methoxybenzal)-2,3-naphthalenedioate (**20d**). This mixture was converted to **19d** after a DBU isomerization. Recrystallization from methanol gave an 82% yield (based on **4d**) of **19d**: mp 85–86 °C; NMR δ 3.73 (s, 3 H, $C_6H_4OCH_3$), 3.93 and 3.98 (s, 6 H, CO_2CH_3), 4.4 (s, 2 H, $ArCH_2$), 6.78 and 7.13 (AB q, 4 H, $C_6H_4OCH_3$), 7.4–8.2 (m, 4 H, aromatic H), 8.62 (s, 1 H, aromatic H_4); IR (Nujol) 1735 and 1720 (C=O), 1300, 1270, 1240, 1130, 1030, 1020, 980, 790, 770, 750 cm^{-1}.

1-Benzyl-1,4-epoxy-3,4-dihydro-2(1*H*)-naphthalenone (16). The acetoxynitrile **15** (500 mg, 1.56 mmol) was dissolved in 25 mL of ethanol containing 500 mg of hydrated sodium sulfide and the solution was refluxed for 12 h. The ethanol was removed, the residue dissolved in ether and water, and the ether layer washed with water and dried ($MgSO_4$). Removal of the solvent gave 240 mg of residue. Recrystallization from ethanol gave 205 mg (52%) of **16**: mp 129–130 °C; NMR δ 2.02 (d, J = 16 Hz, 1 H, endo H), 2.61 (dd, J = 5 Hz, J' = 16 Hz, 1 H, exo H), 3.52 (s, 2 H, $PhCH_2$), 5.64 (d, J = 5 Hz, 1 H, bridgehead H), 7.0–7.6 (m, 9 H, aromatic H); IR ($CHCl_3$) 1760 (C=O), 1500, 1470, 1460, 1050, 690 cm^{-1}.

Reduction of 16 to give 1-Benzyl-1,4-epoxy-1,2,3,4-tetrahydro-*endo*-3-hydroxynaphthalene (28). The ketone **16** (2.0 g, 8 mmol) was reduced by refluxing for 12 h in 250 mL of ether containing 0.50 g (13 mmol) of lithium aluminum hydride. After hydrolysis of the mixture with water, the ether layer was separated and dried ($MgSO_4$) and the solvent removed. The residue was recrystallized from petroleum ether to give 1.9 g (94%) of **28**: mp 86.5–88 °C; NMR δ 0.72 (d, J = 10 Hz, 1 H, OH), 1.03 (dd, 1 H, H_{3N}, $J_{2,3N}$ = 2.5 Hz, $J_{3N,3X}$ = 12 Hz), 2.27–2.75 (m, 1 H, H_{3X}), 3.5 (s, 2 H, $PhCH_2$), 4.5 (t d, 1 H, H_2, $J_{2,3N}$ = 2.5 Hz, $J_{2,3X}$ = 10 Hz, $J_{2,OH}$ = 10 Hz), 5.2 (d, 1 H, H_4, $J_{3X,4}$ = 5.5 Hz), 6.9–7.4 (m, 9 H, aromatic H); IR (Nujol) 3580 (OH), 1055, 730, 670 cm^{-1}.

Acknowledgment. This work was financially supported by the National Science and Engineering Research Council of Canada.

Registry No. **1**, 29539-19-3; **1**, 4,7-dimethyl derivative, 54537-61-0; **1**, 4,7-diphenyl derivative, 54537-64-3; **1**, *p*-methoxy derivative, 64421-15-4; **2a**, 61200-14-4; **2b**, 73194-82-8; **2c**, 73194-83-9; **2d**, 73194-84-0; **3a**, 52540-39-3; **3b**, 73194-85-1; **3c**, 73198-05-7; **3d**, 73194-86-2; *endo*-**4a**, 52540-40-6; *exo*-**4a**, 73245-10-0; *trans*-**4a**, 73245-11-1; **4b**, 73194-87-3; **4c**, 73194-88-4; **4d**, 73194-89-5; *exo*-**5**, 73194-90-8; *endo*-**5**, 73245-12-2; **6**, 73194-91-9; **7a**, 73194-92-0; **7b**, 73194-93-1; **7c**, 73194-94-2; **8**, 73194-95-3; **9**, 73194-96-4; **10**, isomer 1, 73194-97-5; **10**, isomer 2, 73245-13-3; *exo*-**11**, 73194-98-6; *endo*-**11**, 73245-14-4; *exo*-**12**, 73194-99-7; *endo*-**12**, 73245-15-5; *exo*-**13**, 73245-16-6; *endo*-**13**, 73194-59-9; **14**, 73194-60-2; **15**, 73194-61-3; **16**, 73194-62-4; **17**, 73194-63-5; **18**, 73194-64-6; **19a**, 52540-41-7; **19b**, 73194-65-7; **19c**, 73194-66-8; **19d**, 73194-67-9; **20a**, 52540-42-8; **20b**, 73194-68-0; **20c**, 73194-69-1; **20d**, 73194-70-4; **21**, 73200-44-9; **22**, 73194-71-5; **23**, 73194-72-6; **24**, 73194-73-7; **25**, 73194-74-8; **26**, 73194-75-9; **27**, 73194-76-0; **28**, 73194-77-1; **29**, 36441-31-3; **30**, 73194-78-2; 1-hydroxy-1-(*p*-methoxybenzyl)phthalan, 73194-79-3; 3-(*p*-methoxybenzal)phthalide, 4767-61-7; dimethyl acetylenedicarboxylate, 762-42-5; dimethyl maleate, 624-48-6; dimethyl fumarate, 624-49-7; maleic anhydride, 108-31-6; maleic acid, 110-16-7; *p*-benzoquinone, 106-51-4; 1,4-naphthoquinone, 130-15-4; *trans*-1,2-dichloroethylene, 156-60-5; methyl acrylate, 96-33-3; acrylic acid, 79-10-7; acrylonitrile, 107-13-1; α-chloroacrylonitrile, 920-37-6; α-acetoxyacrylonitrile, 3061-65-2; 1-benzylnaphthalene, 611-45-0; 1-benzyl-2-naphthoic acid, 73194-80-6; 1-benzyl-2,3-naphthalenedicarboxylic anhydride, 73194-81-7; acryloyl chloride, 814-68-6.

Synthetic Utility of 3,5,5-Trialkoxy-1,2,4-trichlorocyclopentadiene Diels–Alder Adducts in the Preparation of Highly Substituted Aromatic Quinones

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The Diels–Alder reaction of 3,5,5-trialkoxy-1,2,4-trichlorocyclopentadienes with various dienophiles leads to chloro enol ether adducts that can be used synthetically in several ways. When aromatic products are possible, a trifluoroacetic acid (TFA) initiated rearrangement reaction occurs in which quinones having chloro, alkoxy, and carboalkoxy substituents result. If aromatic products are precluded, normal hydrolysis of the chloro enol ether occurs. In TFA these reactions are exclusively initiated by endo protonation of the chloro enol ether moiety.

The exploitative use of 3,5,5-trimethoxy-1,2,4-trichlorocyclopentadiene (**1**) as a starting material for organic synthesis has been minimal.[1] This is despite the fact that it is a reactive diene in Diels–Alder reactions whose adducts can potentially lead by subsequent selective unmasking to two different carbonyl functions of widely different reactivity. In addition, there are reactive alkyl chloride functions which can be utilized as precursors to other important functional groups of interest. Our recent synthesis of a versatile anthracyclinone precursor analogue is an apt example of the aforementioned methodology.[2] In this paper we hope to show that this same methodology can lead to further types of structural units of potential interest.

The preparation of **1** was first performed by McBee and co-workers,[3] who studied the reaction of methoxide ion with hexachlorocyclopentadiene to produce **2**. This was then converted by excess methoxide ion into **1**. These workers proposed the wrong structure for **1**, but this was rectified by the studies of Chang,[4] MacKenzie,[5] and Johnson[6] in later years. These latter investigations have led to precise experimental procedures that allow for the optimum preparation of diene **1** in substantial amounts, thus providing for its ready accessibility in predictable yields and form.

The Diels–Alder reaction of diene **1** with various dienophiles has been shown to yield the expected endo product under mild conditions.[1-7] Selective acid hydrolysis of the

(1) J. Van Bree and M. J. O. Anteunis, *Tetrahedron*, **33**, 3331 (1977).
(2) U. O'Connor and W. Rosen, *Tetrahedron Lett.*, 601 (1979).
(3) E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav, and H. P. Braendlin, *J. Am. Chem. Soc.*, **84**, 3557 (1962).
(4) W. H. Chang, *J. Chem. Soc.*, 4744 (1965).
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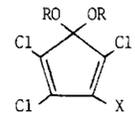
(6) R. I. Kagi and B. L. Johnson, *Aust. J. Chem.*, **28**, 2175 (1975).
(7) R. I. Kagi and B. L. Johnson, *Aust. J. Chem.*, **28**, 2189 (1975).

0022-3263/80/1945-1824$01.00/0

Chart I

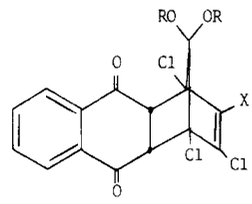


1 X=OCH$_3$, R=CH$_3$

2 X=Cl, R=CH$_3$

3 X=OCH$_3$, R=CH$_2$-

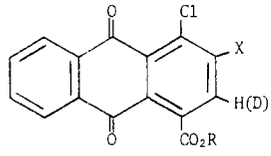
4 X=OCH$_2$CH$_3$, R=CH$_2$-



5 X=OCH$_3$, R=CH$_3$

7 X=OCH$_3$, R=CH$_2$-

9 X=OCH$_2$CH$_3$, R=CH$_2$-



6 X=OCH$_3$, R=CH$_3$

8 X=OCH$_3$, R=CH$_2$CH$_2$Cl

10 X=OCH$_2$CH$_3$, R=CH$_2$CH$_2$Cl

11 X=OCH$_3$ or OH R=CH$_2$CH$_2$O$_2$CCF$_3$

12 X=OCH$_3$ or OH R=CH$_2$CH$_2$OH

endo adduct under a variety of conditions usually leads to an α-chloroketonorbornanone ketal type product. Whether the chloro group is exo or endo is apparently dictated by the conditions chosen or the accessibility of the enol ether to protonation by the acid catalyst. In two instances, however, attempted acid-catalyzed hydrolysis of the Diels–Alder adduct resulted in a cleavage of the strained norbornanone ketal function to yield a carbomethoxy derivative stereospecifically.[1,7] This latter reaction appears to be driven by the stability of the intermediate dioxylium cation and only occurs when strong acid conditions are employed.

In this paper we wish to apply further the aforementioned reaction sequences to a different type of structural unit than that previously employed. Our results indicate that when strongly acidic conditions are applied, aromatic products having a variety of substituents can result, if indeed such a ring system is possible. In addition, we show that the utilization of trifluoroacetic acid (TFA) as the proton source in the selective hydrolysis step preferentially yields the *endo*-protio-*exo*-α-chloro ketone function rather than the thermodynamically more stable *exo*-protio-*endo*-α-chloro ketone.

Results

Diels–Alder Reactions. The cycloaddition reactions of 1, 3, or 4 with the dienophiles maleic anhydride, *p*-benzoquinone, or naphthoquinone were conducted under mild conditions in refluxing benzene. Yields were 60–90%, and the product was always assumed to be the endo product on the basis of the Alder rule and the results of others.[1-7] Physical and spectral data are consistent with the proposed structures, and this is completely enunciated in the Experimental Section (see Chart I).

Hydrolysis and/or Rearrangement Reactions. When some of these Diels–Alder adducts were dissolved in neat trifluoroacetic acid (TFA) at room temperature, a rearrangement reaction occured which could be monitored by proton NMR. The reaction times were found to be dependent upon the identity of the ketal bridge, and, in general, the dimethyl ketals reacted twice as rapidly as the ethylenedioxy ketals. In all cases where TFA-*d* was used, the reaction required an additional period of time, indicating that protonation of the chloro enol ether was probably the rate-determining step.

The hydrolysis product of the naphthoquinone–1 adduct, **5**, has already been described by us.[2] If, however, no water was added to the TFA solvent, the product was completely different. The rearranged structure of the product anthraquinone **6** was deduced from spectral and analytical results and was completely consistent with that proposed. The proton appearing in the NMR at δ 7.3 was the original proton introduced by the acid as verified by its absence in the spectrum when TFA-*d* was utilized. The other major product of this rearrangement reaction was identified as methyl chloride.

When the same conditions were applied to the naphthoquinone–**3** adduct, **7**, the product **8** was derived. The rearranged products of **5** and **7** differed only in the ester grouping, where **8** contained a 2-chloroethyl ester moiety. When the rearrangement reaction was conducted with the naphthoquinone–**4** adduct, **9**, the chloroethyl ester ethyl ether **10** resulted.

In all these reactions minor amounts of other products could be identified in the mass spectra of the crude materials. Although these minor products have not been isolated, they are apparently derived from separate reactions which involve either water or TFA as the ultimate nucleophile rather than chloride ion. Product structures such as **11** or **12** can be proposed as being present in crude **8**.

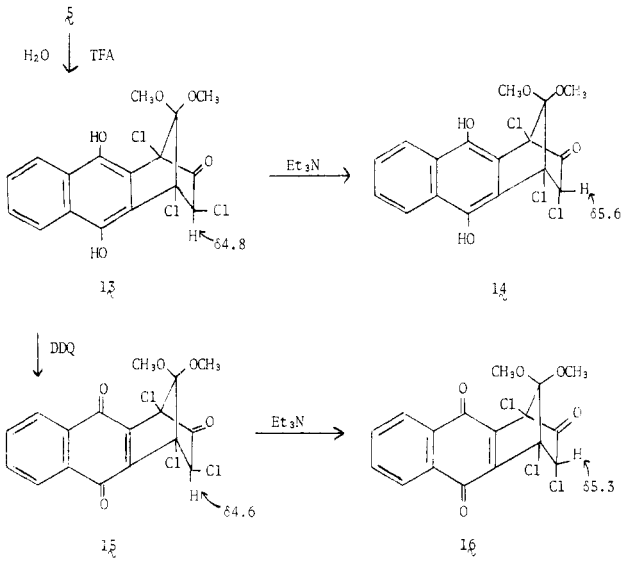
The same rearrangement conditions were applied to the adducts of *p*-benzoquinone and **1**, **3**, or **4** with analogous results. A naphthoquinone was produced having a chlorine, ether, and carboxy ester group in the 1, 2, and 4 positions, respectively. If TFA-*d* was used as solvent, the 3-position was deuterated completely while partial exchange had occurred at positions 6 and 7. Minor products resulting from nucleophiles other than chloride ion were also observed in the crude products of these reactions as well.

In the rearrangement reactions attempted on the maleic anhydride adducts, an inordinate amount of time was required when the system was sealed. If, however, the reaction mixtures were allowed periodic contact with the atmosphere the reaction could be accelerated. The reason for this effect was probably due to the requirement of this reaction for water, but only enough to carry out the necessary hydrolyses. Any more water than the adventitious amount available was detrimental, yielding a complex mixture of materials. Physical and spectral data for all the hydrolysis or rearrangement products are consistent with the proposed structures, and these are elaborated in the Experimental Section.

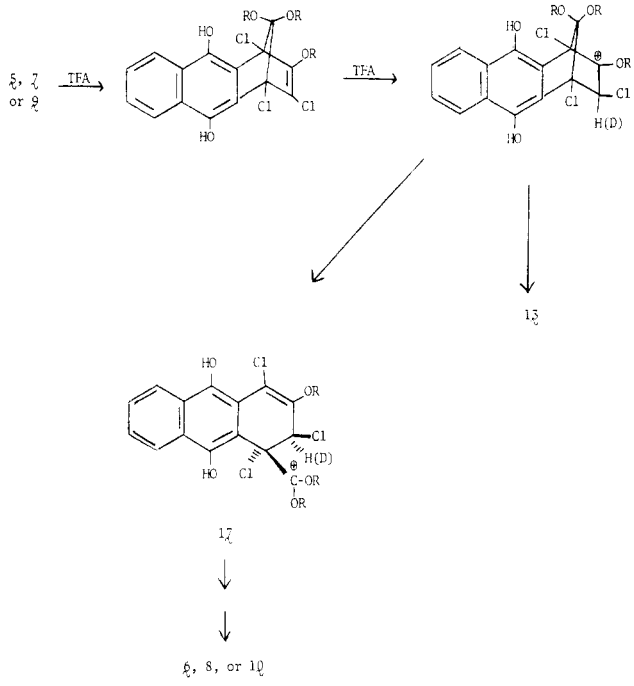
If a potentially aromatic ring is not attached to the norbornane ketal system, then the above-noted rearrangement is not observed. Instead, the system is stable to the conditions and only slow hydrolysis of the chloro enol ether occurs, when water is present. In aqueous TFA the exclusive product is the *exo*-α-chloroketonorbornanone ketal which contrasts with the results of others,[5] who have usually found *endo*-chloro products. Previously we had reported[2] endo protonation of **5** to **13**. This is now confirmed in the selective hydrolysis (in aqueous TFA) of the maleic anhydride adducts of **1** and **3**. Products are produced which have a singlet in the ^{1}H NMR for the α-chloroketo proton. Others[5-7] have found that this proton is a doublet when it is exo because of a W configuration.

The production of the thermodynamically least stable isomer in TFA is of interest. This was shown to be the case in these systems by equilibrating **13** with **14** and **15**

Scheme I



Scheme II



with **16** in the presence of triethylamine (see Scheme I). In both cases a product was derived in which the α-chloroketo proton had shifted downfield, indicating the conversion of an *endo*-α-protio derivative to an *exo*-α-protio derivative. These results and the qualitative observation that the initial protonation was rate determining indicate that the exclusive endo protonation of these systems by TFA is kinetic in nature and probably related to the ability of TFA to stabilize carbenium ions in a bidentate manner.[8]

Discussion

A mechanism that explains the above results is shown in Scheme II by using the naphthoquinone adducts as an example. The first step of the hydrolysis or rearrangement is initiated by rate-determining protonation of the chloro enol ether. The derived carbenium ion can then rearrange to a dioxylium cation or be captured by a nucleophile if one is available. Under the conditions of neat TFA no good nucleophile is present, and thus rearrangement occurs easily. If water is present, normal hydrolysis occurs.[2] Once this reaction has taken place, the subsequent course of events is obscure and can only be conjectured upon at this point.

The noted exclusive endo protonation in trifluoroacetic acid is completely consistent with the derived rearrangement products and the mechanism proposed, since during the course of the reaction the intermediate **17** has a choice of cis elimination of HCl/(DCl) or trans elimination of Cl_2. Obviously the trans dehalogenation dominates with concomitant oxidation of the neighboring intermediate hydroquinone ring system, as shown in Scheme II. The driving force behind this latter intramolecular redox reaction is the resultant aromaticity, but why it occurs in preference to dehydrohalogenation must be investigated.[9]

Conclusion

Exclusive endo protonation is observed in the chloro enol ethers of interest. When the trifluoroacetic acid media contained no other nucleophiles and/or the system had the potential to be aromatic, a rearrangement occured to derive some highly substituted and interesting aromatic quinones. If a good nucleophile was present and/or the ring system had little aromatic potential, then normal, selective hydrolysis of the enol ether was the predominant reaction.[10]

Experimental Section

Elemental analyses were performed by Micro-Analysis Inc. IR spectra were obtained as Nujol mulls or solutions in $CHCl_3$ on a Perkin-Elmer 457 or a Beckman Acculab T.M. 4 spectrophotometer. Proton NMR spectra were measured on a Varian A-60 or a JEOL JNM-C-60 HL Multinuclear spectrometer with Me_4Si as internal standard. The mass spectra were obtained on a Du Pont 490B mass spectrometer. Melting points and boiling points are the uncorrected values. For thin-layer chromatography, silica gel strips (Eastman, with fluorescent indicator) were used and visualized with UV light or iodine.

Preparation of 5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (2). This compound was prepared as described in the literature.[11] From 287 g of freshly distilled hexachlorocyclopentadiene, the desired compound was obtained in 89% yield: bp 62–64 °C (0.2 mm) [lit. bp 79–84 °C (0.6 mm)]; IR (neat) 1640, 1610, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.3 (s).

Preparation of 3,5,5-Trimethoxy-1,2,4-trichlorocyclopentadiene (1). The procedure was based on that previously described.[3] The product was obtained in 80% yield: bp 69–75 °C (0.3–0.5 mm) (lit. bp 102–103 °C (2.5 mm)]; IR (neat) 1640, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.13 (3 H, s), 3.20 (6 H, s).

Preparation of 1,2,4-Trichloro-3-methoxy-5,5-(ethylenedioxy)cyclopentadiene (3). Starting with 1,2,3,4-tetrachloro-5,5-(ethylenedioxy)cyclopentadiene,[12] the diene **3** was prepared by following the procedure of Young.[13] Diene **3** was obtained as a white solid in 65% yield: mp 66–68 °C (lit. mp 70 °C); IR (Nujol) 1660, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.2 (4 H, s), 4.0 (3 H, s).

(8) J. J. Damenberg, *Angew. Chem., Int. Ed. Engl.*, **14**, 641 (1975).

(9) A referee has commented: "The observed preference for 1,2-elimination of Cl_2 rather than HCl from **17** may be independent of the cis or trans nature of these atoms. Product anthraquinones **6**, **8**, and **10** could arise by 1-4, 1-6 and/or 1-8 elimination of two molecules of HCl from **17** or its various keto-tautomers. This obviates the proposed hydroquinone–quinone oxidation after chlorine loss." This may be true, but previous workers have isolated products similar to **17** without resultant aromatization.[1,7]

(10) Recent results in our lab show that juglone and its methyl and acetyl derivatives undergo Diels–Alder reactions with **1**, **3**, and **4** in a nonregiospecific manner; i.e., 1:1 mixtures of the adducts are produced: J. Larson, unpublished results.

(11) P. G. Gassman and J. L. Marshall, "Organic Syntheses", Collect. Vol. V, Wiley, New York, 1973, p 424.

(12) K. MacKenzie, *J. Chem. Soc.*, 5710 (1964).

(13) P. R. Young, Ph.D. Thesis, University of Bristol, England, 1969, p 144. We wish to thank Professor K. MacKenzie for the details of this preparation.

Preparation of 1,2,4-Trichloro-3-ethoxy-5,5-(ethylenedioxy)cyclopentadiene (4). A solution of 1.0 g of KOH in 6 mL of ethanol was added dropwise to a stirred solution of 3.0 g of 1,2,3,4-tetrachloro-5,5-(ethylenedioxy)cyclopentadiene in 10 mL of Me_2SO.[5] As the temperature rose to about 35 °C, KCl began to precipitate. The mixture was stirred at room temperature overnight; the mixture was then poured into 60 mL of H_2O and extracted twice with 50-mL portions of ether. The combined ether extracts were dried over anhydrous $MgSO_4$, filtered and rotary evaporated. The resultant oil crystallized from petroleum ether (bp 30–60 °C) to give 1.0 g of 4 in 33% yield: mp 59–61 °C; IR (Nujol) 1645, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.2 (4 H, s), 4.0 (2 H, q), 1.3 (3 H, t).

General Procedure for the Diels–Alder Cycloaddition Reaction between Dienes 1, 3, or 4 and 1,4-Naphthoquinone, *p*-Benzoquinone, or Maleic Anhydride. A solution of the quinone in benzene in a round-bottomed flask equipped with a stirrer and reflux condenser was placed under nitrogen. To this was added the diene either neat or as a solution in benzene. The mixture was refluxed over an 8–20-h period. After the mixture cooled, the solvent was removed in vacuo and the resultant solid washed with cold methanol and recrystallized.

Preparation of the Diels–Alder Adduct 5. Refluxing 15 g (0.095 mol) of 1,4-naphthoquinone in 250 mL of benzene and 25.9 g (0.1 mol) of diene 1 for 20 h gave 25 g of adduct 5 as a white solid in 60% yield. Recrystallization from acetone gave 16 g of 5: mp 201–204 °C; IR ($CHCl_3$) 1690, 1645, 1600, 1130–1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.3–7.6 (4 H, m), 3.8 (2 H, s), 3.7 (3 H, s), 3.56 (3 H, s), 3.33 (3 H, s); mass spectrum, m/e 381 (M – Cl). Anal. Calcd for $C_{18}H_{15}Cl_3O_5$: C, 51.76; H, 3.62; Cl, 25.46. Found: C, 51.78; H, 3.35; Cl, 25.52.

Preparation of Adduct 7. To 1.3 g (0.008 mol) of 1,4-naphthoquinone dissolved in 27 mL of benzene was added 2.0 g (0.008 mol) of diene 3 as a solution in 20 mL of benzene. The mixture was refluxed for 8 h, and, as it cooled, the adduct 7 crystallized: yield 3.0 g (90%); mp 220–225 °C. Recrystallization from acetone gave 2.4 g of colorless crystals (73% yield): mp 227–230 °C; IR ($CHCl_3$) 1690, 1645, 1600, 1080–980 cm^{-1}; ^1H NMR (TFA) δ 7.9–7.3 (4 H, m), 4.1 (4 H, s), 3.6 (2 H, s), 3.2 (3 H, s); mass spectrum, m/e 379 (M – Cl). Anal. Calcd for $C_{18}H_{13}Cl_3O_5$: C, 52.01; H, 3.15; Cl, 25.59. Found: C, 52.10; H, 3.18; Cl, 25.48.

Preparation of Adduct 9. To a solution of 0.32 g (0.002 mol) of 1,4-naphthoquinones in 20 mL of benzene was added 0.54 g (0.002 mol) of diene 4. The mixture was refluxed for 16 h, cooled, and evaporated to give 0.835 g (97% yield) of the crude adduct 9. Recrystallization from methanol gave 0.80 g (90% yield) of fine colorless crystals: mp 160–165 °C; IR ($CHCl_3$) 1690, 1645, 1040–960 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.5 (4 H, m), 4.25 (4 H, s), 4.0 (2 H, q), 3.7 (2 H, s), 1.0 (3 H, t). Anal. Calcd for $C_{19}H_{15}Cl_3O_5$: C, 53.12; H, 3.49; Cl, 24.56. Found: C, 53.53; H, 3.85; Cl, 25.05.

Preparation of the Diels–Alder Adduct of 1 and *p*-Benzoquinone. To 0.43 g (4.0 mmol) of *p*-benzoquinone in 20 mL of benzene was added 1.03 g (4.0 mmol) of diene 1 dissolved in 10 mL of benzene. The mixture was refluxed for 5 h and then stirred at room temperature overnight. Evaporation of the solvent gave a pale yellow product, 1.4 g (95% yield). Recrystallization from methanol gave 1.1 g (76% yield) of pale yellow crystals: mp 164–167 °C; IR ($CHCl_3$) 1690, 1645, 1620, 1060–950 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.75 (2 H, dd), 4.0 (3 H, s), 3.55 (6 H, s), 3.51 (2 H, s). Anal. Calcd for $C_{14}H_{13}Cl_3O_5$: C, 45.71; H, 3.53; Cl, 29.00. Found: C, 45.44; H, 4.06; Cl, 28.77.

Preparation of the Diels–Alder Adduct of Diene 3 and *p*-Benzoquinone. To 1.08 g (0.01 mol) of *p*-benzoquinone dissolved in 15 mL of benzene was added a solution of 2.60 g (0.01 mol) of diene 3 in 12 mL of benzene. After being refluxed for 20 h, the solution was cooled and evaporated in vacuo to give a yellow product, 2.6 g (71% yield). Recrystallization from methanol gave pale yellow crystals: 2.33 g (63% yield); mp 164–167 °C; IR ($CHCl_3$) 1690, 1645, 1600, 1060–960 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.75 (2 H, dd), 4.2 (4 H, s), 4.0 (3 H, s), 3.55 (2 H, s). Anal. Calcd for $C_{14}H_{11}Cl_3O_5$: C, 45.96; H, 3.03; Cl, 29.13. Found: C, 45.98; H, 3.23; Cl, 28.68.

Preparation of the Diels–Alder Adduct of Diene of 4 and *p*-Benzoquinone. To a solution of 0.07 g (0.5 mmol) of *p*-benzoquinone in 15 mL of benzene was added 0.18 g (0.5 mmol) of diene 4. The mixture was refluxed for 18 h, cooled, and evaporated to give a yellow viscous product. Crystallization from methanol gave yellow crystals: 0.21 g (83% yield); mp 110–114 °C; IR ($CHCl_3$) 1690, 1645, 1620, 1060–960 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.8 (2 H, dd), 4.5–4.2 (6 H, s and q), 3.6 (2 H, s), 1.2 (3 H, t). Anal. Calcd for $C_{15}H_{13}Cl_3O_5$: C, 47.46; H, 3.45; Cl, 28.02. Found: C, 47.72; H, 3.37; Cl, 27.66.

Preparation of the Diels–Alder Adduct of Diene 1 and Maleic Anhydride. To a solution of 0.98 g (0.01 mol) of maleic anhydride in 25 mL of benzene was added 2.60 g (0.01 mol) of 1. The mixture was refluxed overnight and cooled, and the solvent was removed. The resulting solid was recrystallized from petroleum ether (bp 60–90 °C) to yield 3.1 g (86%) of white crystals: mp 161–163 °C (lit.[5] mp 163–165 °C); IR (Nujol) 1860, 1800, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.2 (3 H, s), 3.8 (2 H, s), 3.6 (6 H, s). Anal. Calcd for $C_{12}H_{11}Cl_3O_6$: C, 40.31; H, 3.10; Cl, 29.74. Found: C, 40.30; H, 2.98; Cl, 30.30.

Preparation of the Diels–Alder Adduct of Diene 3 and Maleic Anhydride. To a solution of 0.49 g (0.005 mol) of maleic anhydride in 15 mL of benzene was added 1.29 g (0.005 mol) of 3. The mixture was refluxed for 16 h and cooled, and the solvent was removed. The product was recrystallized from petroleum ether (bp 60–90 °C) to yield 1.12 g (62%) of white crystals: mp 149–151 °C; IR (Nujol) 1860, 1740, 1645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.3 (4 H, s), 4.1 (3 H, s), 3.8 (2 H, s). Anal. Calcd for $C_{12}H_9Cl_3O_6$: C, 40.54; H, 2.55; Cl, 29.91. Found: C, 40.73; H, 2.64; Cl, 29.79.

General Procedure for the Reaction of TFA on the Diels–Alder Adducts. The Diels–Alder adduct, 50 mg, was placed in an NMR tube to which was then added 0.5 mL of TFA. The reaction was monitored by ^1H NMR until no further change was observed in the spectrum. When the mixture cooled, crystalline products were obtained in some cases. Alternatively, the TFA was evaporated in vacuo, yielding yellow solids. The products were recrystallized from methanol. The same procedure was followed with deuterated TFA. Attempts to improve yields in these reactions were not pursued; thus, the reported yields are minimums.

Reaction of TFA with Adduct 5. The product obtained, compound 6, was a yellow crystalline solid: yield 52%; mp 197–199 °C; IR (Nujol) 1730, 1710, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.5–7.8 (4 H, m), 7.43 (1 H, s), 4.16 (3 H, s), 4.06 (3 H, s). Anal. Calcd for $C_{17}H_{11}ClO_5$: C, 61.74; H, 3.35; Cl, 10.72. Found: C, 62.02; H, 3.24; Cl, 10.15.

Reaction of TFA with Adduct 7. The product obtained, compound 8, was a yellow crystalline solid: 55% yield; mp 165–168 °C; IR (Nujol) 1735, 1675, 1600, 1580, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.4–7.7 (4 H, m), 7.3 (1 H, s), 4.65 (2 H, t), 4.03 (3 H, s), 3.85 (2 H, t); mass spectrum, m/e 378, 329 (CH_2Cl), 299 (CH_2O). Anal. Calcd for $C_{18}H_{12}Cl_2O_5$: C, 57.01; H, 3.19; Cl, 18.71. Found: C, 56.81; H, 3.03; Cl, 19.26.

In the NMR of the crude product additional peaks at δ 7.36 (1 H, s) and 4.10 (1 H, s) indicated the presence of a byproduct. Mass spectral data confirmed this as having m/e values of 364, 315 (CH_2Cl), and 285 (CH_2O) which are consistent with structures like 12. Two other side products were observed in the mass spectrum with m/e values of 456 and 442 which are consistent with structures like 11.

Reaction of TFA on Adduct 9. The yellow solid, compound 10, obtained was recrystallized from methanol: yield 47%; mp 169–173 °C; ^1H NMR (TFA) δ 8.5–7.9 (4 H, m), 7.43 (1 H, s), 4.86 (2 H, q), 4.6 (2 H, t), 3.9 (2 H, t), 1.2 (3 H, t); mass spectrum, m/e 392, 285 ($CO_2CH_2CH_2Cl$).

Reaction of TFA on the *p*-Benzoquinone–3 Adduct. The product isolated from this reaction was golden yellow: mp 152–154 °C; IR (Nujol) 1740, 1680, 1600, 1580 cm^{-1}; ^1H NMR ($CDCl_3$) 7.1 (1 H, s), 6.86 (2 H, s), 4.63 (2 H, t), 4.03 (3 H, s), 3.8 (2 H, t); mass spectrum, m/e 328, 249 (OCH_2CH_2Cl). Anal. Calcd for $C_{14}H_{10}Cl_2O_5$: C, 51.01; H, 2.28; Cl, 21.56. Found: C, 51.01; H, 2.36; Cl, 21.16.

Reaction of TFA on the Maleic Anhydride–Diene Adducts. These reactions were run in the same manner as for the other adducts above. However, much more time was required, generally more than 2 weeks, and the NMR tubes had to be opened periodically, i.e., on a daily basis. The products isolated were many because of the added possibility of hydrolyzing the anhydride ring. All products had one characteristic in common,

an endo proton in the ^1H NMR spectrum appearing as a singlet at δ ~4.7. The final ^1H NMR spectra were as follows. Maleic anhydride-1 adduct: δ 4.65 (1 H, s), 4.0 (1 H, d J = 7 Hz), 3.8 (1 H, d J = 7 Hz), 3.7 (3 H, s), 3.6 (3 H, s). Maleic anhydride-3 adduct: δ 4.7 (1 H, s), 4.2 (4 H, s), 3.9 (1 H, d J = 7 Hz), 3.7 (1 H, d J = 7 Hz). (See ref 5 for comparison.)

Oxidation of the Hydroquinone 13 to the Quinone 15 with DDQ. To a solution of 0.22 g (0.53 mmol) of the hydroquinone 13[2] in 40 mL of methanol in a flask fitted with a magnetic stirrer was added 0.23 g (1.0 mmol) of dichlorodicyanoquinone (DDQ) in small portions. After the addition of DDQ was complete, the solution was stirred for an additional 15 min at room temperature, and a yellow solid began to precipitate. When precipitation of the solid was complete, the mixture was filtered to yield the solid quinone: 0.15 g (70% yield); mp 260-263 °C; IR ($CHCl_3$) 1780, 1660, 1580, 1050-920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.5-7.5 (4 H, m), 4.6 (1 H, s), 3.76 (3 H, s), 3.70 (3 H, s).

Triethylamine on Hydroquinone 13. The hydroquinone 13[2] was dissolved in benzene, and to this was added excess triethylamine. From the crude product was obtained a yellowish solid: IR (Nujol) 3400, 1800, 1620, 1100-1000 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.4-7.7 (5 H, m), 7.2 (1 H, s), 5.63 (1 H, s), 3.63 (3 H, s), 3.46 (3 H, s).

Triethylamine on Quinone 15. A few drops of triethylamine were added to a solution of quinone 15 in benzene, and the mixture was stirred for a few hours at room temperature. From the reaction was obtained a dark residue which yielded a yellow solid: IR (Nujol) 1800, 1690, 1590, 1100-1000 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.5-7.5 (4 H, m), 5.3 (1 H, s), 3.76 (3 H, s), 3.7 (3 H, s).

Registry No. 1, 3357-59-3; 1 *p*-benzoquinone adduct, 73286-38-1; 1 maleic anhydride adduct, 49672-95-9; 2, 2207-27-4; 3, 49672-92-6; 3 *p*-benzoquinone adduct, 73286-39-2; 3 maleic anhydride adduct, 73286-40-5; 4, 73286-15-4; 4 *p*-benzoquinone adduct, 73286-16-5; 5, 73346-47-1; 6, 73286-17-6; 7, 73286-18-7; 8, 73286-19-8; 9, 73295-92-8; 10, 73286-20-1; 11 (X = OMe, R = $CH_2CH_2O_2CCF_3$), 73286-21-2; 11 (X = OH, R = $CH_2CH_2O_2CCF_3$), 73286-22-3; 13, 73307-70-7; 14, 73307-71-8; 15, 73286-23-4; 16, 73307-72-9; hexachlorocyclopentadiene, 77-47-4; 1,2,3,4-tetrachloro-5,5-(ethylenedioxy)cyclopentadiene, 2082-08-8; 1,4-naphthoquinone, 130-15-4; *p*-benzoquinone, 106-51-4; maleic anhydride, 108-31-6; 2-(chloroethyl) 4-chloro-5,8-dihydro-5,8-dioxo-3-methoxy-1-naphthalenecarboxylate, 73286-24-5.

One-Step Annelation. A Convenient Method for the Preparation of Diols, Spirolactones, and Spiroethers from Lactones

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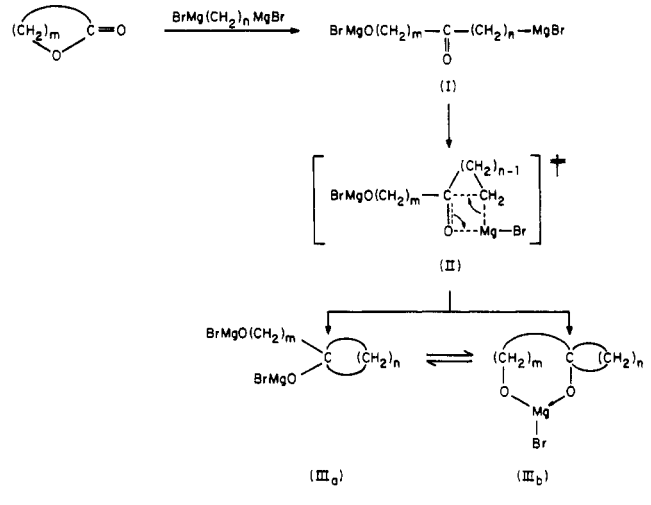
1-(ω-Hydroxyalkyl)cyclopentanols and -cyclohexanols were prepared in one step in high yields from butane-1,4-diyl- and pentane-1,5-diyldimagnesium dibromides and lactones in tetrahydrofuran. This method was found to be general and applicable to lactones of any size (β, γ, δ, and ε) and structure whether aliphatic, aromatic, bicyclic, or spirocyclic. Evidently important steric hindrance close to the carbonyl group prevents annelation and attack on the second nucleophilic center of the Grignard reagent. Furthermore, in the case of oxetan-2-one one obtains, in addition to the corresponding diol, products resulting from scission of the C-O bond. The diols by appropriate transformation afford new routes to spirolactones and spiroethers.

All methods for preparing 1-(ω-hydroxyalkyl)cycloalkanols require several steps which usually result in low overall yields. The only general method applicable to the entire series of such diols would be the reduction of 1-oxaspiroalkan-2-ones. However, the synthesis of such compounds presents serious difficulties.

Other methods require the introduction of the ω-hydroxyalkyl chain to the corresponding cycloalkanone. The products obtained depend upon the order in which the hydroxyl group is introduced into the ω-carbon atom in the chain. Thus for the synthesis of 1-(2-hydroxyethyl)-cycloalkanols the Reformatsky reaction has been used, followed by reduction of the hydroxy esters formed.[1] While the preparation of 1-(3-hydroxypropyl)cycloalkanols was accomplished by three different methods involving reaction of functional organometallic compounds on the cycloalkanones,[2-5] for the synthesis of 1-(4-hydroxybutyl)cycloalkanols, one of these three routes chosen was

Scheme I



the reaction of 3-butenylmagnesium bromide on the cycloalkanones followed by reduction of the double bond by oxidative hydroboration.[6] However, 1-(5-hydroxypentyl)cycloalkanols, as well as other diols, which we have now prepared have not been reported.

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