Although the yields of secondary cyanides are only fair, the fact that they can be easily obtained in a single step may make the reaction useful. Isobutyronitrile, for instance, cannot be made in aqueous alcohol, and is difficult to make by indirect methods. It is doubtful whether this method of preparing *t*-butyl cyanide (pivalonitrile) is practical.

In a few runs part of the excess sodium cyanide was neutralized with sulfuric acid in an attempt to reduce the over-all alkalinity. This reduced the proportion of glycol ether in the product; the effect was small, however, and it was concluded that the alkoxide ion, $HOCH_2CH_2O^-$, which might have been present in the unbuffered solution, was not directly responsible for ether formation.

Experimental

The alkyl halides and ethylene glycol were redistilled before use. The sodium cyanide was Baker Analyzed, 98% minimum.

The general procedure was to mix 150 cc. of ethylene glycol, 0.5 mole of the alkyl halide and 0.55 mole of sodium cyanide in a 500-cc. three-necked flask, and to heat under reflux with constant stirring until the end of the reaction. The initial temperature, measured by a thermometer in the vapor, was always close to the boiling point of the halide, and the end of the reaction was marked by a rapid rise in temperature to a constant value as the last of the halide was used up. In a few runs 0.1 mole of sulfuric acid and an additional 0.2 mole of sodium cyanide were added before heating. In the reaction with *n*-butyl bromide it was observed that the heat of reaction was sufficient to maintain spontaneous reflux at the start.

The liquid products were distilled from the reaction mixture through a three-ball Snyder column. Where further purification of the nitriles was required they were washed with 4 *N* hydrochloric acid, 10% sodium bicarbonate and water, dried and redistilled through a 9-inch or 18-inch packed column. Their properties are listed in Table II. The odor revealed that traces of isocyanide were still present in all cases.

In the runs in which olefin was determined the evolved gases were passed through soda-lime to remove hydrogen cyanide, and condensed in a trap at −80°. The olefins were then converted to the dibromides by passing them into a sodium tribromide solution, prepared from 70 g. of sodium bromide, 112 g. of bromine and 300 cc. of water. The dibromides were washed with sodium carbonate and sodium thiosulfate solutions, dried and weighed.

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RECEIVED OCTOBER 16, 1951

X-Ray Measurements of Terramycin Salts

BY J. ROBERTSON, I. ROBERTSON, P. F. EILAND AND R. PEPINSKY

The hydrochloride of terramycin crystallizes from aqueous solution in the form of yellow elongated plates. These are biaxial negative with parallel extinction, and have the refractive indices $\mu_g = 1.639$, $\mu_m = 1.686$, $\mu_p = 1.721 \pm 0.003$. The highest refractive index is shown when the electric vector vibrates parallel to the direction of elongation (the *a* axis). The crystals are orthorhombic, with space group $P2_12_12_1$, unit cell dimensions $a = 11.19$ Å., $b = 12.49$ Å., $c = 15.68$ Å., and four molecules per cell. The density, found from experiment to be 1.51, gives the value 499 ± 5 for the molecular weight of the asymmetric unit. As it is probable that this unit consists of one molecule of the antibiotic, without water of crystallization, the molecular weight of the free antibiotic, as given by the X-ray data, is 462.5 ± 5. This is in agreement with the molecular weight found approximately by titration methods,[1] and with the formula $C_{22}H_{24}N_2O_9\cdot HCl$, which corresponds to the analysis reported by P. P. Regna and I. A. Solomons.[1]

Terramycin hydrobromide crystallizes as a dihydrate, in space-group $P2_1$. The unit cell dimensions are $a = 12.2$ Å., $b = 11.4$ Å., $c = 18.0$ Å., with β very nearly 90°. There are four molecules per cell, and thus two molecules of $T\cdot HBr\cdot 2H_2O$ in each asymmetric unit.

Since the molecular structure of terramycin is not known, efforts have been exerted toward a complete X-ray analysis. The hydrobromide dihydrate was not suitable for this analysis because of the existence of two molecules in the asymmetric unit, doubling the number of atomic parameters to be determined. The hydrochloride was selected for further study, and a full three-dimensional Patterson synthesis was carried out on X-RAC, the electronic computer for crystal analysis,[2] using data obtained with $CuK\alpha$ radiation. The chloride ion parameters were found to be (0.075, 0.08, 0.00). These ions form nets at $z = 0$ and $z = {}^1/_2$, with the ions 7.0 and 9.9 Å. distant from one another, in sheets which are 15.7 Å. apart.

Attempts at interpretation of the three-dimensional Patterson were made by means of the Vector Convergence Density method, utilizing photographic super-position of displaced Patterson sections.[3] This technique strongly indicated positions of eleven carbon, oxygen or nitrogen atoms in the molecule, and suggested six additional positions of atoms of similar weight. These peaks were all concomitant with acceptable interatomic distances, but their number and distribution were insufficient to suggest a molecular configuration. Atomic coördinates found by the Vector Convergence Density method are now being used to compute structure factor phases for a three-dimensional density map.

This investigation is supported by fellowship grants from Charles Pfizer and Company and the Research Corporation, and under Contract No. N6-onr-26916, T. O. 16 with the Office of Naval Research.

(1) P. P. Regna and I. A. Solomons, *Ann. N. Y. Acad. Sci.*, **53**, 229 (1950).

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DEPARTMENT OF PHYSICS
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RECEIVED NOVEMBER 7, 1951

o-Nitrobenzoates

BY J. U. LOWE

During an investigation of aryl nitro compounds, it became necessary to prepare several *o*-nitrobenzoates; these were prepared in satisfactory yields by the interaction of pure *o*-nitrobenzoyl chloride and the monohydric alcohols.

_o_-Nitrobenzoates.—*o*-Nitrobenzoyl chloride[1] (0.2 mole) and the monohydric alcohol (0.4 mole) were refluxed for 3–7

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(1) K. Auwers and M. Duesberg, *Ber.*, **53**, 1207 (1920).