, *Angew. Chem.*, **76**, 437 (1964).

[3] J. C. Sheehan and G. D. Daves, Jr., *J. Org. Chem.*, **29**, 3599 (1964).

[4] (a) M. Kurihara and N. Yoda, *Tetrahedron Letters*, 2597 (1965); (b) G. Doleschall and K. Lempert, *ibid.*, 1195 (1963); (c) K. Lempert and G. Doleschall, *Monatsh. Chem.*, **95**, 950 (1964).

[5] The catalytic effect of N,N-dimethylformamide on the conversion of carboxylic acids to carboxylic acid chlorides, using phosgene, has been reported by H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, *Helv. Chim. Acta*, **42**, 1653 (1959).

[6] S. Siggia and J. G. Hanna, *Anal. Chem.*, **20**, 1084 (1948).

[7] Analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were determined on a Perkin-Elmer 21 spectrometer.

was achieved, the reaction temperature gradually being increased to reflux. The flask was purged with nitrogen to remove excess phosgene, the solvent was evaporated, and the residue was distilled *in vacuo*. There was afforded 16.75 g (59.2%) of III: bp 100–103° (0.3 mm); mp 30–33°.

Anal. Calcd for $C_8H_4ClNO_2$: C, 52.93; H, 2.22; N, 7.71; Cl, 19.53. Found: C, 53.05; H, 2.42; N, 7.74; Cl, 19.49.

Di-*n*-butylamine titration: Calcd mol wt, 181.56. Found: mol wt, 181.3.

2-Diethylamino-4H-3,1-benzoxazin-4-one (IV, R = C_2H_5).—A solution of 2-isocyanatobenzoyl chloride (3.6 g, 0.02 mole) in benzene (10 ml) was added during 5 min at 24–70° to a solution of diethylamine (2.9 g, 0.04 mole) in benzene (20 ml). On cooling, diethylamine hydrochloride (2.0 g, 91.4%) precipitated and was removed by filtration. The solvent was evaporated and the remaining traces of amine hydrochloride were precipitated with ether and were removed. There was afforded 4.3 g of IV (R = C_2H_5) as a colorless oil: infrared spectra $\lambda_{\max}^{\mathrm{CCl_4}}$ C=O, 1761; C=N, 1667 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.03; H, 6.47; N, 12.84. Found: C, 65.73; H, 6.61; N, 13.00.

2-Di-*n*-butylamino-4H-3,1-benzoxazin-4-one (IV, R = *n*-C_4H_9).—A solution of 2-isocyanatobenzoyl chloride (5.4 g, 0.03 mole) in benzene (25 ml) was added during 5 min at 24–70° to a solution of di-*n*-butylamine (7.7 g, 0.06 mole) in benzene (50 ml). The reaction mixture was worked up in the manner stated above and there was afforded 7.9 g (96.3%) of IV (R = *n*-C_4H_9) as a greenish oil: infrared spectra $\lambda_{\max}^{\mathrm{CCl_4}}$ C=O, 1761; C=N, 1667 cm^{-1}.

Anal. Calcd for $C_{16}H_{22}N_2O_2$: C, 70.04; H, 8.08; N, 10.21. Found: C, 69, 70; H, 8.14; N, 10.25.

Reaction of 2-Isocyanatobenzoyl Chloride with Isopropylamine.—2-Isocyanatobenzoyl chloride (1.8 g, 0.01 mole) was added slowly with stirring to a solution of isopropylamine (1.18 g, 0.02 mole) in benzene (15 ml). The precipitated solid products were collected and the isopropylamine hydrochloride was removed with water. Thus, 0.85 g (41.6%) of **3-isopropylquinazoline-2,4-dione** (VI, R = *i*-C_3H_7) was obtained: mp 193–194° (lit.[8] mp 188°); infrared spectra $\lambda_{\max}^{\mathrm{KBr}}$ NH 3279; C=O 1704, 1639 cm^{-1}.

Evaporation of the mother liquor afforded 1.0 g (49%) of **2-isopropylamino-4H-3,1-benzoxazin-4-one** (V, R = *i*-C_3H_7): mp 138–140° (methanol); $\lambda_{\max}^{\mathrm{KBr}}$ NH 3289; C=O 1736; C=N 1667 cm^{-1}.

Anal. Calcd for $C_{11}H_{12}N_2O_2$: N, 13.72. Found: N, 13.81.

Registry No.—III, 5100-23-2; IV, R = C_2H_5, 14128-51-9; IV, R = *n*-C_4H_9, 14128-52-0; V, R = *i*-C_3H_7, 14128-53-1.

[8] R. P. Staiger and E. C. Wagner, *J. Org. Chem.*, **18**, 1427 (1953).

The Ring Opening and Defluorination of N-Cyclopropyl-α,α,α-trifluoro-*m*-toluamide with Lithium Aluminum Hydride[1]

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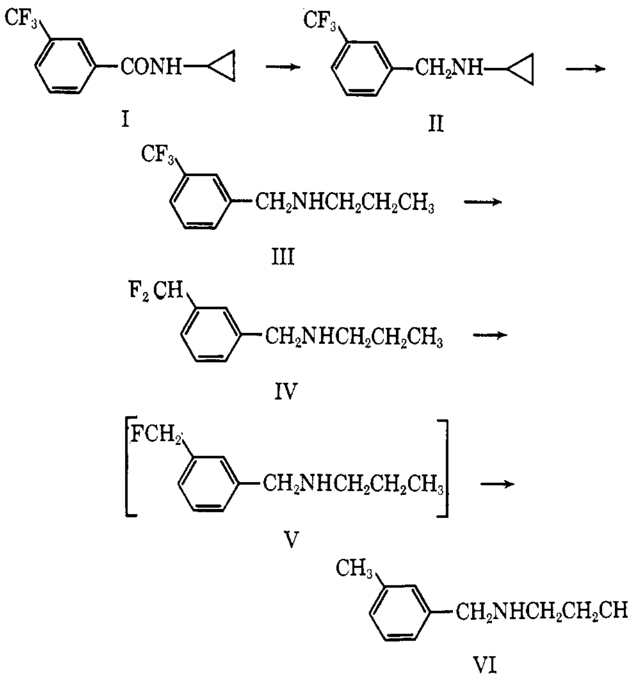
Kaiser and co-workers[2] have reported the opening of the cyclopropane ring in *trans*-N-(2-phenylcyclopropyl)formamide by lithium aluminum hydride and have described a mechanism for this reaction. We have observed that the lithium aluminum hydride reduction of N-cyclopropyl-α,α,α-trifluoro-*m*-toluamide (I) in tetrahydrofuran results not only in an analogous ring opening but also in a stepwise defluorination of intermediate products to give *m*-methyl-N-propylbenzylamine (VI) (Scheme I).

Scheme I



The hydrogenolysis of the aryltrifluoromethyl group was completely unexpected. Moreover, this is not a general reaction, for when *m*-trifluoromethylacetanilide is reduced with a large excess of lithium aluminum hydride, the expected product, N-ethyl-(*m*-trifluoromethyl)aniline, is obtained in good yield. Under the same conditions 2-(trifluoromethyl)phenothiazine and 2-(trifluoromethyl)benzimidazole are recovered essentially unchanged.

Hydrogenolysis of C–F bonds by lithium aluminum hydride in aliphatic systems has been described previously by Papanastassiou and Bruni[3] and by Pettit and Smith.[4] We are unaware of any references to reduction of aryltrifluoromethyl groups with this reducing agent. However, methods for the conversion of aryltrifluoromethyl groups to methyl groups by use of Raney cobalt and nickel alloys[5] and also by electrochemical reduction[6] are known in the literature.

The products obtained by the reaction of I with lithium aluminum hydride were isolated by partition chromatography and identified by comparison of their physical constants with those of authentic materials. The nmr spectra are summarized in Table I. Expected patterns were obtained in each case. The chief distinguishing feature of *m*-(difluoromethyl)-N-propylbenzylamine (IV) was the triplet centered at 6.6 ppm (*J* = 57 cps) which is characteristic for a proton on a carbon atom also bonded to two fluorine atoms.

Product distributions of crude mixtures obtained under a variety of reaction conditions are represented in Table II. The approximate ratios were derived from the nmr spectra.

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[1] Presented in part at the 154th National Meeting of The American Chemical Society, Chicago, Ill., Sept 1967.

[2] C. Kaiser, A. Burger, L. Zirngibl, C. S. Davis, and C. L. Zirkle, *J. Org. Chem.*, **27**, 768 (1962).

[3] Z. B. Papanastassiou and R. J. Bruni, *ibid.*, **29**, 2870 (1964).

[4] G. R. Pettit and R. L. Smith, *Can J. Chem.*, **42**, 572 (1964).

[5] N. P. Buu-Hoi, N. D. Xuong, and N. V. Bac, *Compt. Rend.*, **257** (21), 3182 (1963).

[6] H. Lund, *Acta Chem. Scand.*, **13**, 192 (1959).