tative yield of Diels–Alder adducts of **2** was obtained. The reaction was also complete in refluxing benzene after 10 h. Similarly refluxing **1** with *N*-phenylmaleimide in toluene for 2 h gave adduct quantitatively.

These two facile and complementary routes (base-induced and direct) to isobenzofuran offer ready access to this reactive compound. Both methods can in principle be adapted to in situ formation of **2** with simultaneous formation of adducts. We are currently exploring these and related applications.

Experimental Section

1,3-Dihydro-1-methoxyisobenzofuran (1). A mixture of 2.0 g (0.015 mol) of *o*-phthalyldiol,[8] 80 mL of methanol, 3.4 mL of concentrated sulfuric acid, and 150 mL of pentane was vigorously stirred while 30 mL of 5.25% aqueous NaOCl (commercial laundry bleach) was added over a period of 8 h. After 24 h of additional stirring, the phases were separated, and the aqueous part was washed twice with small portions of pentane. The combined pentane solution was washed with aqueous bicarbonate and dried over potassium carbonate. Evaporation of the solvent gave an oil which was essentially pure **1**; vacuum distillation gave material with bp 32 °C (0.1 torr) in 65% yield. The spectral properties of **1** coincided with those reported by Tidwell.[9]

Isobenzofuran (2). To an ice-cooled solution of 1.43 g of diisopropylamine in 5 mL of benzene was added 6.7 mL of a 2.1 M hexane solution of *n*-butyllithium. The stirred LDA was allowed to warm to near room temperature, and then 0.8 g of **1** in 8 mL of benzene was added over a few minutes. After being stirred for an additional 5 min, the reaction mixture was quenched by adding an equal volume of aqueous NH_4Cl. The organic phase was separated and dried over sodium sulfate.

The yield of **2** in some runs was determined by VPC, using a tetramethylbenzene internal standard on an SE-30 column at 107 °C, conditions where no decomposition of **1** occurred. A sample for NMR analysis was also obtained by preparative VPC under these conditions, giving a spectrum identical with that reported by Warrener.[3] Yields were also determined by adding maleic anhydride to portions of the solutions of **2**; after standing at room temperature for a short time the solvents were removed in vacuo, and the crystalline products were washed with small volumes of cold chloroform. The resultant solids consisted only of Diels–Alder adducts (exo/endo ca. 1:1), as shown by NMR. Yields ranged from 60–69%.

The use of ether in place of benzene as solvent gave a somewhat lower yield (47%).

Allowing longer reaction time with LDA did not materially affect the yield, taking into account the inherent instability of **2**. A benzene–hexane solution of **2** (1.8%) kept at room temperature lost over 60% of **2** after 8 days; a portion of the same solution kept at −20 °C retained over 70% of the original **2** over this same time period. The addition of hydroquinone had little if any stabilizing influence on **2**.

Reaction of 1 with Maleic Anhydride. A mixture of 0.32 g of **1** and 0.50 g (2.3 equiv) of maleic anhydride in 20 mL of toluene was refluxed for 2 h, after which the solvent was removed by rotary evaporation. The crystalline residue was washed with small amounts of cold chloroform to remove the excess maleic anhydride, giving Diels–Alder adducts in essentially pure form (exo/endo = 4/5) and quantitative yield. Fair separation of the isomers was accomplished by dissolving 0.1-g samples in 3 mL of benzene and seeding with the visibly different crystals; on cooling overnight, material related to the seed formed on the walls of the test tubes. The exo product, with assignment based on the absence of bridgehead proton coupling, had mp ca. 212 °C. The endo isomer melted at 172 °C.

A similar reaction of **1** in refluxing benzene followed by NMR showed incomplete loss of **1** after 4 h; no further **1** was seen after 10 h.

N-Phenylmaleimide was also used in refluxing toluene, giving a quantitative yield of exo/endo (5:12) product after 2 h.

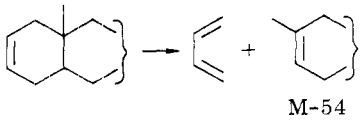
Registry No. **1**, 67536-29-2; **2**, 270-75-7; *o*-phthalyldiol, 612-14-6; maleic anhydride, 108-31-6.

Communications

Mass Spectra of Androstane-7,17-diones

Summary: Steroids with the 7,17-dione structure (**1**) undergo an unusual fragmentation process yielding an intense peak in the mass spectrum at M − 47 (M − CH_3O_2) regardless of the ring A substitution pattern.

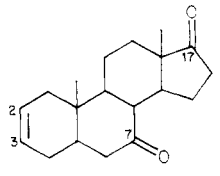
Sir: During the period of rapid advances in the development of organic mass spectrometry, a report appeared[1] which stated that 5α-androst-2-ene-7,17-dione (**1**) was the sole exception to the rule that cyclohexenes would undergo the retro-Diels–Alder reaction[2] which can lead to a peak at M − 54 (loss of butadiene). This is shown in eq 1 for a typical Δ^2 steroid. It was noted that the bicyclic analogue **2** behaved normally as did 5α-androst-2-en-17-one.[3]



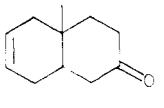
(1)

M-54

These facts have been restated in publications dealing with mass spectrometry to this date.[4] The simplest explanation



1



2

of the data would be that the compound thought to be the Δ^2-olefin was in fact some other compound, perhaps the Δ^3-olefin. (In this case, the retro-Diels–Alder reaction can occur but no fragmentation would be observed. The fragment ion would have the same mass as the parent ion.) Apparently, the sample used for this measurement[1] was obtained from a group of Czech chemists as their report[5]

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is the only one in the literature mentioning the compound. They obtained it as a byproduct from the acetolysis of a 3β-(tosyloxy)-5α-androstane-7,17-dione. Only an elemental analysis was given in support of the structural assignment.

We undertook the resynthesis of 5α-androst-2-ene-7,17-dione to verify both the structure and the measurement. We used dehydroepiandrosterone (3β-hydroxyandrost-5-en-17-one) as the starting material and followed this scheme: esterification of the 3β-alcohol function; allylic oxidation at C-7 with a chromium trioxide–3,5-dimethylpyrazole complex;[6] hydrogenation of the Δ^5 double bond; saponification of the 3β-ester; tosylate formation at C-3; and the elimination of *p*-TsOH with potassium acetate in acetic acid. Each compond in the sequence had physical and spectral properties which were in complete accord with literature precedents.[5,7] The anomalous behavior described[1] in 1963 was accurate.

The availability of the mass spectra of six different 5α-androstane-7,17-diones revealed, however, that the true anomaly was *not* in the fragmentation which was not observed but in the remarkable reaction which does occur and which totally dominates the spectra of this series of related compounds. Each spectrum has as its most intense fragment peak a signal at M – 47. The 3β-acetate does not have the expected M – 60 for the loss of acetic acid.[8] The 3β-alcohol does not have a significant peak at M – 18 for the loss of water.[9] The tosylate has a peak at M – 47 as well as at M – (47 + *p*-TsOH).[9] The alkene,[9] the 3,7,17-triketone,[10] and the unsubstituted A-ring compound[11] each show a base peak at M – 47. Similar compounds of the 7-one,[12] 17-one,[13] and 6,17-dione[10] series do not show the M – 47 peak but give more rational fragmentation patterns.

M – 47 must be the loss of one carbon, three hydrogens, and two oxygens. High-resolution mass measurements[14] on the unsubstituted A-ring compound verify this fact. Literature sources[8,10] indicate that these components may be lost as a single entity since metastable ions are noted which correspond to the expected "mother → daughter" transition. This is in keeping with the thought that a two-step process involving multiple bond fissions to the same carbon (for example, loss of water followed by loss of HCO, or vice versa) would not dominate these spectra to the extent that it totally suppresses other well-known facile reactions (loss of acetic acid, loss of water, loss of butadiene). While the earlier workers[8,10] noted that the loss of 47 mass units was characteristic of the 7,17-dione system, they did not refer to the evidence from the metastable ions which they recorded nor did they note the overwhelming influence of this fragmentation process.

5α-Cholest-2-en-7-one was also prepared[15] and while its spectrum is dominated by D-ring cleavages, one can observe the results of the retro-Diels–Alder reaction (M – 54).

A preliminary deuterium-labeling experiment gave a sample of 3β-hydroxy-5α-androstane-7,17-dione, which is 50% d_5 (6,6,8β,16,16), 34% d_4 (6,6,16,16), 12% d_3, and 4% d_2.[12] For this sample, it appears that the major fragmentation was loss of CHD_2O_2 (M – 49). Our work to understand this unprecedented fragmentation process and its specificity continues.

Acknowledgment. We thank the University Research Council of the University of West Florida for a grant.

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3-(Phenylseleno)-2-propenal as a Versatile Unit for Oxetane Ring Formation

Summary: Treatment of 1-alkyl-3-(phenylseleno)-2-propen-1-ol with 2 equiv of MCPBA followed by sodium hydroxide in aqueous methanol gave 2-alkyl-3-methoxyoxetane in good yield.

Sir: Oxetane ring formation has received extensive attention especially in connection with the synthesis of thromboxane A_2 derivatives.[1] For the preparation of oxetanes, photochemical reaction of olefins with carbonyl compounds (Paterno–Büchi reaction)[2] and ring closure of 1,3-diol derivatives[3] have been widely employed. Recently sodium *S,S*-dimethyl-*N*-(*p*-toluenesulfonyl)sulfoximine has also been used as a convenient reagent for the conversion of carbonyl compounds to oxetanes via their oxirane derivatives.[4]

We have been interested in the novel reactivity[5] of phenyl vinyl selenoxides and have described their unique cyclopropanylation reaction with ketone enolates.[6] Fur-

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