Table II. Activation Parameters of the Retro-Diene Reaction

	cyclohexane	dichloromethane	acetonitrile
$\Delta H^{\ddagger}$ (±5), kJ/mol	107.0	106.2	104.5
$\log A$	12.13	12.24	11.87
$\Delta S^{\ddagger}$ (±5),[a] J mol^{-1} K^{-1}	−22.0	−20.0	−26.9
$\Delta G^{\ddagger}$,[a] kJ/mol	111.4	110.0	111.0
$\Delta V^{\ddagger}$ (±1.0), cm^3/mol	−2.0	−1.0	−3.4

[a] At 353 K.

volve the quasi-simultaneous breaking of two σ bonds.

Because the instability of the epimeric adduct mixture at temperatures well compatible with the usual high-pressure experimental conditions, we were prompted to study the temperature and the pressure effect on the rate of reaction 1.

At temperatures ≥70 °C, the thermolysis was found to be irreversible, at least within reaction periods not exceeding 3 days. The standard first-order rate law is obeyed within the examined temperature and pressure range. The kinetics was followed by ^{1}H NMR spectroscopy by taking into account the proton in α position of the formed 2-methylfuran (7.30 ppm) and the methylene protons in CH_2Cl_2, serving as an internal standard (5.25 ppm). Table I summarizes the thermolysis rate data.

Arrhenius plots afford $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, while $\Delta V^{\ddagger}$ is deduced from the initial slope of the graph reproducing the response to pressure of ln k according to Evans and Polanyi's equation (Table II).

While $\Delta H^{\ddagger}$ has rather low values, the magnitude of the present $\Delta S^{\ddagger}$ values lies at the lower limit of the usual reported literature values which are generally low, positive or negative.[10] It is concluded that there are no important modifications of rotational or vibrational degrees of freedom in the transition state. Both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values may be in accordance with a process in which the transition state occurs early along the reaction coordinate. However, $\Delta V^{\ddagger}$ offers the most conclusive interpretation.

Since electrostriction effects are highly improbable in this type of reaction [only minor changes in rate constant are introduced by varying the polarity of the medium (Table I)], $\Delta V^{\ddagger}$ is a good measure of the progression of the reaction.[11] For the reverse reaction 1, we find a zero or a slightly negative value which is doubtless indicative of an early transition state so far as *the volume profile* is concerned, in contradiction with the hypothesis of a biradical or a biradicaloid intermediate, though the adduct is a rather unsymmetrical molecule for which it may be conceivable that the weaker C–C bond is cleaved first before attainment of the transition state. The present $\Delta V^{\ddagger}$ values give good evidence for the concerted breaking of the two bonds previously deduced by Seltzer[12] on the basis of secondary isotope effects.

It should be noted that bond cleavage is usually characterized by a large volume increase as examplified by the $\Delta V^{\ddagger}$ (10 cm^3/mol) for O–O breaking.[13] However, the present $\Delta V^{\ddagger}$ values are clearly related to the location of the transition state along the reaction coordinate.

The interesting observation is that the retro-Diels–Alder reaction seems to be slightly accelerated by pressure though the monitoring of procedure allows only a precision not better than 1 cm^3/mol. The result should not be surprising, since the former $\Delta V^{\ddagger}$ value we calculated for the forward reaction (conducted in CH_2Cl_2) was indicative of a minimum in the volume profile ($|\Delta V^{\ddagger} - \overline{\Delta V}| = 1.9$ cm^3/mol).[14] For reaction 1, we get $|\Delta V^{\ddagger} - \overline{\Delta V}| \simeq 1.0$ cm^3/mol. The agreement is satisfactory and could give support for the operation of secondary orbital interactions we invoked to rationalize the tighter transition state compared to the final state. However, the results can also support the possibility of a slight increase in polarity in the transition state, as suggested by le Noble.[15] This question needs further investigation, for the difference $|\Delta V^{\ddagger} - \Delta V|$ is too small here to enable a definitive discussion.

In conclusion, the present kinetic and thermodynamic date are doubtless in favor of an early transition state for the retro-Diels–Alder reaction of *endo*- and *exo*-1-methyl-2-cyano-7-oxabicyclo[2.2.1]hept-5-ene and are in excellent agreement with the concerted scheme postulated previously for the forward reaction.

Registry No. *endo*-1, 1727-98-6; *exo*-1, 56561-73-0.

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Benzylic Oxidation with 2,3-Dichloro-5,6-dicyanobenzoquinone in Aqueous Media. A Convenient Synthesis of Aryl Ketones and Aldehydes

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Received July 26, 1982

2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) has found extensive synthetic application as an oxidant in organic chemistry.[1-4] Oxidation of arylalkanes with DDQ proceeds via a mechanism thought to involve initial hydride abstraction from a benzylic or allylic site to generate a carbonium ion intermediate which can lose a proton to afford an olefinic product (Scheme I).[2,5] The method has important application in the preparation of dihydro aromatic compounds such as 7,8-dihydrobenzo[*a*]pyrene (**2**), re-

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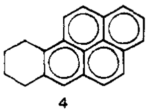
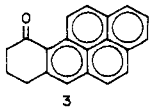
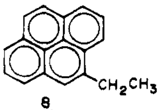
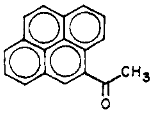
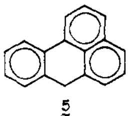
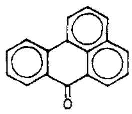
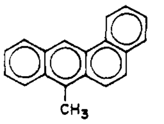
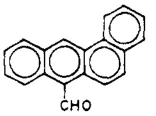
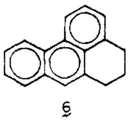
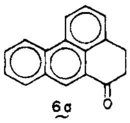
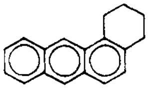
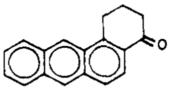
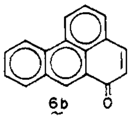
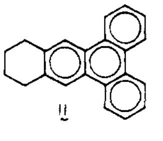
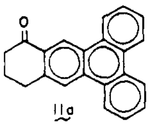
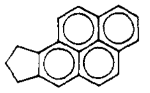
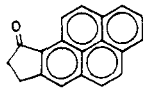
Table I. Oxidation of Arylalkanes with DDQ in Aqueous Media[a]

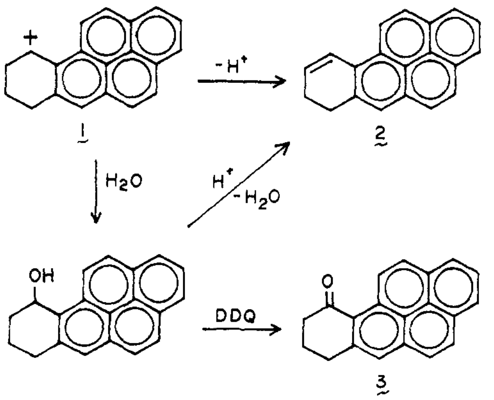
hydrocarbon	product[b]	yield,[c] %	hydrocarbon	product[b]	yield,[c] %
 4	 3	40 (75)[d]	 8		48[h]
 5		87[e]	 9		63 (0)[i]
 6	 6a	39 (0)	 10	 10a	37 (0)[j]
	 6b	19 (70)[f]	 11	 11a	43 (0)[k]
 7		71 (74)[g]	1-methylpyrene 9-methylphenanthrene 1-methylnaphthalene	1-formylpyrene 9-formylphenanthrene 1-formylnaphthalene	33 20 0

[a] Two procedures were employed. **Method I.** To a solution of DDQ (1.5 mmol) in 40 mL of $CHCl_3$ at 65 °C was added 2 mL of water. This solution was stirred for 10 min, and then the hydrocarbon (0.5 mmol) dissolved in 2 mL of $CHCl_3$ was added. This solution was stirred for 3-16 h, cooled, and poured onto a short column of neutral alumina. Elution with dioxane gave the ketone which was crystallized or further purified if necessary by chromatography on Florisil. **Method II.** To a suspension of DDQ (3 mmol) in 30 mL of aqueous dioxane was added a solution of the hydrocarbon (1 mmol) in 2 mL of dioxane. This solution was heated at reflux for 16 h and then worked up as Method I. Since HCN is a product of decomposition of DDQ in water, these reactions were conducted in an efficient hood. [b] NMR spectra of all products matched those of the authentic compounds given in references cited. [c] Yields are for Method I (Method II yields in parentheses). [d] Mp 175-176 °C (EtOAc) (lit.[14] mp 175-177 °C); NMR spectrum.[11] Method I also yielded benzo[a]pyrene (47%). [e] Reaction in $CHCl_3$ or CH_2Cl_2 for 30 min; mp 169-170 °C (lit.[15] mp 170-171 °C). [f] Mp 137-139 °C; 270-MHz proton NMR spectrum.[13] [g] Mp 206-208 °C (EtOAc); NMR spectrum.[16] [h] Reaction in $CHCl_3$ for 16 h gave the ketone and the related alcohol (1:1, 64%). Treatment of this mixture with excess DDQ in refluxing $CHCl_3$ gave 4-acetylpyrene, mp 129-130 °C (EtOAc) (lit.[17] mp 132.5 °C). [i] Mp 145-146 °C (EtOAc) (lit.[18] mp 147.5-148 °C); NMR δ 7.4-9.1 (m, 10, aromatic), 9.3 (s, 1, H_{12}), 11.45 (s, 1, CHO). [j] Mp 196-197 °C (EtOAc) (lit.[19] mp 196-197 °C); the NMR spectrum of 10a was consistent only with the assigned isomer structure.[10] Benz[a]anthracene (56%) was the major product. [k] Mp 203-205 °C (EtOAc) (lit.[20] mp 189-190 °C); NMR spectrum.[20] Method II gave only dibenz[a,c]anthracene (42%).

quired as intermediates in the synthesis of the biologically active dihydrodiol metabolites of carcinogenic polycyclic hydrocarbons.[6-8]

In principle, if the carbonium ion intermediates (e.g., 1) could be trapped by reaction with water, this would furnish benzylic alcohols expected to undergo further oxidation with DDQ to yield ketones (Scheme I). While the use of DDQ in aqueous media for the benzylic oxidation of arylalkanes has not been reported, several examples of oxidations with DDQ in methanol have been described.[9,10] Preliminary investigations in our laboratory of oxidations of arylalkanes with DDQ in methanol showed these reactions to be complicated by formation of secondary products, particularly methyl enol ethers, phenol methyl ethers, and dimethyl ketals, and to afford relatively low yields of the desired ketones.[11]

Scheme I



We now report a convenient new synthesis of aryl ketones and aldehydes through oxidation of the corre-

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(8) Harvey, R. G. *Acc. Chem. Res.* **1981**, *14*, 218.

(9) Oxidation of 6-hydroxytetralin with DDQ in methanol is reported to furnish 6-hydroxytetralone: Findlay, J. W.; Turner, A. B. *Chem. Ind. (London)* **1970**, 158.

(10) Oxidation of 8,9,10,11-tetrahydrobenz[a]anthracene with DDQ in methanol gives 8-oxo- and 11-oxo-8,9,10,11-tetrahydrobenz[a]anthracene along with lesser amounts of the methyl ethers of 8- and 11-hydroxybenz[a]anthracene: Fu, P. P.; Cortez, C.; Sukumaran, K. B.; Harvey, R. G. *J. Org. Chem.* **1979**, *44*, 4265.

(11) Following completion of these studies, Fu et al. reported that attempted oxidation of 7,8,9,10-tetrahydrobenzo[a]pyrene with DDQ in methanol failed to afford 3; an analogous reaction with DDQ in formic acid gave 3 in moderate yield (40%): Fu, P. P.; Clark, J. D.; Huang, A. Y. *J. Chem. Res., Synop.* **1982**, 121.

sponding alkyl-substituted and dihydro aromatic polycyclic hydrocarbons with DDQ in aqueous media. In Table I are summarized the results of oxidation of a series of polycyclic hydrocarbons with DDQ in aqueous dioxane and/or chloroform. Despite the reported instability of DDQ in water,[4] good yields of aryl ketones and aldehydes were generally obtained.

Where more than one benzylic site is present in the molecule (**4**, **6**, **7**, and **10**), reaction takes place, apparently regiospecifically, on the carbon atom which affords the most stable carbocation intermediate,[2,6] theoretically predictable from the calculated delocalization energies.[12]

Dehydrogenation of the initially formed ketone products with DDQ was observed only in the case of 1,10-trimethylenephenanthrene (**6**), oxidation of which with DDQ in aqueous dioxane gave 6*H*-benzanthracen-6-one[13] (**6b**) as the major product. The anticipated primary product, 4,5-dihydro-6*H*-benzanthracen-6-one, could be detected when a smaller excess of DDQ or a shorter reaction time was employed. The resistance of ketones **3**, **10a**, and **11a** to formation of phenolic dehydrogenation products is most likely a consequence of electronic inhibition of formation of the necessary carbonium ion intermediate by the electron-withdrawing carbonyl function.

Yields were dependent upon both the solvent and the ability of the polycyclic aromatic ring system to stabilize the positive charge in the intermediate cation. In accord with expectation, larger fused-ring systems such as pyrene were more effective in this regard than smaller ring systems such as phenanthrene and naphthalene. Solvent effects were often dramatic. In some cases superior yields were obtained with dioxane than with chloroform as a cosolvent, and in other cases the contrary was observed. Other solvents (tetrahydrofuran, dimethyl sulfoxide, dimethylformamide, diglyme) were found to afford generally lower yields. Ohki et al.[21] observed earlier that the rate of oxidation of benzylic alcohols with DDQ was greater in chloroform than in dioxane or other solvents. This effect was ascribed to the relative abilities of these solvents to enhance initial charge-transfer complexation between the alcohol and DDQ. A similar effect appears to be operative in these reactions. The lower yields of ketones observed in some cases with chloroform as the solvent may be due to enhanced rates of secondary reactions, e.g., dehydrogenation of **4** and **10** to benzo[*a*]pyrene and benz[*a*]anthracene, respectively.

Many of the ketones in Table I are intermediates in the synthesis of the mutagenic and carcinogenic dihydrodiol and diol epoxide metabolites of the parent hydrocarbons. In most cases, the method reported herein represents the most convenient synthesis of these biologically important molecules.

Acknowledgment. Support for this research by NIH Grants CA 09183 and CA 14599 is gratefully acknowledged.

Registry No. **3**, 57652-65-0; **4**, 17750-93-5; **5**, 199-94-0; **6**, 4389-09-7; **6a**, 4389-14-4; **6b**, 80252-14-8; **7**, 82979-72-4; **8**, 66778-03-8; **9**, 2541-69-7; **10**, 4483-98-1; **10a**, 38393-90-7; **11**, 25486-89-9; **11a**, 39081-06-6; DDQ, 84-58-2; 7*H*-benz[*de*]anthracen-7-one, 82-05-3; 7,8-dihydro-9*H*-cyclopenta[*a*]pyren-9-one, 82979-73-5; 4-acetylpyrene, 22245-47-2; benz[*a*]anthracene-7-carboxaldehyde, 7505-62-6.

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Platinum-Catalyzed Acylative Cleavage of Cyclic Ethers

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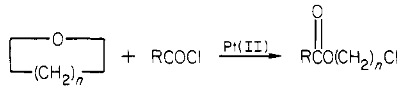
Received August 3, 1982

Although it has been possible to effect acylative cleavage of ethers since the turn of the century by using Lewis acid catalysis,[2] recent work has been directed toward developing mild and selective methods for this potentially useful reaction.[3-5] Very recently a method for the catalysis of acylative cleavage of cyclic ethers using a mixture of a triorganotin halide and a palladium(II) catalyst was reported.[6] The mechanism for the reaction involves bis(triphenylphosphine)palladium(0) as the catalytically active species which first oxidatively adds the acyl halide and then transfers it to the ether substrate. We now report that platinum(II) and rhodium(I) complexes also catalyze this reaction in an exothermic process which occurs even in the absence of any added reducing agent.

Results and Discussion

Cyclic ethers are readily cleaved under mild reaction conditions by acyl halides in the presence of platinum(II) complexes (eq 1). The reactions are usually exothermic



(1)

and, when conducted stoichiometrically with respect to ether and acyl halides, sometimes require external cooling. For this reason the ether was generally used in excess to serve as a heat sink.

The reaction between tetrahydrofuran (**1**) and acetyl chloride (**2**) is typical and yields 4-chlorobutyl acetate in good yield (Table I, reaction 1). This reaction is complete as soon as the mixture cools to room temperature (i.e., 2 h; see Table I, reaction 3). It is catalyzed readily not only by Zeise's salt, $K[PtCl_3(C_2H_4)]$ (**3**), but also by $[Rh(C_2H_4)_2Cl]_2$ (reaction 6). In contrast, *trans*-$[Pt(C_2H_4)pyCl_2]$ is a very poor catalyst for the reaction (reaction 5). The results obtained by using acetyl bromide as the acylating agent parallel those obtained with **2** (reaction 4). On the other hand, the reaction between **1** and benzoyl chloride is not exothermic, and the mixture must be refluxed for 2 h to achieve complete reaction.

The effect of ring size on ether reactivity parallels that reported earlier in the palladium-catalyzed cleavage.[6]

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[6] Pri-Bar, I.; Stille, J. K. *J. Org. Chem.* **1982**, *47*, 1215.

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