REACTION OF 6, 8-DI-tert-BUTYLSPIRO[4,5]DECA-1-OXA-5, 8-DIENE-2, 7-DIONE WITH ACID AGENTS

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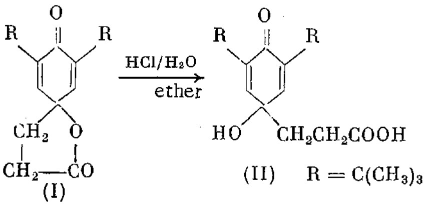
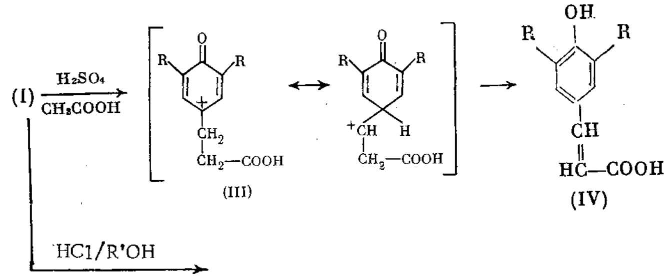
Ketolactone (I) is an interesting object for studying the rules of the dienone–phenol transformations of cyclohexadienones (under the influence of acid agents). Like any cyclohexadienone, this compound in the presence of acid agents can undergo the dienone–phenol rearrangement. At the same time the presence of a lactone group in the (I) molecule should substantially affect the character of the processes that take place here. In this connection it seemed important to ascertain the rules for the reaction of (I) with acid agents. It was established that, depending on the "hardness" of the acid, the results of their action on (I) can be different. Here an opening of the lactone ring occurs initially, with a retention of the cyclohexadienone structure. Thus, in aqueous-ether HCl solution the lactone group of (I) is opened to give quinol (II), which is stable under the given conditions.

Aromatization of the system occurs when spirodienone (I) is treated with a mixture of sulfuric and acetic acids, but in a different direction than in the classical dienone–phenol rearrangement, which proceeds by the mechanism of anionotropic shift of one of the geminal substituents



(I) (II) $R = C(CH_3)_3$

in the six-membered ring [1]. In this case the sole reaction product is acid (IV), which is apparently formed by the isomerization of the intermediate carbocation (III) to a cation of the benzyl type (see next scheme). In the PMR spectrum of (IV) the vinyl protons are split into a doublet with a J constant=14 Hz. This gives reason to assume that the trans-cinnamic acid (IV) is formed. Esters (V) and (VI) are formed when an alcohol solution of spirodienone (I) is treated with HCl, in which connection an increase in the yield of (VI) is facilitated by a decrease in the reaction temperature. These data are in good agreement with a possible isomerization of cation (III) in the six-membered ring and subsequent nucleophilic attack by either chlorine ion or HCl. The formation of esters (V) and (VI) in the given case can be explained by the esterification of the corresponding carboxylic acid. The discussed transformations of spirodienone (I) in acid media can be depicted by the following scheme:



(III) (IV)

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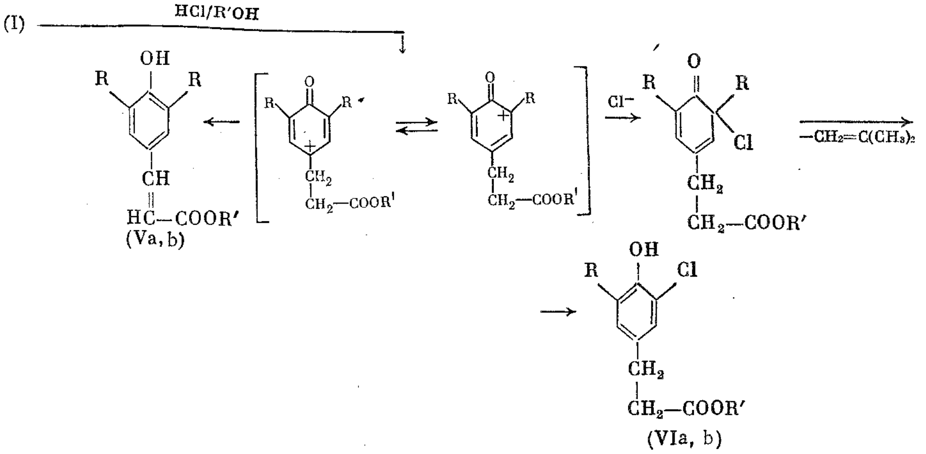

$R = C(CH_3)_3$; R′ = Me (a); Et (b)

The fact of cleaving a tert-butyl group in a quinoid chloride in acid media was described previously [2].

EXPERIMENTAL

The PMR spectra were taken on a JNM-60 MHz spectrometer (internal standard = HMDS); the IR spectra were taken on a UR-20W spectrometer in CCl_4 solution.

4-Hydroxy-4-(2-carboxyethyl)-2,6-di-tert-butylcyclohexa-2,5-dien-2-one (II). A stream of HCl was passed for 5 min into a solution of 2.76 g (0.01 mole) of (I) [3] in 60 ml of water-saturated ether, after which the mixture was kept for 10 h at 20°C, neutralized, and the ether was distilled off. We obtained 2.59 g (88%) of (II), mp 150-152° (benzene – methanol), and IR spectrum (CCl_4, ν, cm^{-1}): 1655, 1670, 1720 (C = O). Ultraviolet spectrum (hexane, λ_{max}): 242 nm (log 3.94). PMR spectrum (CCl_4, δ, ppm): 1.2 s (18 H), 1.38 m (2H), 2.27 m (2H), 6.40 s (2H). Found: C 69.50; H 8.85%, $C_{17}H_{26}O_4$. Calculated: C 69.36; H 8.90%.

trans-4-Hydroxy-3,5-di-tert-butylcinnamic acid (IV). To a solution of 2.76 g (0.01 mole) of (I) in 50 ml of AcOH was added 1 ml of H_2SO_4, the reaction mixture was kept for 40 min at 90°, cooled, treated with 150 ml of water, and the precipitate was separated and recrystallized from a 2 : 1 benzene – hexane mixture to give 2.72 g (~100%) of (III), mp 218-219°, cf. [4].

Methyl Ester of trans-4-Hydroxy-3,5-di-tert-butylcinnamic Acid (Va) and Methyl Ester of 3-tert-Butyl-5-chloro-4-hydroxyphenylpropionic Acid (VIa). Gaseous HCl was passed for 10 min into a solution of 2.76 g (0.01 mole) of (I) in 60 ml of MeOH, the mixture was kept for 2 h at 60°, cooled, treated with 150 ml of water, and the obtained oil was separated. Recrystallization from hexane gave 2.55 g (88%) of (Va), mp 117-118°, cf. [5]. Fractional distillation of the mother liquor in vacuo gave 0.2 g (8%) of (VIa), bp 125° (1 mm), n_D^{20} 1.5190; d_{20}^4 1.4279. Infrared spectrum (CCl_4, ν, cm^{-1}): 3640, 3500 (OH), 1745 (C = O). Ultraviolet spectrum (hexane, λ_{max}): 279 nm (log 3.36). PMR spectrum (CCl_4, δ, ppm): 1.25 s (9H), 2.48 m (4H), 3.42 s (3H), 6.18 s (OH), 6.80 s (H), 6.84 s (H). Found: C 62.43; H 7.37; Cl 12.88%. $C_{14}H_{19}ClO_3$. Calculated: C 62.10; H 7.07; Cl 13.01%.

When the reaction is run under the conditions of cooling the reaction mixture in the range from −5 to −10°, the yield of (VIa) is 85%.

Ethyl Ester of trans-4-Hydroxy-3,5-di-tert-butylcinnamic Acid (Vb) and Ethyl Ester of 3-tert-Butyl-5-chloro-4-hydroxyphenylpropionic Acid (VIb). In a similar manner, from 2.76 g (0.01 mole) of (I) and HCl in EtOH at 60°C we obtained 2.23 g (72%) of (Vb), mp 154-155°. PMR spectrum (CCl_4, δ, ppm); 1.45 s (18H), 1.32 m (3H), 4.26 m (2H), 5.40 s (OH), 6.15 d (H), 7.31 s (2H), 7.72 d (H), J = 14 Hz, cf. [5]. Fractional distillation in vacuo gave 0.57 g (20%) of (VIb) as a viscous liquid with bp 131° (1 mm). PMR spectrum (CCl_4, δ, ppm): 1.25 s (9H), 2.61 m (4H), 1.12 m (3H), 4.00 m (2H), 5.97 s (OH), 6.80 s (H), 6.84 s (H). Found: C 63.52; H 7.84; Cl 12.21%. $C_{15}H_{21}ClO_3$. Calculated: C 63.26; H 7.43; Cl 12.45%.

CONCLUSIONS

1. The action of acid agents on 6,8-di-tert-butylspiro[4.5]deca-1-oxa-5,8-diene-2,7-dione results in the initial opening of the lactone ring with a retention of the cyclohexadiene structure, and then the isomerization of the thus formed carbonium ion with migration of the carbonium ion center in two directions, and specifically in the six-membered ring and in the side chain.

2. The migration direction of the intermediately formed carbonium ion depends on the temperature.

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HYDRATION OF 3-METHYL-3-NORCARENE EPOXIDES UNDER ACID AND BASIC CATALYSIS CONDITIONS

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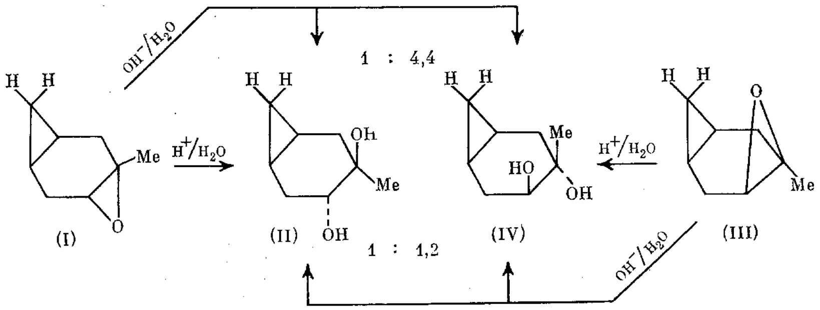
Rearrangement of the bicyclo[4.1.0]heptane system to the bicyclo[3.1.0]hexane system is characteristic for the 3,4-disubstituted carane derivatives with a β-oriented substituent on C^3, which rearrangement proceeds via the transannular participation of the cyclopropane ring (CPR) as the internal nucleophile under electrophilic catalysis conditions [1]. A convenient object for observing the rearrangement is cis-3,4-epoxycarane in the acid hydration reaction. For the isomeric trans-3,4-epoxycarane the product with an altered carbon skeleton was detected in insignificant amount [2]. To ascertain in this structural transformation the role of geminal methyl groups in the CPR we studied the behavior of the model 3-methyl-3-norcarene (3-MNC) epoxides [3], devoid of geminal substituents, under hydration conditions.

The hydration of 3-MNC-3 trans-epoxide (I), which was run in the presence of an acid, gives a mixture of 3-methyl-4-norcaranones (22%) [4] and a crystalline diol. Its bicyclic structure and secondary-tertiary nature of the OH groups are in agreement with the IR and PMR spectral data. The conversion of the diol monotosylate to the cis-epoxide (III) by treatment with methanolic caustic solution confirms for it the structure of 3β,4α-dihydroxy-3-methylnorcarane (II). The hydration of cis-epoxide (III) under the same conditions gave mainly a liquid diol, in which, according to the PMR spectrum, is present a CPR, and also a secondary and a tertiary OH group. Due to the difficulty of obtaining the monotosylate, we were unable to establish its structure by the method used for (II).



By analogy with the behavior of the carane epoxide [5] in the corresponding reaction, the structure of 3α,4β-dihydroxy-3-methylnorcarane (IV) or of a rearranged product can be proposed for the diol; the structure of 3β,4β-dihydroxy-3-methylnorcarane is excluded, since the corresponding product was synthesized earlier [6]. The structure of (IV) for the isolated diol can be confirmed by counter synthesis from the trans-epoxide (I), using alkaline conditions for the hydration, since it is known [7] that the predominant opening of the epoxide ring in acid and alkaline media goes at different C–O bonds. Actually, when (I) is heated in aqueous alkali the same liquid diol (IV) and diol (II) are formed in a 4.4:1 ratio, which confirms the structure of (IV) for the first

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