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PHOTOCHEMISTRY OF NONAROMATIC HETEROCYCLES.

COMMUNICATION 1. PHOTOTRANSFORMATIONS OF 2,2-DIMETHYLTETRAHYDROPYRAN-4-ONE IN METHANOL IN THE PRESENCE AND ABSENCE OF TITANIUM TETRACHLORIDE

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The photoreaction of aliphatic ketones with methanol in the presence of $TiCl_4$ leads to primary—tertiary 1,2-glycols; ketals of these 1,2-glycols with the starting ketones are formed as by-products in this reaction [1, 2]. To obtain derivatives of tetrahydropyran suitable for the synthesis of spiro-bisheterocyclic systems, we studied the photoreaction of 2,2-dimethyltetrahydropyran-4-one [1] with NaOH in the presence of $TiCl_4$.

During the irradiation of a 0.1 M solution of ketone (I) in MeOH with an equimolar amount of $TiCl_4$ (quartz, 18-22°C, argon), a mixture of isomeric ketals (II) and (II') in a ratio of 1:1 was obtained in a yield of 42%, as the only reaction product (data of PMR and GLC analyses). The expected glycol (III) could not be obtained under these conditions. Attempts to obtain glycol (III) by suppressing the ketalization by adding bases (MeONa or pyridine, cf. [1, 2]) proved to be unsuccessful.

The structure of the spiroketals (II) and (II') follows from the spectral data, obtained directly with respect to their mixture. In the PMR spectrum of the mixture a double set of signals is observed, corresponding to the CH_3 groups and protons at C^3, C^5, and C^6, while the protons of the CH_2 group of the dioxolane ring resonate in the form of an AB quartet (Table 1). In the mass spectrum of the mixture of (II) and (II') there are intense ions with m/z 270 M^+, 255 $[M - CH_3]^+$, 184 [ion a], and 128 [ion b]. During the hydrolysis of the mixture by 80% AcOH, glycol (III) was obtained in a 60% yield. Oxidation of (III) with $NaIO_4$ gives ketone (I) in a yield of 85%.

Unexpectedly, the yield of (III) was found to be considerably better in an experiment with the irradiation of a solution of ketone (I) in the absence of $TiCl_4$. In this case, two products were obtained, glycol (III) and 2,2-dimethyltetrahydropyran-4-ol (IV), in yields of 43 and 42.5%, respectively. Alcohol (IV) was identified by spectral data and by comparison with a sample obtained by the reduction of (I) with $NaBH_4$. The structure of glycol (III),

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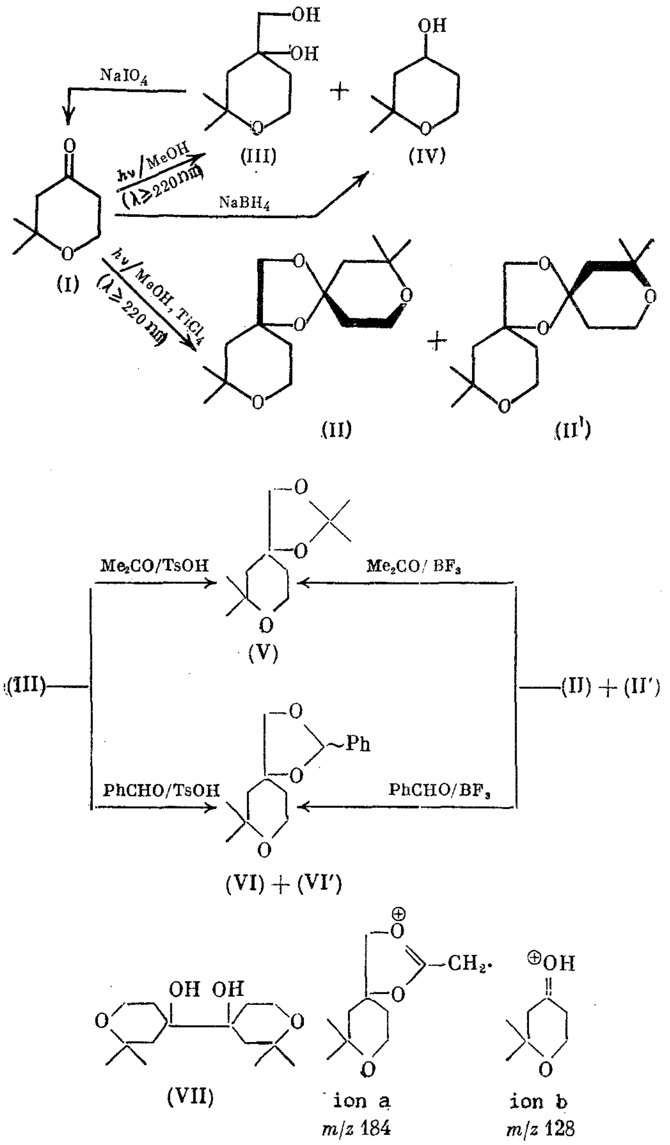
TABLE 1. IR and PMR Spectra of 4-Hydroxymethyl-2,2-dimethylpyran-4-ol (III) and Its Derivatives

Compound	ν, cm^{-1} (in $CHCl_3$)	δ, ppm, J, Hz (in $CDCl_3$)					
		4-CH_2OR	2,2-$(CH_3)_2$	3-CH_2	5-CH_2	6-CH_2	very strong
(III)	3600 sh 3550–3250, 3410 v.s 385, 1370, 1200, 1070 (max), 1040, 900	3,46–3,80 m (2H)	1,13 s (3H) 1,35 s (3H)	1,50 br.s (2H)	1,42 m (2H)	3,83–4,02 m (2H)	3,25 br.s (2H, (OH groups)
(II) + (II′)	1390, 1370, 1200, 1150, 1100 (max), 1075, 960	3,68 & 3,80 (AB-q, 2H, J_{AB} = =8)	1,17 s, 1,19 s 1,26 s 1,30 s 1,34 s, 1,37 s 1,40 s (in total 12H)	1,64 1,66 br.s (in (in total 4H)	1,52 & 1,73 1,54 & 1,64 (two AB-q, in total 4H, J_{AB} ≈ 13)	3,63–3,96 m (4H)	
(V)	1385, 1370 s, 1200, 1165, 1070 (max)	3,60 & 3,72 (AB-q, 2H, J_{AB} = =9)	1,08 s (3H) 1,25 s (3H)	1,55 br.s (2H)	1,45 & 1,65 (AB-q 2H, J_{AB} = =13)	3,58 m (1H), 3,82 m (1H)	1,29 s (3H) 1,31 s (3H)
(VI) + (VI′)	3090, 3075, 3030 1385, 1370, 1200 s, 1150, 1100 (max), 1070, 1040, 960, 930, 860	3,60 & 3,82 (ABq, 2H, J_{AB} = =8,5)	1,23 s, 1,25 s 1,39 s 1,41 s (in total 6H)	1,56, 1,61 br.s (in total 2H)	1,52 & 1,74 1,54 & 1,67 (two AB-q, acetal H), J_{AB} = 12	3,63 m (1H) 3,90 m (1H)	5,79 s, 5,83 s (in total 1H, acetal H), 7.19–7,45 m (5H, Ph)

and thus also the structure of spiroketals (II) and (II'), was verified by spectral data for (III) and two of its dioxolane derivatives (V) and (VI), obtained in the reaction of (III) with acetone or benzaldehyde in the presence of p-toluenesulfonic acid. The same dioxolanes (V) and (VI) were obtained from a mixture of (II) and (II') by the action of acetone or a solution of benzaldehyde in benzene in it in the presence of BF_3 etherate (see Scheme 1).

Scheme 1



In the PMR spectra of glycol (III) and its dioxolane derivatives, signals of the same type are observed (see Table 1). In the spectra of the latter compounds, CH_2 unit of the dioxolane ring appears in the form of an AB quartet, while in (III) itself, the corresponding signal is complex in form because of the coexistence of forms with different types of hydrogen bonds. THe strong H bond in (III) is also indicated by the IR spectrum and ^{13}C NMR spectrum, where a double set of signals is observed. The main peak in the mass spectrum of (III) at m/z 129 corresponds to the $[M - CH_2OH]^+$ ion. The absorption maximum in the IR spectra of (II), (V), and (VI) is present at 1100 cm^{-1} (the dioxolane OCO grouping).

It should be noted that during the irradiation of (I) in MeOH, pinacone (VII), whose formation should have been expected in analogy with known examples of the reductive dimerization of aliphatic ketones in alcohols (cf. [3, 4]), was not detected. At the same time, a direct photoinduced addition of MeOH to the keto group, leading to a primary—tertiary 1,2-glycol, was observed preferentially for certain α-dicarbonyl compounds [5, 6].

EXPERIMENTAL

The irradiation was carried out in an immersible photochemical reactor with a DRT-375 lamp, placed inside a cooling water jacket made of quartz, at 18-20°C, in an argon atmosphere. The TLC was carried out on silica gel, and GLC on an LKhM-8MD apparatus with a flame-ionization detector [stainless steel column, $\ell = 3.0$ m, $d_{ext} = 4$ mm, 4% XE-60 on Chromaton N-AW (HMDS), grain size 0.16-0.20 mm, flow rate of N_2 50 ml/min, evaporator temperature 275°C, thermostat temperature from 100°C with a 1.5 deg/min program]. The PMR and ^{13}C NMR spectra were run on a Bruker spectrometer (250 MHz) in $CDCl_3$; the IR spectra, on UR-10 spectrophotometer in $CHCl_3$; and the mass spectra, on a Varian CH-6 apparatus. The products were preparatively separated on silica gel L (40-100 μm). Before being used, the solvents were purified and made absolute according to [7].

2,5-Di(3',3'-dimethyl-4'-oxacyclohexano)dioxolanes (II) and (II'). A solution of 5.76 g (45 mmoles) of (I) and 8.54 g (45 mmoles) of $TiCl_4$ in absolute MeOH (total volume 420 ml) was irradiated for 18 h, then evaporated in vacuo, and neutralized with 10% $NaHCO_3$. The aqueous layer was extracted by ethyl acetate; the extract was dried over $MgSO_4$ and evaporated to yield 3.2 g of a yellow oil. Purification by preparative chromatography [a 5:1:1 hexane–benzene–acetone mixture, elution by ethyl acetate (EA) of a zone with R_f 0.75] gave 2.5 g of a mixture of ketals (II) and (II'), free of impurities, in the form of a viscous colorless liquid with n_D^{20} 1.4710 and R_t 3.50 min. In the PMR spectrum (see Table 1), two sets of signals with almost equal intensity were observed. For the IR spectrum see Table 1. Mass spectrum, m/z (relative intensity, %): 270 (25) M^+, 255 (33) $[M - CH_3]^+$, 226 (31), 225 (40), 213 (15), 197 (52), 185 (100), 184 (79) (ion a), 167 (38), 155 (27), 139 (38), 128 (93) (ion b).

The GLC analysis of the (II) + (II') mixture in a 20-min regime at 100°C, followed by a 1.5 deg/min program, gave two peaks in a 1:1 ratio.

4-Hydroxymethyl-2,2-dimethyltetrahydropyran-4-ol (III). a) A) A 0.50-g portion of a (II) + (II') mixture was added to 20 ml of an 80% AcOH, and the solution was boiled for 90 min, and then evaporated in vacuo, while benzene was added in portions. The dark residue (0.32 g) was purified by preparative TLC (hexane–EA, 1:1, elution by EA of a zone with R_f 0.23). Yield, 0.17 g of glycol (III) in the form of a colorless viscous liquid with R_t 26.7 min and n_D^{20} 1.4800. Yield 60%. Mass spectrum m/z (relative intensity, %): 160 (2.5) M^+, 145 (80) $[M - CH_3]^+$, 144 (25), 129 (100) $[M - CH_2OH]^+$, 127 (58), 116 (13), 99 (42), 86 (45), 85 (44), 71 (91). ^{13}C NMR spectrum (δ, ppm, in acetone-d_6): $24.7 < 24.8$ and 26.4 (gem-CH_3), $32.9 > 33.6 < 34$, (C^5), $40.2 \approx 40.3 < 43.8$ (C^3), $58 > 58.2$ (CH_2OH), 70.6 and 71.6 w (C^2), $71.3 < 72.2$ (C^6): multiple set of signals of the same type with unequal intensity indicates the presence of several conformers and/or associates in the solution. For the IR spectrum and PMR spectrum see Table 1.

b) A solution of 10.0 g of (I) in 450 ml of absolute MeOH was irradiated for 12 h, and the solvent was distilled in vacuo. The residual yellow oil (12.0 g) was chromatographed in portions of 0.60 g on a preparative plate, 32 × 20 cm in size (hexane–EA, 1:1). Compound (III) was isolated by elution by EA from the zone with R_f 0.23 and was identical with the above-described sample, yield 43%.

2,2-Dimethyltetrahydropyran-4-ol (IV) was isolated by elution by EA from the zone with R_f 0.34, in the form of a colorless oil with R_t 5.75 min and n_D^{20} 1.4709, in a yield of 42.5%. PMR spectrum (δ, ppm): 1.14 s (3H), 1.19 s (3H), narrow m (2H, 3-CH_2), 1.55-1.80 m (2H, 5-CH_2), 3.30 br. s (1H, OH), 3.65-3.73 m (2H, CHOH + 6-CH_2), 3.91 m (1H, 6-CH_2). IR spectrum (ν, cm^{-1}): 3600, 3430, 1370, 1080 v.s) (secondary OH), 1040, 960.

Reduction of Ketone (I). A 0.05-portion (1.3 mmoles) of $NaBH_4$ was added to a solution of 0.51 g (4 mmoles) of (I) in 10 ml of an 80% aqueous alcohol, and the mixture was left to stand overnight. The mixture was neutralized by adding dropwise 5% HCl, the alcohol was distilled off, and the residue was extracted by EA. The extract was washed with water, dried over $MgSO_4$, and evaporated, and the residue (oil, 0.47 g) was chromatographed on preparative plate (hexane–EA, 1:1). From the zone with R_f 0.34, 0.45 g of (IV) was obtained that was identical with the above-described sample.

Oxidation of Glycol (III). A 0.43-g portion (2 mmoles) of $NaIO_4$ was added to a solution of 0.32 g (2 mmoles) of (III) in 10 ml of water, and after 1 h, the mixture was extracted by ether. The extract was washed with water and dried over $MgSO_4$, and after distillation in a flange flask, 215 mg of (I) was obtained; the compound was identified by TLC, GLC, and PMR spectra.

2,2-Dimethyl-5-(3',3'-dimethyl-4'-oxacyclohexano)dioxolane (V). a) A 0.30-g portion of (III) and 0.13 g of p-$CH_3C_6H_4SO_3H$ were added to 10 ml of absolute acetone, and the mixture was left to stand for 24 h. Acetone was removed in vacuo, the residue was dissolved in EA, and the solution was washed with 5% $NaHCO_3$ and water to a neutral reaction and dried over $MgSO_4$. After distillation of the solvent, the residue (0.33 g) was chromatographed on a preparative plate (hexane—EA, 8:1), and ketal (V) was eluted by EA from the zone with R_f 0.54, colorless oil with R_t 4.0 min. Yield, 0.315 g (84%). For the IR and PMR spectra, see Table 1.

b) A 17-mg portion of BF_3 etherate was added to a solution of 0.8 g of a (II) + (II') mixture in absolute acetone. The mixture was left to stand for 12 h, the solvent was distilled off in vacuo, and hexane was added to the residue. The mixture was filtered, and the hexane solution was evaporated. The residue (0.38 g) was chromatographed as described above. Yield, 0.29 g (50%) of ketal (V), which was identical with the above-described sample.

2-Phenyl-5-(3',3'-dimethyl-4'-oxacyclohexano)dioxolane (VI). A 0.30-g portion of (III) 0.132 g of p-$CH_3C_6H_4SO_3H$, and 1 ml of PhCHO were added to 20 ml of absolute benzene. The mixture was held for 24 h, benzene was distilled in vacuo, and the residue was dissolved in EA and washed with 5% $NaHCO_3$ and water, dried over $MgSO_4$, and evaporated. The residue (0.42 g) was chromatographed on a preparative plate (benzene—hexane—EA, 6:2:1), and 0.39 g (90%) od dioxolane (VI) was eluted by EA from the zone with R_f 0.60 in the form of a colorless oil with R_f 39.5 min. Judging from a double set of the same type of signals in the PMR spectra, compound (VI) contains an appreciable amount of stereoisomer (VI).

b) A 17-mg portion of BF_3 etherate was added to a solution of 0.80 g of the (II) + (II') mixture in 20 ml of absolute benzene, and then, in the course of 1 h, 2 ml of PhCHO was added. After 24 h, benzene was distilled in vacuo, and the dark residue was washed with hexane (3 × 10 ml), hexane was evaporated, and the residue (0.7 g) was chromatographed on a plate, as described above. Yield, 0.34 g (70%) of a sample which was identical with the preceding one. For the IR spectrum and PMR spectrum, see Table 1. On storage, acetal (VI) gradually hydrolyzes by atmospheric moisture with the formation of PhCHO, whose autooxidation accelerates further hydrolysis.

CONCLUSIONS

1. The photolysis of 2,2-dimethyltetrahydropyran-4-one in methanol in the presence of an equimolar amount of $TiCl_4$ leads to the formation of stereoisomer 2,5-di(3',3'-dimethyl) 4'-oxacyclohexano)dioxolanes.

2. In the absence of $TiCl_4$, the irradiation of 2,2-dimethyltetrahydropyran-4-one in methanol leads to 4-hydroxymethyl-2,2-dimethyltetrahydropyran-4-ol and 2,2-dimethyltetrahydropyran-4-ol.

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