A Novel Degradation of a Benzene Ring

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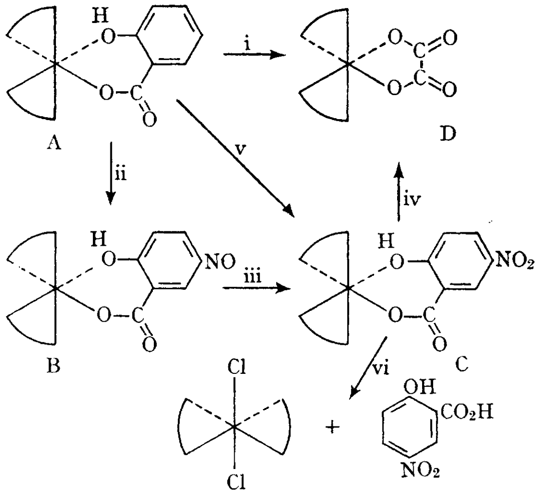
IN experiments on chemical correlation of the optical configurations of octahedral complexes, we have discovered a remarkable degradation of chelated salicylate. When salts of the red cation, salicylatobisethylenediaminecobalt(III), A, are treated with concentrated nitric acid, the final product, formed in very good yield (*ca.* 90%) is the oxalatobisethylenediaminecobalt(III) cation, D.

This product, isolated as its nitrate, has been characterized by analysis, and by electronic and infrared spectra, and by plots of molar conductivity against concentration. These physical properties are quantitatively identical with those of an authentic sample of D, as are the chemical properties, such as solubilities of salts.

Two intermediates (the Scheme) have been isolated by working under milder conditions. These are a green, weakly paramagnetic compound B, tentatively formulated as shown, which we have not obtained pure, the contaminant being C, and the brown compound C, of 5-nitrosalicylate, which decomposes in concentrated hydrochloric acid as shown. Salts of C are identical with authentic samples of salts of the (5-nitrosalicylato)-bisethylenediaminecobalt(III) ion, made from 5-nitrosalicylic acid and salts of the bisaquobis-ethylenediaminecobalt(III) ion. The electrophilic substitution in the salicylate ion is markedly modified in A, where we obtain only the 5-nitro-compound. Direct nitration of free salicylic acid leads to a mixture of 5- and 3-nitro-compounds, which are difficult to separate.

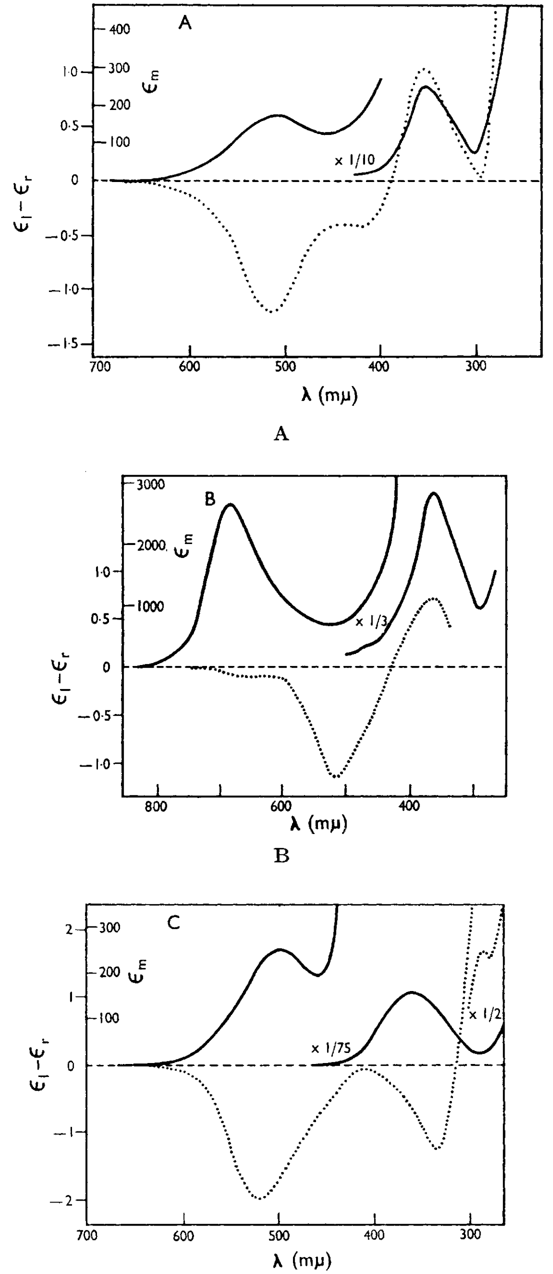
Some pointers to the mechanism of this degradation are available. B and C, when obtained from optically active (+)-A [resolved through either (+)-camphorsulphonate or (+)-bromocamphorsulphonate] are strongly optically active; the relevant spectra are shown in the Figure. However, D made from optically active A or C is racemic. This loss of optical activity argues that the oxalate unit must be formed with rupture of at least one of the chelate bonds to cobalt, since[1] the bisethylenediaminecobalt moiety readily loses its optical activity under these conditions. This conclusion is modified by the fact that while the preformed oxalato-complex D is surprisingly stable in concentrated nitric acid, it cannot be made from its components under these conditions. In the degradation of 5-nitrosalicylate to oxalate, therefore, only one of the chelate bonds is broken.



SCHEME. *The conversion of the salicylato-complex to the oxalato-complex.*

Reagents: i, Conc. HNO_3, hot, 15 hr.; ii, 0·5 M HNO_3, cold 1 hr.; iii, H_2O; iv, As (i); v, Conc. HNO_3, cold; vi, Conc. HCl, hot

The conversion of the three-carbon unit in the chelate ring of the salicylate complex to the two-carbon unit of oxalate probably involves decarboxylation, since a small yield (< 10%) of picric acid is occasionally obtained in reaction (iv). Picric acid is known to arise from salicylic acid by decarboxylation under strong nitrating conditions, and we assume it (or a decarboxylated precursor, such as 2,4-dinitrophenol, which is then nitrated further) to arise from the intermediate of reaction (iv).



A

B

.C

FIGURES

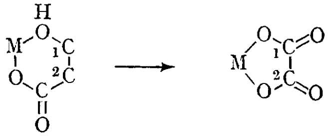
FIGURE. *The absorption (——) and circular dichroism (. . . .) spectra of the complex cations*:

A, (−)-$[Co\,en_2(SalH)]^{2+}$

B, (−)-$[Co\,en_2(5\text{-}NO\text{-}salH)]^{2+}$

C, (−)-$[Co\,en_2\,(5\text{-}NO_2\text{-}salH)]^{2+}$

Extensions of this novel reaction are being studied, together with its mechanism, which may well be associated with the tautomeric possibilities for the nitrophenols. The present observations incidentally give a chemical correlation of the optical configurations of A, B, and C, which agrees with an empirical rule[2] proposed recently.



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[1] K. Garbett, R. D. Gillard, and P. J. Staples, *J. Chem. Soc.* (*A*), 1966, 201.
[2] R. D. Gillard, *Chem. in Britain*, 1967, 1.