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SPIRO EPOXY KETONES.

2.* THERMAL TRANSFORMATIONS OF 2-BENZYLIDENEINDAN-1,3-DIONE α-OXIDE

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2-Phenyl-3,3,4,4-diphthaloyloxetane is formed when solutions of 2-benzylideneindan-1,3-dione α-oxide in benzene or carbon tetrachloride are heated, while 5-oxo-3-phenyl-2,2-phthaloyl-2,3-dihydroindeno[2,3-b][1,4]dioxine is formed when solutions in dioxane are heated.

2-Benzylideneindan-1,3-dione α-oxide (I) undergoes thermal 1,3-dipolar cycloaddition reactions with most electron-deficient olefins [1]. Continuing our study of the reactivity of α-oxide I we have observed interesting transformations when solutions of it in benzene, CCl_4, and dioxane are refluxed.

In benzene and carbon tetrachloride the principal reaction product is 2-phenyl-3,3,4,4-diphthaloyloxetane (IV), the structure of which was established on the basis of spectral data. The mass spectrum contains a molecular-ion peak with m/z 394, as well as intense peaks of ions formed in the fragmentation of M^+: diphthaloylethylene (m/e 288) and benzaldehyde (m/z 106). Alternative fragmentation of the molecular ion gives triketoindan and the 2-benzylideneindan-1,3-dione ion with m/z 234. The ion with m/z 250, which corresponds to a fragment of α-oxide I, is also extremely intense. The characteristic doublet of the absorption frequencies of the carbonyl groups of an indandionyl fragment (1730 and 1765 cm^{-1}) is observed in the IR spectrum of IV. In addition to multiplets of aromatic protons, the PMR spectrum contains a singlet at δ 4.55 ppm. This shift of the signal of the 2-H proton to strong field as compared with the signal of the methylidyne proton of α-oxide I (4.72 ppm) is probably explained by the anisotropic effect of the carbonyl group of the substituent in the 3-position of the oxetane. An analysis of molecular models shows that the 2-H proton falls into the cone of positive anisotropy.

A mixture of 5-oxo-3-phenyl-2,2-phthaloyl-2,3-dihydroindeno[2,3-b][1,4] dioxine (VI) and oxetane IV in a ratio of 7:1 is formed when α-oxide I is refluxed in dioxane. The structure of VI was established by spectral and chemical methods. The molecular mass determined by mass spectrometry is 394, and the given substances are isomers. The presence of a cyclic ether C—O—C grouping in indenodioxine VI is confirmed by the presence of an $[M - 16]^{+\cdot}$ fragment ion with m/z 378 [2]. In addition, the mass spectrum contains intense peaks of ions with m/z 105 and 106 ($PhC{\equiv}O^+$ and $PhCHO^{+\cdot}$, respectively), 250 (ion after the elimination of a phthaloyl fragment), and 306 and 278 (fragmentation of the phthaloyl fragments of the molecular ion). Absorption frequencies of the carbonyl groups of the indandionyl part (1730 and 1750 cm^{-1}), of a keto group conjugated with a C═C bond (1690 cm^{-1}), and of an aromatic ring and a C═C bond (1610 cm^{-1}) are observed in the IR spectrum of VI. A singlet and a methylidyne proton at 6.1 ppm and a multiplet of aromatic protons are present in the PMR spectrum.

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*See [1] for Communication 1.

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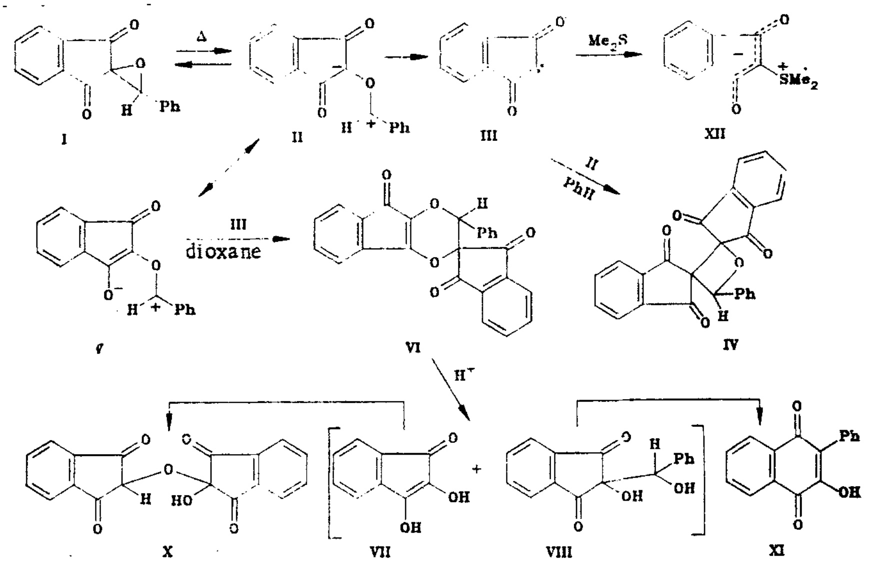
Hydrolysis of indenodioxine VI led to hydrindanthine X and 2-hydroxy-3-phenyl-1,4-naphthoquinone (XI), which were identical to genuine samples (with respect to their IR spectra and TLC data). When VI is treated with 70% H_2SO_4, unstable (under these conditions) 2-hydroxyindan-1,3-dione (VII) and diol VIII are probably formed in the first step of the reaction. It is known [3] that VII is readily converted to hydrindanthine X, while diol VIII in an acidic medium undergoes rearrangement to naphthoquinone XI. The possibility of the latter transformation is confirmed by the fact that in the hydration of α-oxide I in the presence of sulfuric acid naphthoquinone XI is also formed instead of the expected diol VIII.



The proposed scheme for the formation of IV and VI includes a step involving fragmentation of carbonyl ylid II that initially arises from α-oxide I to carbene III and benzaldehyde. The latter was detected from the PMR spectrum of the reaction mixture. The only evidence for the existence of the carbene is the formation, although in only low yield (6%), of dimethylsulfonium ylid XII when the reaction is carried out in the presence of dimethyl sulfide, since carbenes generated in such a way do not give an EPR signal [4], while carbonyl ylid II itself proves to be more reactive with unsaturated compounds [1]. One should note the insignificant yield of ylid XII obtained in the photolysis of 2-diazoindan-1,3-dione in the presence of dimethyl sulfide [5] as well as the absence of cycloaddition adducts in the reaction of diaroylcarbenes or their resonance 1,3-dipoles with olefins [6]. We also did not detect diphthaloylethylene – the product of dimerization of carbene III, which has a characteristic red-violet color and is only slightly soluble in organic solvents [7] – in the reaction mixture.

Calculations show that such fragmentation of carbonyl ylids is thermally forbidden [8]. The experimental data are in satisfactory agreement with this conclusion [9]. A single instance of the formation of aldehydes in the thermolysis of oxopyrazolinespirooxiranes has been described, but the nature of the intermediates was not discussed in detail [10].

It has been previously shown that the yield of products of fragmentation of carbonyl ylids increases in the case of the successive action of UV and visible light on the corresponding oxiranes [11]. However, IV and VI were also formed when α-oxide I was refluxed in the dark, i.e., this process has purely thermal nature. This sort of anomalous fragmentation of carbonyl ylids is due, in our opinion, to the following factors: 1) to a decrease not only in the difference between the highest occupied molecular orbital (HOMO) and the lowest vacant molecular orbital (LVMO) of the ylid but also in the energies of these orbitals because of the presence of substituents that decrease the electron density on the carbonyl ylid, which is known to promote its fragmentation [8]; 2) to the existence of ylid II in both planar and nonplanar conformations, since the thermal formation of a carbene and an aldehyde, which is forbidden for the planar conformation [8] (compare, for example, with diazomethane, for the thermal fragmentation of which deviation from the plane of the methylene group is also necessary [12]), is possible precisely in the latter case.

In benzene and carbon tetrachloride ylid II reacts with carbene III to give oxetane IV. A similar [3 + 1]-cycloaddition process has been described, for example, for azomethinylids generated from the corresponding aziridines [13]. Not only 1,3-dipole II but also the resonance 1,5-dipole V prove to be reactive in dioxane. The reaction of V with carbene III leads to indenodioxine VI. Similar behavior (but in intramolecular processes) was noted for carbonyl ylids formed in the photolysis of epoxychalcones [14]. Attempts to intercept the 1,5-dipole were unsuccessful, since 1,3-dipole II reacts with dipolarophiles in dioxane.

Thus we have found that carbonyl ylid II thermally generated from 2-benzylideneindan-1,3-dione α-oxide can undergo fragmentation to carbene III and benzaldehyde. Carbene III in benzene and CCl_4 reacts with ylid II to give 2-phenyl-3,3,4,4-diphthaloyloxetane, while in dioxane the reaction of the former with 1,5-dipole V leads to 5-oxo-3-phenyl-2,2-phthaloyl-2,3-dihydroindeno[2,3-b][1,4]dioxine (in addition to oxetane IV).

EXPERIMENTAL

The IR spectra (KBr pellets) were recorded with a Specord IR-75 spectrometer. The PMR spectra were obtained with a Tesla BS-467 spectrometer (60 MHz). The mass spectra were recorded with a Hewlett–Packard 5985 spectrometer. Thermoderivatography was accomplished with a Paulik–Paulik–Erdey apparatus. Thin-layer chromatography was carried out on Silufol UV-254 plates. Column flash chromatography was accomplished with an 11 by 2.8 cm column packed with Silpearl silica gel (elution with chloroform).

2-Phenyl-3,3,4,4-diphthaloyloxetane (IV). A 1-g (4 mmole) sample of α-oxide I [15] was refluxed for 35 h in 100 ml of absolute benzene or CCl_4 in an argon atmosphere, after which the solvent was partially evaporated, and the product was precipitated with hexane to give 0.53 g (67%) of oxetane IV with mp 180-181°C (from benzene, with decomposition) and R_f 0.37 [$CHCl_3$–ethyl acetate (20:1)]. IR spectrum: 1730, 1765 (C=O); 1190, 1050 cm^{-1}. PMR spectrum (d_6-acetone): 4.55 (1H, s, 2-H), 7.22-8.14 ppm (13H, m). Mass spectrum, m/z: 105 (100), 106 (48), 234 (45), 250 (70), 288 (31), M^+ 394 (8). Found: C 76.7; H 3.4%. $C_{25}H_{14}O_5$. Calculated: C 76.1; H 3.6%.

5-Oxo-3-phenyl-2,2-phthaloyl-2,3-dihydroindeno[2,3-b][1,4]dioxine (VI). A 0.5-g (2 mmole) sample of α-oxide I was refluxed for 20 h in 50 ml of absolute dioxane in an argon atmosphere, after which the solvent was evaporated, and the residue was treated with benzene. The precipitated slightly soluble VI was removed by filtration, washed on the filter with benzene, and recrystallized from ethanol to give 0.29 g (74%) of indenodioxine VI with mp 214-215°C (from ethanol, with decomposition) and R_f 0.41 [$CHCl_3$–ethyl acetate (4:1)]. IR spectrum: 1610 (C=C); 1690, 1730, 1750 cm^{-1} (C=O). PMR spectrum (d_6-DMSO): 6.1 (1H, s, 3-H), 7.20-8.25 ppm (13H, m). Mass spectrum, m/z: 105 (100), 106 (28), 250 (50), 278 (35), 306 (31), M^+ 394 (9). Found: C 69.8; H 4.6; H_2O 8.2 (from the derivatogram). $C_{25}H_{14}O_5 \cdot 2H_2O$. Calculated: 69.8; H 4.2; H_2O 8.4%.

The benzene solution was partially evaporated and the residue was treated with hexane to give 0.043 g (11%) of oxetane IV.

Hydrolysis of Indenodioxine VI. A 0.2-g (0.46 mmole) sample of VI was mixed with 15 ml of 70% H_2SO_4. After the development of a light-brown coloration, the mixture was heated slightly to dissolve the precipitate completely, and the solution was poured into 50 ml of ice water. The precipitate was removed by filtration, washed with water until the wash water was neutral, and dried to give 0.1 g (71%) of naphthoquinone XI with mp 146-147°C (from aqueous ethanol) (mp 145-146°C [16]). The acidic filtrate was neutralized with sodium bicarbonate solution; at pH 4 the mixture was yellow, at pH 6 it was pink, and at pH 11 it was blue. This procedure gave 0.05 g (60%) of hydrindanthine X with mp 231-233°C (dec.) (mp 230-235°C (dec.) [3]).

2-Hydroxy-3-phenyl-1,4-naphthoquinone (XI). A 0.2-g (0.8 mmole) sample of α-oxide I was mixed with 70% H_2SO_4. After the α-oxide had dissolved, the mixture was poured into 40 ml of ice water. The reaction product was removed by filtration, washed on the filter with water until the wash water was neutral, and dried to give 0.16 g (80%) of naphthoquinone XI with mp 146-147°C (from aqueous ethanol).

2-Dimethylsulfoniaindan-1,3-dionide (XII). A mixture of 0.5 g (2 mmole) of α-oxide I, 0.44 ml (6 mmole) of Me_2S, and 15 ml of benzene in a sealed ampul was heated for 40 h at 80-85°C. After removal of the solvent and excess dimethyl sulfide, the reaction mixture was chromatographed with a column to give (in the order of elution) 0.09 g (61%) of PhCHO, 0.12 g of unchanged α-oxide I, 0.14 g (46%) of oxetane IV, and 0.017 g (6%) of ylid XII Compound XII had mp 165-166°C (mp 166-167°C [17]).

In the case of the reaction in dioxane ylid XII was detected only by TLC because of the formation of a difficult-to-separate mixture.

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