SEVEN-MEMBERED ACETALS BASED ON cis-2,3-DICHLORO-2-BUTENE-1,4-DIOL

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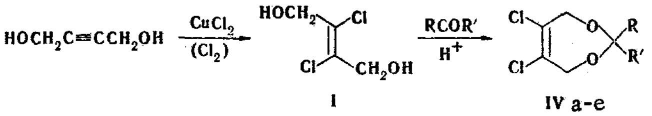
cis-2,3-Dichloro-2-butene-1,4-diol was obtained by reduction of dichloromaleic anhydride with lithium aluminum hydride. Condensation of the diol with carbonyl compounds leads to seven-membered unsaturated acetals, viz., 5,6-dichloro-1,3-dioxa-5-cycloheptenes.

Only a few publications devoted to the synthesis of seven-membered acetals that contain a carbon–carbon double bond in the 5 position are known. cis-2-Butene-1,4-diol [1-3], cis-3-hexene-2,5-diol [3], and 1,2-bis(hydroxymethyl)-1,4-cyclohexadiene [4] have been subjected to condensation with a carbonyl component. The narrow assortment of unsaturated acetals is due to limitations associated with the synthesis of the starting glycols themselves, which are obtained either by cis hydrogenation of acetalenic diols or from carbonyl systems with known cis configurations.

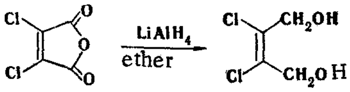
To increase the number of known unsaturated 1,4-glycols we worked out the synthesis of cis-2,3-dichloro-2-butene-1,4-diol and obtained a number of cyclic acetals based on it.

2,3-Dichloro-2-butene-1,4-diol (I) has been described in a number of patents [5-7]. It was synthesized by chlorination of 2-butyne-1,4-diol with molecular chlorine or $CuCl_2$; however, data on its geometrical configuration have not been presented.



IV a $R=C_6H_5$; b $R=p\text{-}ClC_6H_4$; c $R=p\text{-}NO_2C_6H_4$; d $R=(CH_3)_2C$; e $R,R'=(CH_2)_5$; a-d $R'=H$

To determine the configuration of diol I we reduced dichloromaleic anhydride with $LiAlH_4$, since it is known that the double bond is not involved in analogous reactions, and hydrogenolysis of the C_{sp}—Cl bond does not occur [8]. A melting-point depression was observed for a mixture of II with I prepared by the method in [9], and this constitutes evidence for the formation of both geometrical isomers (I is the trans form)



II

The method of dipole moments [10] has been used to establish the configuration of vicinal dichlorides of the ethylene series; however, its use for the establishment of structures I and II is not a rigorous procedure because of the presence of irregular polar hydroxymethyl groups in these compounds. We found that IR spectroscopy can be successfully used for this purpose. Thus the band of stretching vibrations of a C=C bond is absent in the spectrum of I, whereas in the case of II, on the other hand, an intense band appears at 1627 cm^{-1}, and this serves as an unambiguous confirmation of the structural conclusions in favor of isomeric glycols.

It seemed of interest to use the spectral test to ascertain the geometry of 2,3-dibromo-2-butene-1,4-diol (III) obtained* by bromination of 2-butyne-1,4-diol [11]. It was found that it has a trans configuration (the band of multiple-bond stretching vibrations is absent).

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Structures I and III are in complete agreement with the literature data on the stereochemistry of the halogenation of sterically unhindered acetylenes. It was established that the trans forms are the only products or the preponderant products both in the case of chlorination with $CuCl_2$ [12] and in the case of bromination [13].

2-R-5,6-Dichloro-1,3-dioxa-5-cycloheptenes (IVa-e) were obtained by condensation of II with carbonyl compounds in acidic media with separation of the resulting water. We used toluene in place of benzene, which is usually employed in such condensations, and this decreased the reaction time considerably and led to a smaller degree of resinification. Data on the conformation of the acetals obtained will be presented in a separate communication.

EXPERIMENTAL

cis-2,3-Dichloro-2-butene-1,4-diol (II). A solution of 1.7 g (0.045 mole) of $LiAlH_4$ in 150 ml of ester was added dropwise to 5 g (0.03 mole) of dichloromaleic anhydride in 50 ml of absolute ether, and the mixture was stirred for 2 h. It was then treated with 15% NaOH solution as in [14], and the ether layer was washed with a saturated solution of Na_2CO_3 and dried over $MgSO_4$. The residue after removal of the ether by distillation was crystallized from benzene to give 2.35-2.60 g (50-55%) of a product with mp 89-90°C. Found: C 30.3; H 4.0; Cl 45.1%. $C_4H_6Cl_2O_2$. Calculated: C 30.6; H 3.9; Cl 45.2%.

2-Phenyl-5,6-dichloro-1,3-dioxa-5-cycloheptene (IVa). A 2-g (0.01 mole) sample of diol II and 1.35 g (0.01 mole) of benzaldehyde were refluxed in 50 ml of toluene with a catalytic amount of p-toluenesulfonic acid with separation of the water in a Dean–Stark adapter. The mixture was cooled and washed with 10% $NaHCO_3$ solution, the solvent was removed by distillation, and the residue was recrystallized from methanol to give 3 g (96%) of a product with mp 53°C. IR spectrum: 1647 cm^{-1} (C=C). Found: C 54.1; H 4.2%. $C_{11}H_{10}Cl_2O_2$. Calculated: C 53.9; H 4.1%.

2-(p-Chlorophenyl)-5,6-dichloro-1,3-dioxa-5-cycloheptene (IVb). This compound, with mp 66-68°C (from methanol), was similarly obtained in 86% yield. IR spectrum: 1645 cm^{-1} (C=C). PMR spectrum, $\delta(CCl_4)$: 4.33 (4H, s, CH_2), 5.73 (1H, s, CH), and 7.30 ppm ($4H_{arom}$, s). Found: C 47.7; H 3.3; Cl 38.0%. $C_{11}H_9Cl_3O_2$. Calculated: C 47.3; H 3.3; Cl 38.1%.

2-(p-Nitrophenyl)-5,6-dichloro-1,3-dioxa-5-cycloheptene (IVc). This compound, with mp 113-114°C (from ethyl acetate), was similarly obtained in 80% yield. IR spectrum: 1644 cm^{-1} (C=C). Found: C 45.5; H 3.0; N 5.0%. $C_{11}H_9Cl_2NO_4$. Calculated: C 45.5; H 3.1; N 4.8%.

2-tert-Butyl-5,6-dichloro-1,3-dioxa-5-cycloheptene (IVd). This compound, with mp 59-61°C (from methanol), was similarly obtained in 57% yield, except that toluene was used in place of benzene. IR spectrum: 1646 cm^{-1} (C=C). PMR spectrum, $\delta(CCl_4)$: 0.92 (9H, s, CH_3), 4.27 (1H, s, CH), and 4.43 ppm (4H, m, CH_2). Found: Cl 35.5%. $C_9H_{14}Cl_2O_2$. Calculated: Cl 35.5%.

3,4-Dichloro-1,6-dioxaspiro[6,5]dodec-3-ene (IVe). This compound, with mp 69-70°C (from methanol), was obtained in 97% yield by the method used to prepare IVa. IR spectrum: 1654 cm^{-1} (C=C). Found: C 51.0; H 5.5; Cl 30.0%. $C_{10}H_{14}Cl_2O_2$. Calculated: C 50.7; H 5.9; Cl 29.9%.

LITERATURE CITED

1. J. Soulier, M. Farines, A. Laguerre, and A. Boanfos-Bastouill, Bull. Soc. Chim. Fr., 1763 (1975).
2. G. B. Sterling, E. J. Watson, and C. E. Pawloski, US Patent No. 3116298; Chem. Abstr., 60, 6856g (1964).
3. M. H. Gianni, M. Adams, H. G. Kuivila, and K. Wursthorn, J. Org. Chem., 40, 450 (1975).
4. Y. Gaoni and N. Shoef, Bull. Soc. Chim. Fr., 485 (1977).
5. A. Echte and H. Gunster, West German Patent 1152395 (1961).
6. H. Kleinert, DP 58505 (1967).
7. Gaetano F. D'Alelio, US Patent No. 3664992 (1972); Ref. Zh. Khim., 4N37 (1973).
8. A. Hajos, Komplexe Hydride und ihre Anwendung in der Organischen Chemie, Deutschen Verlag der Wissenschaften, Berlin (1966).
9. H. Kleinert and H. Furst, J. Prakt. Chem., 36, 252 (1967).
10. A. Debon, S. Masson, and H. Thuiller, Bull. Soc. Chim. Fr., 2493 (1975).
11. L. D. Bergel'son, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1066 (1960).

12. S. Uemura, H. Okazaki, A. Onoe, and M. Okano, J. Chem. Soc., Perkin Trans. I, 676 (1977).
13. S. Uemura, H. Okazaki, and M. Okano, J. Chem. Soc., Perkin Trans. I, 1278 (1978).
14. L. Fieser and M. Fieser, Reagents for Organic Synthesis, Vol. 2, Wiley (1969).

SYNTHESIS OF DERIVATIVES OF SOME CONDENSED SYSTEMS THAT INCLUDE FURAN RINGS AND INVESTIGATION OF THEM BY THE LANTHANIDE-SHIFT-REAGENT METHOD

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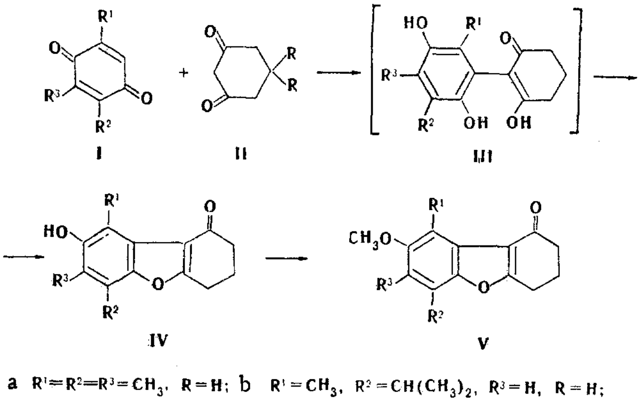
Derivatives of some condensed systems that include furan rings were obtained by condensation of 1,4-benzoquinones with cyclic β-diketones under the conditions of the Michael reaction. The structure of the methoxy derivatives of tetrahydrobenzofuran were established from the PMR spectra with the aid of europium(III) tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate). The location of the europium ion in the adduct of the lanthanide shift reagent (LSR) with the substrate was determined.

It is known that oxygen-containing heterocycles such as benzo- [1-8] and dibenzofurans [9, 10], as well as benzodifurans [11-14], can be formed in the reaction of p-benzoquinones with β-dicarbonyl compounds or their derivatives. The condensation may take place in the presence of bases (under the conditions of the Michael reaction) and Lewis acids or under the conditions of the Nenitzescu reaction with enamino derivatives of β-dicarbonyl compounds.

We carried out the condensation of alkyl-substituted 1,4-benzoquinones with cyclic β-diketones under the conditions of the Michael reaction and isolated a number of tetrahydrodibenzofuran and benzodifuran derivatives. The structures of the reaction products depend substantially on the structure of the β-diketone used, the ratio of the reacting components, and the conditions under which the condensation is carried out. Thus the reaction of equimolar amounts of quinones I and cyclohexane-1,3-dione (II, R = H) in the presence of piperidine or sodium methoxide leads to 1-oxo-8-hydroxy-1,2,3,4-tetrahydrodibenzofurans IVa-c, which are obtained evidently as a result of intramolecular cyclization of 1,4-addition products III (e.g., see [15]). Compound IVb is formed by refluxing the reaction mixture for 6 h, while isomeric IVc and IVa are obtained by allowing a methanol solution of an equimolar mixture of the reagents to stand at 20°C for a few hours. Methoxy derivatives Va-c, which are readily soluble in chloroform and are therefore more convenient for the measurement of the PMR spectra, were prepared from the corresponding hydroxy compounds IVa-c and dimethyl sulfate. If a methanol solution of dimedone (II, R = CH_3) and thymoquinone (Ib) in a molar



a $R^1=R^2=R^3=CH_3$, R=H; b $R^1=CH_3$, $R^2=CH(CH_3)_2$, $R^3=H$, R=H;
c $R^1=CH(CH_3)_2$, $R^2=CH_3$, $R^3=H$, R=H

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