DIOXOLANIUM SALTS

SYNTHESIS AND REACTIONS WITH SOME NUCLEOPHILIC REAGENTS

L. V. Mezheritskaya and G. N. Dorofeenko

A new method was developed for the synthesis of dioxolanium salts by the condensation of 1,2-glycols of the pinacol series with aliphatic acid anhydrides in the presence of perchloric acid. The dioxolanium ring is opened to form monoacylates of the starting pinacols under the influence of water, alcohol, and ammonia. A method was developed for the acetylation of aromatic compounds by dioxolanium salts.

Dioxolanium salts are a peculiar class of nonaromatic salts in which the cation is a carbonium-ioncontaining $\int_{C}^{1+i} d$ system. The presence of a stabilized carbonium ion in the molecules of dioxolanium salts makes them convenient subjects for a study of the reactivity and behavior of carbonium ions. In addition, the high electrophilicity of the dioxolanium salts opens up prospects for their use for various synthetic ends.

The known methods for the synthesis of dioxolanium salts are based on removal of an alkoxy group or a hydride ion from 1,3-dioxolanes [1,2] or on the cyclization of β -chloro- or β -alkoxyethyl esters of carb-oxylic acids [1,3].

We propose a simple method for the synthesis of dioxolanium salts by the acylation of 1,2-glycols of the pinacol series by aliphatic acid anhydrides in the presence of 70% perchloric acid [4] via the scheme



TABLE 1. Dioxolanium Perchlorates (IV).

Com- pound	R'=R"	R	mp (from acetic acid)	Empirical formula	Found, %			Calc., %			Yield.
					с	н	CI	с	н	СІ	%
a b c d e f g	(CH ₂) ₅ (CH ₂) ₅ (CH ₂) ₅ (CH ₂) ₅ (CH ₂) ₅ CH ₃ CH ₃ CH ₃	CH_3 C_2H_5 C_3H_7 $CH(CH_3)_2$ C_4H_9 CH_3 CH_5 CH_5	112 110 109 107 106 133 129	$C_{14}H_{23}ClO_6$ $C_{15}H_{25}ClO_6$ $C_{16}H_{27}ClO_6$ $C_{16}H_{27}ClO_6$ $C_{17}H_{29}ClO_6$ $C_8H_{15}ClO_6$ $C_9H_{17}ClO_6$	51,81 53,00 54,99 55,03 55,78 39,75 42,13	7,41 7,61 7,64 8,02 8,06 6,16 6,53 6,06	10,76 10,12 10,02 10,36 9,73 14,38 13,55	52,08 53,49 54,77 55,96 39,59 42,11	7,13 7,48 7,75 7,75 8,01 6,23 6,67 7,07	10,95 10,52 10,10 10,10 9,71 14,61 13,81	$63 \\ 50 \\ 75 \\ 65 \\ 64 \\ 93 \\ 40 \\ 72$

Rostov-on-Don State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1023-1026, August, 1971. Original article submitted September 17, 1970.

© 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00. In the first step of the reaction, the acylium cation (I) reacts with the pinacol to form its monoacylate (II), which splits out a water molecule in acid media and is converted to a carbonium ion (III). The latter attacks the nucleophilic oxygen of the ester grouping to form a dioxolanium salt (IV).

The reaction proceeds under mild conditions during the slow addition of an equimolecular amount of 70% perchloric acid to a solution of the pinacol in excess acid anhydride. Data on the yields and properties of the salts obtained are presented in Table 1.

The IR spectra of all of the synthesized dioxolanium salts contain two intense bands at 1529-1536 and 1495-1508 cm⁻¹. Since absorption in this region is not characteristic for dioxolane derivatives of this type

[5], the indicated frequencies can be assigned to the vibrations of the 0 regulation of the dioxolanium

salt molecule. In addition, bands corresponding to the vibrations of alkyl radicals (1380-1391, 1174, and 740-770 cm⁻¹), methylene groups in the cyclohexyl substituents (1438-1442 cm⁻¹), and the ClO_4^- anion (1096-1110 cm⁻¹) are present in the spectra of the dioxolanium salts.

It might have been expected that pinacol rearrangement should have occurred under the conditions used to carry out the reaction under consideration. However, we could not obtain data that constituted evidence in favor of this conversion during the synthesis of the dioxolanium salts.

The rate of the pinacol rearrangement is probably considerably less than the rate of acylation of the hydroxyl group by the acyl cation, as a result of which the dioxolanium salt forms.

The pinacol rearrangement does occur in the case of the less active (in comparison with the acyl cation) diethoxycarbonium ion [6]. We therefore isolated only 2,6-di-tert-butylpyrylium perchlorate (V) in 18% yield in an attempt to obtain the 2-unsubstituted dioxolanium salt by the reaction of pinacol with ethyl orthoformate in the presence of perchloric acid:



In this case, the pinacolone formed as a result of the pinacol rearrangement apparently reacts, as previously demonstrated [7,8], with the diethoxycarbonium ion to give a γ -unsubstituted 2,6-di-tert-butyl-pyrylium salt.

Under the influence of weak nucleophilic reagents (water, aqueous alcohol, and ammonium hydroxide), the dioxolanium salts react readily with opening of the heteroring to form quantitative yields of the mono-acylates (II) of the starting pinacols.

However, the reactions of the dioxolanium salts in which the primary cyclic structure is retained are of greatest interest. These sorts of transformations have not been studied adequately at all and are known only in the case of the nucleophilic addition of alkoxy or cyano groups to the 2-position of the heteroring [1].



We have detected a new reaction of dioxolanium salts with compounds that have aromatic structures. It was shown that the dioxolanium salts are capable of electrophilic substitution with activated aromatic compounds, similar to acylium and carbonium ions [9,10].

The reaction proceeds through the formation of 2,2-disubstituted dioxolanes (cyclic ketals), the acid hydrolysis of which leads to the corresponding ketones.

Thus the corresponding acetophenones were obtained by refluxing equimolecular amounts of 2,4,4,5,5-pentamethyldioxolanium perchlorates with phenols (anisole, resorcinol dimethyl ether) in acetic acid for 1 h with subsequent hydrolysis of the reaction mixture with 5% hydrochloric acid.

Some heterocyclic compounds (indole) react similarly.

The yields of the ketones range from 30 to 67%. 2,4-Dimethoxyacetophenone is obtained in lower yields via this method, which is probably explained by the steric effect of the methoxy group in the ortho position relative to the carbon atom undergoing attack.

Further study of this reaction will make it possible to establish the range of its application.

EXPERIMENTAL

<u>2,4,4,5,5-Pentamethyldioxolanium Perchlorate (IVf)</u>. A 5.1 ml (0.05 mole) sample of acetic anhydride was added to 1.13 g (0.005 mole) of pinacol hexahydrate, and 0.5 ml (0.005 mole) of 70% perchloric acid was added dropwise with cooling. After 10-15 min, the mixture was diluted with ether, and the product was filtered and crystallized with glacial acetic acid to give 1.13 g (93%) of a product with mp 133 deg. IR spectrum: 1533, 1505, 1388, 1099, 945 cm⁻¹.

Compounds IVg,h were similarly obtained.

<u>2,6-Di(tert-butyl)pyrylium Perchlorate (V)</u>. A 0.6 ml (0.006 mole) sample of 70% perchloric acid was added to a mixture of 1.36 g (0.006 mole) of pinacol hydrate and 20 ml of ethyl orthoformate, and the mixture was heated on a water bath (80 deg) for 10 min. The mixture was cooled and diluted with ether, and the resulting colorless crystals were filtered and recrystallized from acetic acid to give 0.3 g (18%) of a product with mp 224-225 deg. IR spectrum: 1626, 1550, 1450, 1100 cm⁻¹. Found: C 53.62; H 9.52; Cl 11.52%. C₁₃H₂₁ClO₅. Calculated: C 53.34; H 9.19; Cl 12.13%.

Dicyclohexylpinacol Monoacetate. Water (10 ml) and 5 ml of ether were added to 0.65 g (0.002 mole) of IVa, and the mixture was shaken until the substance dissolved completely in the ether. The ether solution was separated and evaporated to give 0.45 g (94%) of light-yellow crystals with mp 59-60 deg (from aqueous alcohol). IR spectrum: 3425, 1707, 1442, 1373, 1244, 1152 cm⁻¹. Found: C 69.92; H 10.03%. $C_{14}H_{24}O_{3}$. Calculated: C 69.96; H 10.06%.

The following compounds were similarly obtained. Dicyclohexylpinacol monopropionate was obtained in 94% yield and had mp 44-46 deg. IR spectrum: 3394, 1709, 1443, 1374, 1207, 1146, 750 cm⁻¹. Found: C 71.73; H 10.60%. $C_{16}H_{28}O_3$. Calculated: C 71.60; H 10.51%. Dicyclohexylpinacol monobutyrate was obtained in 92% yield and had mp 20 deg. IR spectrum: 3400, 1707, 1451, 1374, 1193, 1153, 911 cm⁻¹. Found: C 71.98; H 10.85%. $C_{17}H_{30}O_3$. Calculated: C 72.29; H 10.70%. Pinacol monoacetate was obtained in 80% yield and had bp 38 deg (5 mm). IR spectrum: 3455, 1700, 1442, 1380, 1250, 1151, 945 cm⁻¹. Found: C 60.27; H 10.12%. $C_8H_{16}O_3$. Calculated: C 59.97; H 10.06%.

<u>p-Methoxyacetophenone</u>. Anisole [1.1 ml (0.01 mole)] was added to a hot solution of 2.43 g (0.01 mole) of IVf in 10 ml of glacial acetic acid. The mixture was refluxed for 1 h, 20 ml of 5% hydrochloric acid was added, and the mixture was refluxed for another 25-30 min. It was then cooled and extracted with ether. The ether extract was washed with sodium carbonate and water and dried with anhydrous sodium sulfate. The solvent was removed by distillation, and the residue was vacuum distilled to give 1 g (67%) of p-meth-oxyacetophenone with bp 135 deg (15 mm) and mp 38 deg. The 2,4-dinitrophenylhydrazone had mp 220 deg [11].

<u>3-Acetylindole</u>. This was similarly obtained from 1.2 g (0.005 mole) of IVf and 0.6 g (0.005 mole) of indole. The crystalline reaction product that precipitated after hydrolysis was filtered, washed with ether, and recrystallized from benzene to give 0.4 g (51%) of a product with mp 190 deg. The oxime had mp 143-144 deg [11].

2,4-Dimethoxyacetophenone Oxime. This was similarly obtained from 1.2 g (0.005 mole) of IVf and 0.7 ml (0.005 mole) of resorcinol dimethyl ether. The ketone that formed after hydrolysis of the interme-

diate dioxolane was converted to 0.3 g (31%) of the oxime with mp 124 deg (mp 125 deg [11]).

The IR spectra of mineral oil pastes of the synthesized samples were recorded with an IKS-14 spectrophotometer from 600 to 3600 cm^{-1} (LiF and NaCl prisms).

LITERATURE CITED

- 1. H. Meerwein, K. Bodenbenner. P. Borner, F. Kunert, and K. Wunderlish, Lieb. Ann., 632, 38 (1960).
- 2. H. Meerwein, V. Hederish, H. Morschel, and K. Wunderlish, Lieb. Ann., 635, 1 (1960).
- 3. H. Meerwein and K. Wunderlish, Angew. Chem., 69, 481 (1957).
- 4. G. N. Dorofeenko and L. V. Mezheritskaya, Zh. Obshch. Khim., 38, 1192 (1968).
- 5. Bergmann and Pinchas, Rec. Trav. Chim., 71, 161 (1952).
- 6. L. S. Povarov, Usp. Khim., <u>34</u>, 1491 (1965)
- 7. V. V. Mezheritskii and G. N. Dorofeenko, Zh. Organ. Khim., 3, 1533 (1967).
- 8. V. V. Mezheritskii and G. N. Dorofeenko, Khim. Geterotsikl. Soedin., No. 2, 232 (1970).
- 9. G. N. Dorofeenko, Yu. A. Zhdanov, V. I. Dulenko, and S. V. Krivun, Perchloric Acid and Its Compounds in Organic Synthesis [in Russian], Izd. Rost. Univ., (1965), pp. 47, 53.
- 10. S. V. Krivun, Dokl. Akad. Nauk SSSR, 180, 615 (1968).
- 11. Dictionary of Organic Compounds, Oxford University Press (1966).