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Abstract

Full Text

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STUDIES IN THE STEREOCHEMISTRY OF CYCLIC COMPOUNDS

CYCLOPENTENEDIONE-1,3 IN DIENE-SYNTHESIS REACTIONS

(Presented by Academician M. M. Shemyakin, 19 XII 1959)

For the synthesis and study of the stereochemistry of polycyclic compounds, including those related to natural products, cyclopentenedione-1,3 (I) is of unquestionable interest; a brief communication on its preparation was recently published (¹). One of the possible aspects of the synthetic use of this unsaturated cyclic β-diketone is its application as a dienophile in diene condensations with various dienes. Being a carbocyclic analogue of maleic anhydride, this dienophile may be successfully used for constructing polycyclic systems containing a five-membered ring with carbonyl groups in the α-position relative to the site of ring fusion, which is extremely important both for the synthesis of compounds related to steroids and for the study of the stereochemistry of hydrindanone systems.

The starting product for obtaining cyclopentenedione-1,3 (I) is cyclopentadiene, which readily gives the dibromide (II); the transformations of the latter into the diacetate (III) and then into a mixture of isomeric cyclopentenediols (IV) have been described previously (²). Oxidation of these diols to cyclopentenedione-1,3 is best carried out with chromic anhydride in acetic acid, and under these conditions a sufficiently pure diketone (m.p. 35–36°) can be obtained in yields up to 30%.

$$\text{cyclopentadiene} \longrightarrow \underset{(II)}{\text{dibromide}} \longrightarrow \underset{(III)}{\text{diacetate}} \longrightarrow \underset{(IV)}{\text{diol}} \longrightarrow \underset{(I)}{\text{cyclopentenedione-1,3}}$$

Cyclopentenedione-1,3 (I) readily enters into a diene-synthesis reaction with butadiene and, already at room temperature, gives in good yield the corresponding cis-adduct (V), the structure and configuration of which was proved by oxidation of the corresponding hydrindandione-1,3 (VI) to the known cis-cyclohexane-1,2-dicarboxylic acid. In an analogous manner, condensation of the diketone with isoprene proceeds with formation of the adduct (VII), and also with cyclopentadiene, leading to the corresponding adduct (VIII), which on hydrogenation with a Pd catalyst adds 1 mole of hydrogen, giving the corresponding endomethylenehydrindandione-1,3 (IX).

According to infrared spectra, the resulting adducts are completely enolized in solution, which agrees with recently published results (^{6}).

[Chemical reaction schemes and structural formulas labeled (I), (V), (VI), (VII), (VIII), (IX), (X), and (XI) are shown at the top of the page.]

Cyclopentenedione-1,3 (I) readily condenses with 1-vinyl-Δ'-cyclohexene and 6-methoxy-1-vinyl-$\Delta^{3,4}$-dihydronaphthalene, forming in good yields the corresponding tri- and tetracyclic diketones (X) and (XI), the latter possessing a structure extremely interesting for further study and related to steroid compounds. The ease and comparative simplicity of obtaining the adducts described have made them fully accessible for the study of various chemical transformations, which is the subject of our further work.

Experimental Part

Oxidation of cyclopentenediole-1,3 (IV). To a solution, cooled with ice water, of 6.3 g of cyclopentenediole-1,3 (^{2}) (b.p. 107—108°/0.7 mm, n_D^{20} 1.5025) in 50 ml of acetic acid, a solution of 8.4 g of chromic anhydride in 100 ml of acetic acid is added over 15 min. The solvent is distilled off; 100 ml of $2N$ H_2SO_4 is added to the residue; the oxidation product is extracted with benzene and, after removal of the solvent, the residue is distilled in vacuo. 1.5 g of cyclopentenedione-1,3 (I) is obtained, b.p. 60°/1 mm, n_D^{20} 1.5045, which crystallizes immediately and has m.p. 35—36° (^{1}); yield 26%. By the same method, diketone (I) is also obtained in 25% yield on oxidation of pure cis-cyclopentenediole-1,3.

Found, %:	C 61.98; 61.92;	H 4.56; 4.62
$C_5H_4O_2$. Calculated, %:	C 62.50;	H 4.16

Condensation of cyclopentenedione-1,3 (I) with butadiene. A solution of 2.5 g of cyclopentenedione-1,3 (I) and 15 g of butadiene in 15 ml of benzene, in the presence of a small amount of pyrogallol, is kept for two weeks at room temperature. The crystalline precipitate that separates is filtered off, giving 2.46 g of adduct (V), which after crystallization from abs. methanol has m.p. 157.5—158.5°.

Found, %:	C 71.90; 71.87;	H 6.63; 6.71
$C_9H_{10}O_2$. Calculated, %:	C 71.98;	H 6.71

Hydrindandione-1,3 (VI) and its oxidation. A solution of 1.62 g of (V) in 50 ml of alcohol is hydrogenated over a Pd catalyst. After absorption of 1 mole of hydrogen, the hydrogenation ceases; the solvent is distilled off and 1.63

g of hydrindandione-1,3 (VI) is obtained, which after crystallization from abs. methanol has m.p. 86—86.5°.

Found, %: C 70.73; 71.01; H 8.18; 7.97
$C_9H_{12}O_2$. Calculated, %: C 71.02; H 7.95

For oxidation, to a cooled solution of 0.45 g of hydrindandione-1,3 (VI) in 3.5 ml of 10% NaOH there is gradually added (over 15 min.) a cooled solution of 1 g of bromine in 17 ml of 10% NaOH. The mixture is stirred at 0° for 1 hour; the neutral products are extracted with ether, and the alkaline solution is saturated with CO_2 and evaporated in vacuo to half the initial volume. The precipitate that separates on cooling is filtered off and thoroughly extracted with dry acetone. After distilling off the acetone, 0.1 g of *cis*-cyclohexane-1,2-dicarboxylic acid is obtained, m.p. 186.5–187.5°, which gave no depression with an authentic sample (^{3}).

Condensation of cyclopentenedione-1,3 (I) with isoprene. A solution of 0.48 g of cyclopentenedione-1,3 (I) and 3.4 g of isoprene in 5 ml of benzene, in the presence of a small amount of pyrogallol, is kept in an ampoule at room temperature for one month. The benzene is distilled off in vacuo, and from the remaining oil, after treatment with ether, 0.71 g of a crystalline reaction product is isolated, m.p. 83–87°, crystallization of which from nitromethane gives pure adduct (VII), m.p. 84.5–85.5°.

Found, %: C 73.15; 72.89; H 7.49; 7.47
$C_{10}H_{12}O_2$. Calculated, %: C 73.14; H 7.37

Condensation of cyclopentenedione-1,3 (I) with cyclopentadiene. To a solution of 0.24 g of cyclopentenedione-1,3 (I) in 3 ml of benzene there is added 1.2 g of freshly distilled cyclopentadiene, and the crystalline reaction product that separates is filtered off. 0.40 g of adduct (VIII) is obtained, which after crystallization from absolute methanol has m.p. 178–178.5°.

Found, %: C 74.10; 74.36; H 6.22; 6.16
$C_{10}H_{10}O_2$. Calculated, %: C 74.05; H 6.22

0.16 g of adduct (VIII) in a solution of 10 ml of absolute alcohol is hydrogenated over a Pd catalyst. After absorption of 1 mole of hydrogen the hydrogenation ceases; the solvent is distilled off and 0.15 g of endomethylenehydrindandione-1,3 (IX) is obtained, which after crystallization from absolute methanol has m.p. 166–166.5°.

Found, %: C 73.46; 73.45; H 7.40; 7.22
$C_{10}H_{12}O_2$. Calculated, %: C 73.14; H 7.37

Condensation of cyclopentenedione-1,3 (I) with 1-vinyl-Δ^1-cyclohexene. To a solution of 0.48 g of cyclopentenedione-1,3 (I) in 2.5 ml of benzene there is added 1.62 g of 1-vinyl-Δ^1-cyclohexene (^{4}), and the mixture is kept at room temperature for one week. The benzene is distilled off, the viscous dark oil is treated with dry ether, and 0.6 g of a crystalline product is obtained, m.p. 113–117°. After recrystallization from nitromethane, pure adduct (X) has m.p. 120–121°.

Found, %: C 76.20; 76.28; H 7.80; 7.75
$C_{13}H_{16}O_2$. Calculated, %: C 76.44; H 7.90

Condensation of cyclopentenedione-1,3 (I) with 6-methoxy-1-vinyl-Δ^3,^{4}-dihydronaphthalene. To a solution of 0.48 g of cyclopentenedione-1,3 (I) in 2.5 ml of benzene there is added a solution of 1 g of 6-methoxy-1-vinyl-Δ^3,^{4}-dihydronaphthalene ([5]) in 2.5 ml of benzene, and the mixture is left for 24 hours at room temperature. 1 g of crystalline reaction product is obtained, m.p. 205–207° (with decomp.). The adduct (XI) recrystallized from absolute methanol has m.p. 206.5–207.5°.

Found, %: C 76.49; 76.32; H 6.63; 6.46
$C_{18}H_{18}O_3$. Calculated, %: C 76.57; H 6.43.

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