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benzylic alcohol function, and *a priori* may give rise to either one or both types of oxidation.

We have now found that benzoin splits into benzaldehyde and benzoic acid when exposed to ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, in aqueous acetonitrile. Similarly, anisoin, toluoin, *p*-phenylbenzoin, and 1-naphthoin provide the corresponding aldehydes and acids. However, no furfural has been isolated or identified when furoin was subjected to the same conditions. The major product obtained was 2-furoic acid.

Generally, two mole-equivalents of the oxidant are sufficient to give good yields of the products. In the case of furoin, the starting material was not completely consumed unless four equivalents of ceric ammonium nitrate were employed. A small amount (5%) of furil has been isolated from this reaction. When equimolar amounts of furoin and ceric ammonium nitrate were allowed to react, the neutral organic material recovered (55%) consisted of furil and furoin in the ratio of $\sim 1:10$. It was demonstrated that furfuryl alcohol did not furnish furfural during oxidation. The failure to observe any furfural in the crude oxidation products of furoin may indicate its destruction by nitric acid which was produced in the course of the reaction.

The results reported here essentially parallel those of the lead tetraacetate reaction. Thus, the reaction may be represented by the following mechanistic scheme.

Table 1. Ceric Ammonium Nitrate Cleavage of Benzoins

Ar-CH-C-Ar HO O	$Ar - CH = N - NH - NO_2$ O_2N		Ar-C00H	
Ar	Yield %	m. p.	Yield %	m. p.
-	80	242243°	86	121°
—∕>осн₃	87	254255°	88	184–185°
-√>сн₃	87	240~241°	86	175177
-	78	238-240°	81	225 - 227
	82	254~255°	84	158~-161°
6)			83	130 132°

Cleavage of Benzoins; General Procedure:

To a stirred solution of benzoin (1 mmol) in acetonitrile (4.5 ml) was added in one portion a solution of ceric ammonium nitrate (1.10 g, 2 mmol) in water (1.5 ml). The reaction mixture was

Ceric Ammonium Nitrate Oxidation of Benzoins

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Ceric ammonium nitrate oxidation of alcohols^{1,2,3} has received considerable attention in recent years. Two different reaction courses are available in which fragmentation or direct oxidation to carbonyl compounds are observed. Cyclopropylcarbinols⁴ and primary benzylic and related alcohols⁵ are oxidized to aldehydes, 2-aryl-1-phenylethanols⁶ undergo C—C bond fission to yield benzaldehyde and products derived from the benzyl moiety, whereas alkylphenylcarbinols⁷ afford a mixture of benzaldehyde and alkyl phenyl ketone. These results entail pertinent interests in the reaction of ceric ammonium nitrate with benzoins which bear a

heated at 60° for 10 min, poured into brine, and extracted with ether (40 ml). Direct treatment of the ethereal extract with a stock 2,4-dinitrophenylhydrazine solution precipitated the 2,4-dinitrophenylhydrazone of the aldehyde. The carboxylic acid was isolated from the filtrate by extraction with aqueous sodium hydroxide, acidification, and solvent extraction. It was finally purified by either recrystallization or sublimation. All products were characterized by comparison with authentic compounds.

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