

sorption spectrum was essentially identical with that reported earlier for III¹² and indicated the following maxima: λ_{\max} 232 m μ , ϵ 21550; λ_{\max} 289 m μ , ϵ 16300; λ_{\max} 325 m μ , ϵ 18300.

A solution of 50 g. of III in 500 ml. of boiling glacial acetic acid was treated with 100 ml. of 48% hydrobromic acid, and the mixture was boiled under reflux for 3 hr. and allowed to cool. The reaction mixture was concentrated to one-half volume under reduced pressure, and the residue was diluted with 3 l. of water and allowed to stand overnight. The heavy precipitate was filtered, washed, and air dried to yield 44 g. of product as light yellow crystals. Recrystallization from water gave bright yellow crystals melting at 113° with gas evolution, solidifying, and remelting at 233–235°. Analysis indicated the monohydrate of I. The ultraviolet absorption spectrum was identical with that of the dihydrate.

Anal. Calcd. for C₁₄H₁₂O₇: C, 57.54; H, 4.14. Found: C, 57.25; H, 4.57.

Acetylation of either the monohydrate, the dihydrate, or the parent anhydrous I with acetic anhydride in pyridine, and recrystallization from ethanol gave yellow needles of 3,3',4,4'-tetraacetoxybenzyl (IV) melting at 133–134°: λ_{\max} 268 m μ , ϵ 21000.

Anal. Calcd. for C₂₂H₁₈O₁₀: C, 59.73; H, 4.10. Found: C, 59.73; H, 4.15.

Methylation of any of the three forms of I with dimethyl sulfate and alkali and recrystallization of the product from glacial acetic acid yielded yellow crystals melting at 220–221° and not depressing a mixed melting point with authentic II.⁴

3,3',4,4'-Tetrahydroxybenzoin (V). A solution of 5 g. of I dihydrate in 200 ml. of hot water was treated with 25 ml. of glacial acetic acid and 5 g. of granulated tin. The mixture was heated on the steam bath for 1.5 hr. and filtered. The precipitate was washed with hot water, and the combined filtrate and washings were concentrated under reduced pressure. After standing at room temperature, the solution deposited 1.2 g. of tan crystals which were recrystallized from water in the presence of decolorizing carbon to yield light tan needles of V hemihydrate melting at 186–188°. The ultraviolet absorption spectrum was identical with that of authentic veratrolin (VI) and indicated the following maxima: λ_{\max} 232 m μ , ϵ 19750; λ_{\max} 281 m μ , ϵ 14780; λ_{\max} 325 m μ , ϵ 17250.

Anal. Calcd. for C₁₄H₁₈O_{6.5}: C, 58.90; H, 4.46. Found: C, 58.92; H, 4.59.

Acetylation with acetic anhydride in pyridine yielded 3,3',4,4'-tetrahydroxybenzoin pentaacetate (VII) as colorless needles from ethanol melting at 182–183°.

Anal. Calcd. for C₂₄H₂₂O₁₁: C, 59.26; H, 4.56. Found: C, 59.68; H, 4.32.

3,3',4,4'-Tetrahydroxydeoxybenzoin (VIII). A solution of 5 g. of I dihydrate in 200 ml. of hot water was treated with 10 g. of granulated tin and then slowly with 10 ml. of concd. hydrochloric acid. The mixture was heated on the steam bath 1.5 hr. and filtered. The precipitate was washed with hot water, and the combined filtrate and washings were concentrated under reduced pressure. After standing several days at room temperature the solution deposited 2.2 g. of dark crystals which were recrystallized from water in the presence of decolorizing carbon to yield light tan crystals of VIII monohydrate melting at 196–198° and having the following maxima in its ultraviolet absorption spectrum: λ_{\max} 231 m μ , ϵ 18800; λ_{\max} 281 m μ , ϵ 11950; λ_{\max} 310 m μ , ϵ 8720. The ultraviolet absorption spectrum was identical with that of deoxyvanilloin (IX).

Anal. Calcd. for C₁₄H₁₄O₆: C, 60.43; H, 5.07. Found: C, 60.59; H, 5.19.

Acetylation with acetic anhydride in pyridine yielded 3,3',4,4'-tetraacetoxydeoxybenzoin (X) as light yellow needles from ethanol melting at 127–128° and having the following maximum in its ultraviolet absorption spectrum:

λ_{\max} 293 m μ , ϵ 26950. The spectrum was essentially identical with that of deoxyvanilloin diacetate (XI).

Anal. Calcd. for C₂₂H₂₀O₈: C, 61.68; H, 4.71. Found: C, 61.55; H, 4.74.

VIII was also prepared by reduction of I dihydrate with tin amalgam and hydrochloric acid¹³ in either aqueous or dilute ethanolic solution.

3,3',4,4'-Tetrahydroxybibenzyl (XII). A solution of 5 g. of I dihydrate in 200 ml. of hot water was treated with 10 g. of zinc dust and heated to boiling. The mixture was removed from the source of heat and treated portionwise with 40 ml. of concd. hydrochloric acid. The solution decolorized after the first addition. The mixture was allowed to stand 5 min. after the last addition and filtered hot. The zinc residue was washed with water, and the combined filtrate and washings were concentrated by distillation under reduced pressure. The concentrated solution deposited crystals upon standing at room temperature. The crystals were filtered and recrystallized from water to give 4.0 g. of XII as tan crystals melting at 151–152°. The ultraviolet absorption spectrum had a maximum at 283 m μ (ϵ 6750) and was essentially identical with that of bivanillyl (XIII) except for a slight maximum in the latter at 230 m μ .

Anal. Calcd. for C₁₄H₁₄O₄: C, 68.28; H, 5.73. Found: C, 68.31; H, 6.15.

Acetylation and recrystallization from ethanol yielded 3,3',4,4'-tetraacetoxybivanillyl (XIV) melting at 148–149° and having the following maxima in its ultraviolet absorption spectrum: λ_{\max} 266 m μ , ϵ 1680; λ_{\max} 272 m μ , 1660.

Anal. Calcd. for C₂₂H₂₂O₈: C, 63.76; H, 5.35. Found: C, 63.70; H, 5.33.

Unsuccessful reductions of I. Attempted reductions of I with zinc and ammonium chloride, aluminum and hydrochloric acid, aluminum amalgam and ammonium hydroxide, tin amalgam and hydrochloric acid, sodium borohydride, sodium trimethoxyborohydride in alkaline solution, sodium hydrosulfite in alkaline solution, zinc and sodium hydroxide, and Raney nickel alloy in sodium hydroxide solution under conditions reported previously^{4,10,13} resulted in either the recovery of starting material or in the production of highly colored tarry materials from which no crystalline products could be isolated.

THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WIS.

(13) I. A. Pearl and W. M. Dehn, *J. Am. Chem. Soc.* **60**, 57 (1938).

Decomposition of Acyl Nitrates. Reaction of Trifluoroacetic Anhydride with Nitric Acid

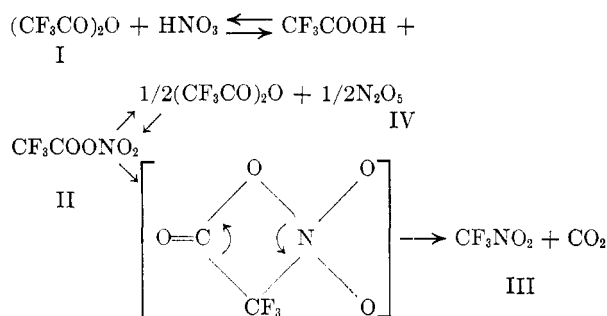
ROBERT BOSCHAN

Received January 29, 1960

A low yield of fluoropicrin (III) has been obtained from the reaction of trifluoroacetic anhydride (I) with nitric acid at 100°. The formation of this material very likely proceeds *via* the intermediate trifluoroacetyl nitrate (II), which decomposes as shown in a manner similar to that previously postulated in the conversion of alkyl chloroformates to nitrate esters¹ and of dialkyl carbamyl

(12) I. A. Pearl and E. E. Dickey, *J. Am. Chem. Soc.* **74**, 614 (1952).

(1) R. Boschan, *J. Am. Chem. Soc.*, **81**, 3341 (1959).



chlorides to nitramines² by treatment with silver nitrate. Probably the reason for the low yield of III is the reversible conversion to nitrogen pentoxide (IV). The formation of IV from I and nitric acid has been demonstrated previously³; IV would certainly decompose very rapidly at 100°, thus preventing the formation of III.

The reactions of perfluorobutyric anhydride and of perfluorosuccinic anhydride with nitric acid were tried, but in neither case was any nitro compound found in appreciable amount. Probably in these cases IV is formed and decomposes too rapidly to allow formation of nitro compounds. Neither of these anhydrides is completely miscible with nitric acid as is I, and this would doubtlessly affect the reversibility of the reaction in which IV is formed.

EXPERIMENTAL

Reaction of trifluoroacetic anhydride with nitric acid. A mixture of 21.0 g. (0.10 mole) of trifluoroacetic anhydride and 6.3 g. (4.20 cc., 0.10 mole) of 100% nitric acid was placed in a hydrogenation bomb liner and inserted in a stainless steel bomb. The heater was turned on, and in less than an hour the reaction mixture was up to 100°. The mixture was maintained at this temperature for about an additional 5.5 hr., and then was gradually allowed to cool to ambient temperature and allowed to remain overnight. The gas was bled into a standard nitrometer tube (240 cc.) and then into a liquid nitrogen trap. Fourteen fillings of the nitrometer tube (total 3360 cc.) were required to bleed all the gas from the bomb. The gases were passed through a molecular sieve vapor phase chromatography column which irreversibly removed carbon dioxide, nitrogen dioxide, and water. A pure sample of fluoropicrin was thus obtained and eluted from the column. Three 5-cc. aliquots of the original gas sample yielded sufficiently pure fluoropicrin to give a good infrared spectrum. The amount of helium (which had been used as carrier gas in the vapor phase chromatograph) and air in the gas sample were determined by mass spectrometry. The weight of the gas sample was measured by weighing the gas sample tube before and after evacuation. From these data it was calculated that 0.815 g. (7.09%) of pure fluoropicrin was obtained in the reaction.

The fluoropicrin was characterized by means of its infrared and mass spectra. The infrared spectrum showed the reported⁴ asymmetrical stretch vibration peaks at 6.13 μ and 6.18 μ and the symmetrical stretch vibration peak at 7.78 μ . The entire infrared spectrum was similar to the reported⁵ spectrum of 1-chloro-1,1,2,2-tetrafluoro-2-nitroethane.

(2) W. P. Norris, *J. Am. Chem. Soc.*, **81**, 3346 (1959).

(3) J. H. Robson, *J. Am. Chem. Soc.*, **77**, 107 (1955).

(4) R. N. Haszeldine and J. Jander, *J. Chem. Soc.*, 4172 (1953).

(5) R. N. Haszeldine, *J. Chem. Soc.*, 2525 (1953).

The mass spectrum showed the expected cracking pattern for a compound with the structure trifluoronitromethane.

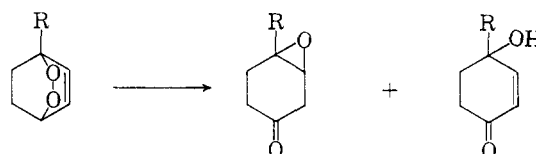
CHEMISTRY DIVISION
U. S. NAVAL ORDNANCE TEST STATION
CHINA LAKE, CALIF.

Pyrolysis of 9(11)-Dehydroergosterol Peroxide Acetate

WERNER BERGMANN¹ AND MARTIN B. MEYERS²

Received February 17, 1960

The thermal or base-catalyzed treatment of epidioxide rings attached to secondary-secondary or secondary-tertiary carbon atoms ordinarily gives rise to disproportionation into either or both a β,γ -epoxy ketone and/or a keto-allylic alcohol³:



Where the epidioxide ring is attached to two tertiary carbon atoms, as in ergosterol peroxide (I), there must be a rearrangement for disproportionation to take place. This is observed when I is refluxed in a hydrocarbon solvent at around 200°. Two major products are formed, ergost-22-ene-5,6 α -epoxy-7-one-3 β -ol (II) and ergosta-8,22-diene-5,6 α -epoxy-3 β ,7 α -diol (III), where the oxygen function has migrated from C₈ to C₇.⁴ The assignment of the nuclear double bond to the Δ^8 position was made by oxidation of the 3-monoacetate of III to 3 β -acetoxyergosta-8,22-diene-5,6 α -epoxy-7-one (IV), which when treated with potassium iodide in glacial acetic acid gave the known 3 β -acetoxyergosta-5,8,22-triene-7-one (V). It was thought that further support for the correctness of this assignment could be made by pyrolysis of 9(11)dehydroergosterol peroxide acetate (VI), which by proceeding in analogous manner to ergosterol peroxide (I) would produce the β,γ -epoxy ketone VII and VIII: Basic isomerization of VII should then lead to IV.

(1) Deceased.

(2) Central Research Laboratories, General Mills, Inc., 2010 East Hennepin Avenue, Minneapolis 13, Minnesota.

(3) (a) W. Bergmann and R. J. Conca, *J. Org. Chem.*, **18**, 1104 (1953); (b) E. J. Agnello, R. Pinson, Jr., and G. D. Laubach, *J. Am. Chem. Soc.*, **78**, 4756 (1956); (c) R. B. Woodward and R. H. Eastman, *J. Am. Chem. Soc.*, **72**, 339 (1950); (d) T. G. Halsall, W. J. Rodewald, and D. Willis, *Proc. Chem. Soc.*, 1958, 231.

(4) W. Bergmann and M. B. Meyers, *Chem. & Ind. (London)*, 1958, 655; *Ann.*, **620**, 46 (1959).