

The formation of the solvates may also be of value as diagnostic features of rotenone and may be of some application in analytical procedures. Thus in the extraction of derris root with carbon tetrachloride, the rotenone-solvent compound crystallizes from the evaporated extract and may be separated, dried and weighed in the air without heating in the oven, the weight being calculated to that of rotenone.

Summary

Under ordinary conditions rotenone forms with benzene, carbon tetrachloride and chloroform crystalline solvates containing one molecule of rotenone to one of solvent, and with acetic acid a solvate containing two molecules of rotenone to one of solvent.

No crystalline solvates were formed with acetone, chlorobenzene, ethyl acetate, ethyl alcohol and ethylene dichloride.

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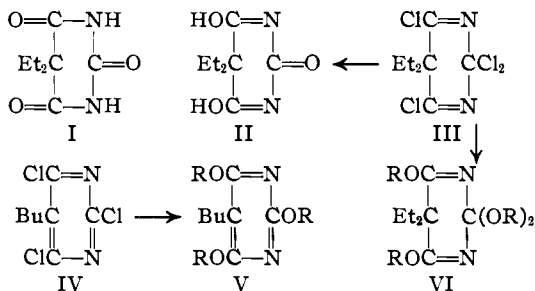
OXYGEN ETHERS OF BARBITAL

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The formula commonly assigned to barbital (5,5-diethylbarbituric acid) represents the keto-lactam structure (I). On theoretical grounds this structure should be more stable than the isomeric enol-lactim (II). At least one of the lactam groupings has the properties of an imide, since a monosodium salt can be prepared which reacts with alkyl halides to form N-alkylated barbital. If the sodium salt exists as the tautomeric enol, it should yield an oxygen ether, but no such oxygen ethers have thus been obtained. After alkylation of one lactam the resulting 1,5,5-trialkylbarbituric acid again behaves as an imide, the remaining lactam forming a sodium salt which reacts as before. It is thus possible to prepare a 1,3,5,5-tetraalkylbarbituric acid.¹



¹ Dox and Jones, THIS JOURNAL, 51, 316 (1929).

From analogy to similar structures, *e. g.*, isatin, carbostyryl, etc., the tautomeric enol-lactim (II) should be the less stable form. Nevertheless, its oxygen ethers, once formed, should be relatively stable, though possibly subject to molecular rearrangement under drastic treatment.

In a previous paper² the hydrolysis of 2,2,4,6-tetrachloro-5,5-diethyl-dihydropyrimidine (III) was discussed. Replacement of the four chlorines by hydroxyl, followed by loss of water at C-2, should yield the tautomeric barbital (II). Aside from a quantitative liberation of hydrochloric acid, the only product obtained was diethylmalononitrile, the logical decomposition product of the unstable tautomer. Whether this tautomer exists momentarily as an intermediate product cannot as yet be stated with certainty. In view of the results obtained in the analogous alcoholysis of this tetrachloro derivative, the tentative explanation which assumes the momentary existence of an unstable tautomer acquires greater validity.

The substitution of alkoxy for chlorine in a chlorinated derivative of an alkylbarbituric acid is recorded in one instance. V. Merckatz³ treated 2,4,6-trichloro-5-ethylpyrimidine with sodium methoxide and obtained 2,4,6-trimethoxy-5-ethylpyrimidine. No evidence, beyond the method of preparation, was offered in support of the oxygen ether structure of the product. The possibility of rearrangement to an isomeric N-alkyl structure was not mentioned. In the case of tautomeric barbital, which represents a dihydropyrimidine and has two double bonds instead of three, the possibility of rearrangement is a more serious consideration.

Experimental

The reaction described by v. Merckatz, in which the three chlorines of 2,4,6-trichloro-5-ethylpyrimidine were replaced by methoxyl, was first tried with the homologous 2,4,6-trichloro-5-*sec.*-butylpyrimidine (IV),² using several alkoxides. The chlorinated pyrimidine was treated with the equivalent of sodium dissolved in the appropriate absolute alcohol. The reaction began almost immediately, as shown by the evolution of heat and the precipitation of sodium chloride. The mixture was heated in a steam-bath for two to four hours, then treated with water and the separated oily product distilled at atmosphere pressure.

2,4,6-TRIALKOXY-5-*sec.*-BUTYLPYRIMIDINES (V)

Alkoxy	B. p., °C.	Formula	Nitrogen, %	
			Calcd.	Found
Methoxyl	245-250	C ₁₁ H ₁₈ O ₃ N ₂	12.39	12.35 12.34
Ethoxyl	260-264	C ₁₄ H ₂₄ O ₃ N ₂	10.44	10.29 10.28
Propoxyl	285-290	C ₁₇ H ₃₀ O ₃ N ₂	9.03	9.27 9.22
Butoxyl	310-315	C ₂₀ H ₃₆ O ₃ N ₂	7.95	8.09

² Dox, *THIS JOURNAL*, **53**, 1559 (1931).

³ V. Merckatz, *Ber.*, **52**, 876 (1919).

Proof of structure was not attempted, since the proof given for the tetraalkoxy derivative below should be equally applicable here.

The 2,2,4,6-tetrachloro-5,5-diethylidihydropyrimidine (III), obtained by treatment of barbitol with phosphorus pentachloride, reacted in the same manner with sodium ethoxide and sodium butoxide. The oily products were separated as above, but distilled at 3 mm. instead of atmospheric pressure.

2,2,4,6-TETRAALKOXY-5,5-DIETHYLDIHYDROPYRIMIDINES (VI)

Alkoxy1	B. p., °C. (3 mm.)	Formula	C	Calcd., %			Found, %	
				H	N	C	H	N
Ethoxyl	122-123	C ₁₆ H ₂₀ O ₄ N ₂	61.15	9.55	8.92	60.12	9.49	8.88
Butoxyl	180-183	C ₂₄ H ₃₆ O ₄ N ₂	67.60	10.80	6.57	67.36	10.56	6.71

Both are high-boiling liquids, the tetrabutoxy derivative being considerably more viscous than its lower homolog.

Proof of structure was obtained by examining the products of hydrolysis. A homogeneous solution of 1.3885 g. of the tetraethoxy derivative in 10 cc. of concentrated hydrochloric acid was heated in a sealed tube for five hours at 140-150°. Considerable pressure was released on opening the tube and the contents, consisting of an aqueous solution and a supernatant oil, were separated in a small funnel. The oil was washed with water and dried with calcium chloride. It was acid to litmus, boiled at 192-193°, and its titration value represented a molecular weight of 114. These properties identify the substance as diethylacetic acid, boiling point 195°, molecular weight 116. It is obviously a secondary product resulting from loss of carbon dioxide from diethylmalonic acid, the direct product of hydrolysis.

Evaporation of the aqueous layer of the reaction mixture left a white crystalline residue. After washing this with absolute alcohol, the yield was 0.4472 g. A portion was analyzed and found to contain 66.22% Cl; calculated for NH₄Cl, 66.36% Cl. The ammonium chloride actually recovered and analyzed accounts for 94.5% of the nitrogen present in the original material. If, however, the substance had been the isomeric N-alkyl derivative, hydrolysis by hydrochloric acid would have yielded ethylamine hydrochloride instead of ammonium chloride. The alcoholic washings from the ammonium chloride gave no picronic acid reaction for ethylamine. From another preparation which had been distilled at 260-265° under atmospheric pressure, a very small amount of ethylamine was obtained on hydrolysis, barely enough for analysis of the chloroplatinate and melting point of the picronate. The amount was estimated at less than 2% of the total nitrogen. The recovery of ammonium chloride, as before, was almost quantitative.

It is thus apparent that the substance is actually an oxygen ether with alkyl linked to oxygen and not to nitrogen. The isomeric N-alkyl deriva-

tive if present occurs in mere traces. The tetraethoxy and tetrabutoxy derivatives obtained as above are of especial interest as representing the first known derivatives of the hypothetical tautomeric barbital. They possess in addition to ether linkages in positions 4 and 6, an acetal structure in the 2-position. Hence they may be regarded as acetals of the ethers of enolic barbital. The isomeric 1,3,5,5-tetraethylbarbituric acid, but without the acetal grouping in position 2, has been prepared by Fischer and Dilthey⁴ from ethyl diethylmalonate and *sym.*-diethylurea. This also was a high-boiling liquid.

Summary

2,2,4,6-Tetrachloro-5,5-diethyldihydropyrimidine, a product obtained by chlorination of barbital with phosphorus pentachloride, reacts with sodium alkoxides to form the corresponding 2,2,4,6-tetraalkoxy-5,5-diethyldihydropyrimidines. Hydrolysis by concentrated hydrochloric acid converts the tetraalkoxy derivative into diethylacetic acid and ammonium chloride, the latter in almost quantitative yield, showing that the alkyl is actually linked to oxygen. These tetraalkoxy derivatives represent acetals of the ethers of a hypothetical enolic barbital.

A series of 2,4,6-trialkoxo derivatives was also prepared from 2,4,6-trichloro-5-*sec.*-butylpyrimidine.

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[CONTRIBUTION FROM THE SWAN-MYERS DIVISION OF ABBOTT LABORATORIES]

STUDIES ON POLLEN AND POLLEN EXTRACTS. VII. A GLUCOSIDE FROM CERTAIN GRASS POLLENS

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The existence of glucosides in pollen has been previously recognized. Heyl¹ found the coloring substances of ragweed pollen to be entirely glucosidic, and was able to isolate and identify glucosides of quercetin and isorhamnetin in the alcoholic extract. More recently, Fukuda² has isolated a glucoside of isorhamnetin from an alcoholic extract of the pollen of *Typha angustata* Bory et Chaub.

A new glucoside has been isolated in this Laboratory from two grass pollens. The first preparation of this compound was made from the pollen of orchard grass (*Dactylis glomerata* L.) and for this reason we are proposing the name "dactylin." An identical compound was found to separate from an extract of timothy pollen (*Phleum pratense* L.).

⁴ Fischer and Dilthey, *Ann.*, **335**, 349 (1904).

¹ F. W. Heyl, *THIS JOURNAL*, **41**, 1285-1289 (1919).

² Masao Fukuda, *Chem. Abstracts*, **22**, 1993 (1928), from *Bull. Soc. Chem. Japan*, **3**, 53-56 (1928).