SYNTHESIS OF cis-5-ARYL-4-AROYL-1,3-DIOXOLANES

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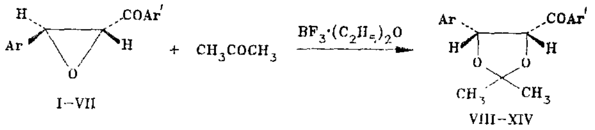
UDC 547.729.7:541.634

The reaction of trans-3-aryl-2-aroyloxiranes containing electron-acceptor substituents in the aryl group with acetone under acid-catalysis conditions gives the corresponding cis-1,3-dioxolanes.

trans-3-Aryl-2-acyloxiranes containing electron-donor or weak electron-acceptor substituents in the aryl group react with acetone in the presence of catalytic amounts of boron trifluoride etherate to form mixture of cis- and trans-2,2-dimethyl-5-aryl-4-benzoyl-1,3-dioxolanes [1, 2]. It has been noted that the ratio between the cis and trans isomers in the mixture is determined by the reaction mechanism, which is close to S_N1, and the simultaneous isomerization of the cis-1,3-dioxolanes to the trans isomers under the conditions of the reaction [2, 3].

In the present work we studied the interaction of a number of trans-3-aryl-2-aroyloxiranes (I-VII) containing electron-aceptor substituents in the aryl group with acetone in the presence of boron trifluoride etherate. In all cases, cis-2,2-dimethyl-5-aryl-4-aroyl-1,3-dioxolanes (VIII-XIV) (Table 1) were obtained as the only reaction product.



I–VII

VIII–XIV

I, VIII Ar=4-$CH_3OCOC_6H_4$, Ar′=C_6H_5; II, IX Ar=2,4-$Cl_2C_6H_3$, Ar′=C_6H_5; III, X Ar=3-$NO_2C_6H_4$, Ar′=C_6H_5; IV, XI Ar=4-$NO_2C_6H_4$, Ar′=C_6H_5; V, XII Ar=4-$NO_2C_6H_4$, Ar′=4-$CH_3OC_6H_4$; VI, XIII Ar=4-$NO_2C_6H_4$, Ar′=4-$CH_3C_6H_4$; VII, XIV Ar=4-$NO_2C_6H_4$, Ar′=4-ClC_6H_4

The reaction of 3-aryl-2-aroyloxiranes with ketones in the presence of Lewis acids may be viewed as nucleophilic substitution at the benzyl center. The mechanism of a nucleophilic substituent reaction in substrates of the benzyl type is known [4] to be strongly dependent on the electronic nature of the substituents in the aromatic ring. Strong electron-acceptor substituents shift the reaction mechanism into the S_N2 region, and, as a result, only cis-1,3-dioxolanes VIII-XIV form from trans-oxiranes I-VII in our case. The isomerization of the cis-1,3-dioxolanes to the corresponding trans isomers [2] is practically not observed in the presence of the strong electron-acceptor substituents in the aromatic ring of the benzyl center of 1,3-dioxolanes VIII-XIV.

TABLE 1. 1,3-Dioxolanes VIII-XIV

Compound	Reaction time, days	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
			C	H	N		C	H	N	
VIII	1	180—181	70,6	6,1	—	$C_{20}H_{20}O_5$	70,4	5,9	—	80
IX	3	127—128	61,9	4,7	—	$C_{18}H_{16}Cl_2O_3$	61,6	4,6	—	64
X	6	127—128	66,3	5,4	4,6	$C_{18}H_{17}NO_5$	65,9	5,2	4,3	75
XI	9	157—158	66,2	5,3	4,6	$C_{18}H_{17}NO_5$	65,9	5,2	4,3	75
XII	11	137—139	63,9	5,5	4,2	$C_{19}H_{19}NO_6$	63,7	5,4	3,9	59
XIII	13	144—145	67,0	5,8	4,3	$C_{19}H_{19}NO_5$	66,7	5,6	4,1	68
XIV	14	164—165	60,0	4,7	4,3	$C_{18}H_{16}ClNO_5$	59,8	4,5	3,9	28

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TABLE 2. Proton-Magnetic-Resonance Spectra of 1,3-Dioxolanes VIII-XIV

Compound	$\delta_{2\text{-}CH_3}$ (s), ppm	$\delta_{4\text{-}H}$ (d), ppm	$\delta_{5\text{-}H}$ (d), ppm	J_{45}, Hz	$\delta_{R(Ar)}$, ppm	$\delta_{H(Ar)}$(m), ppm
VIII	1,57; 1,77	5,83	6,18	7,8	3,84	7,08—7,80
IX	1,54; 1,77	5,88	6,14	7,8	—	6,97—7,74
X	1,61; 1,84	5,90	6,20	7,8	—	7,24—8,00
XI	1,57; 1,84	5,54	5,84	7,8	—	7,10—7,85
XII	1,57; 1,77	5,84	6,14	7,8	3,80	6,74—8,00
XIII	1,57; 1,77	5,87	6,17	7,8	2,30	7,07—8,04
XIV	1,60; 1,80	5,90	6,17	7,8	—	7,27—8,05

The structure of 1,3-dioxolanes VIII-XIV was confirmed by the PMR spectra (Table 2). The spin—spin coupling constant of the 4- and 5-H protons in these 1,3-dioxolanes is equal to 7.8 Hz, which is characteristic of cis-2,2-dimethyl-5-aryl-4-benzoyl-1,3-dioxolanes [2].

EXPERIMENTAL

The PMR spectra were obtained on Varian HA-100D-15 and JNM-PS-100 spectrometers with the use of 5-10% solutions of the samples in $CDCl_3$ or acetone-d_6 with HMDS as an internal reference. The course of the reaction and the individuality of the compounds obtained were monitored with the aid of TLC on Silufol UV-254 plates (3:2:1 ether—hexane—chloroform).

trans-3-Aryl-2-aroyloxiranes I-IV and VII. A solution of 0.1 mole of the aromatic aldehyde and 0.1 mole of phenacyl bromide in 100 ml of absolute ethanol is given a dropwise addition over the course of 30 min of a solution of 0.1 mole of sodium ethoxide in 25 ml of absolute ethanol at 10-15°C. The reaction mixture is stirred for 15 min and diluted with water, dried, and crystallized from acetone or ethanol. The following oxiranes are obtained: I [85% yield, mp 117-118°C. PMR spectrum (acetone-d_6): 3.97 (3H, s, CH_3OOC), 4.40 (1H, d, J = 2 Hz, CH), 4.70 (1H, d, J = 2 Hz, CH), 7.57-8.24 (9H, m, arom.). Found: C, 71.9; H, 5.3%, Calculated for $C_{17}H_{14}O_4$: C, 71.7; H, 5.1%], II [74% yield, mp 103-104°C. PMR spectrum ($CDCl_3$): 4.12 (1H, d, J = 2 Hz, CH), 4.31 (1H, d, J = 2 Hz, CH), 7.20-8.11 ppm (8H, m, arom). Found: C, 61.9; H, 3.6; Cl, 24.0%. Calculated for $C_{15}H_{10}Cl_2O_2$: C, 61.5; H, 3.4; Cl, 24.2%], III (70% yield, mp 117-118°C [5]), IV (80% yield, mp 150-151°C [6]), VII (85% yield, mp 159-160°C [6]).

trans-3-(4-Nitrophenyl)-2-aroyloxiranes V and VI. A solution of 0.1 mole of the respective chalcone in a mixture of 200 ml of ethanol and 200 ml of dioxane is given an addition of a solution of 1 g of sodium hydroxide in 15 ml of ethanol and then a dropwise addition of 40 ml of 30% hydrogen peroxide at 40-45°C. At the conclusion of the reaction (TLC) the mixture is diluted with water, and the precipitate is separated, washed with water, dried, and crystallized from chloroform. Oxiranes V (75% yield, mp 145-146°C [6]) and VI (70% yield, mp 149-150°C [6]) are obtained.

cis-5-Aryl-aroyl-1,3-dioxolanes VIII-XIV. A solution of 0.01 mole of oxirane 1-VII in 75-100 ml of acetone is given an addition of 1-2 ml (0.008-0.016 mole) or boron trifluoride etherate. At the conclusion of the reaction (TLC) the solution is evaporated to 1/3 of its original volume, neutralized by a solution of sodium hydroxide in methanol, and diluted with water, and the precipitate formed is separated, washed with water and isopropanol, dried, and crystallized from isopropanol or a mixture of the latter with acetone.

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BISACYLATION OF THE ANHYDRIDE AND ESTERS OF 4-METHYL-1,2,3,4-TETRAHYDROPHTHALIC ACID

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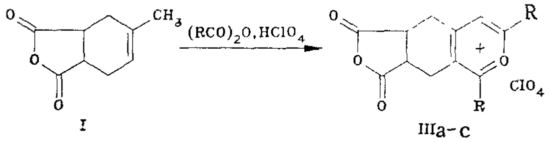
UDC 547.584'833.3'814

The bisacylation of the anhydride and esters of 4-methyl-1,2,3,4-tetrahydrophthalic acid by anhydrides of carboxylic acids in the presence of perchloric acid results in the formation of derivatives of 1,3-dialkyl-6, 7-dicarboxy-5,6,7,8-tetrahydro-2-benzopyrylium salts. Some reactions of the salts obtained, including their recyclization under the action of nucleophiles, have been studied. A convenient preparative method for the synthesis of 6,7-dicarboalkoxy-5,6,7,8-tetrahydroixoquinolines has been developed.

The increased interest in pyrylium salts in the past decade has resulted in the appearance of a large number of publications on their synthesis and reactions. The advances in this field have been reflected in several reviews, among which we should mention the most extensive [1-3].

In our opinion, one of the promising areas for the further development of the chemistry of pyrylium salts is the study which we began of the synthesis paths and the properties of functionally substituted pyrylium salts [4-7].

In order to further develop this work, as well as to synthesize new biologically active compounds, we studied the bisacylation of functionally substituted cyclic olefins, viz., the anhydride (I)* and esters (II) of 4-methyl-1,2,3,4-tetrahydrophthalic acid, which are functional derivatives of 1-methycyclohexene. The bisacylation of 1-methylcyclohexene itself was previously carried out by Praill and Whithear [9], who obtained 1,3-dimethyl-5,6,7,8-tetrahydro-2-benzopyrylium perchlorate with a 30% yield. We obtain pyrylium salts III with approximately the same yield by acylating I with carboxylic acid anhydrides in the presence of perchloric acid.



III a $R=CH_3$, b $R=C_2H_5$, c $R=C_3H_7$

The structures of perchlorates III were confirmed by their IR spectra, which displayed the characteristic absorption bands of a cyclic anhydride (1860 and 1790 cm^{-1}) and a pyrylium cation (1640, 1550, 1510, and 1460 cm^{-1}). When compound IIIa is heated in methanol, it is converted into dimethyl ester IVa, which is converted under the action of ammonium into the corresponding derivative of 5,6,7,8-tetrahydroiaozuinoline (Va). The data from the PMR spectrum of compound Va [4] unequivocally prove the structures of salts III, whose PMR spectra could not be obtained due to their poor solubility.

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*For a preliminary report, see [4].

Institute of Physical Organic Chemistry and Carbon Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk 340114. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1318-1321, October, 1984. Original article submitted December 14, 1983; revision submitted March 12, 1984.

0009-3122/84/2010-1078$08.50