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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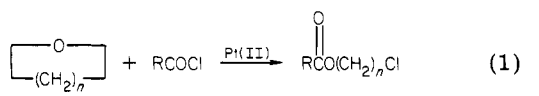
Although it has been possible to effect acylative cleavage of ethers since the turn of the century by using Lewis acid catalysis,[2] recent work has been directed toward developing mild and selective methods for this potentially useful reaction.[3-5] Very recently a method for the catalysis of acylative 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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Table I. Acylative Cleavage Reactions

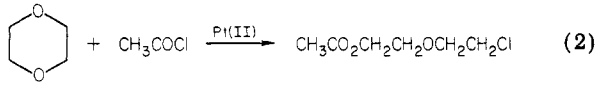
rxn	ether (mol)	acyl halide (mol)	catalyst (mmol)	temp, °C (time, h)[b]	product (% isolated yield)[c]
1	tetrahydrofuran, 1 (0.56)	CH_3COCl, 2 (0.11)	$K[Pt(C_2H_4)Cl_3]$, 3 (1.3)	ambient (24)	$CH_3CO_2CH_2(CH_2)_2CH_2Cl$ (72)
2	1 (0.55)	C_6H_5COCl (0.11)	3 (1.4)	67 (2)	$C_6H_5CO_2CH_2(CH_2)_2CH_2Cl$ (71)
3	1 (0.62)	2 (0.21)	3 (1.4)	ambient (2)	$CH_3CO_2CH_2(CH_2)_2CH_2Cl$ (75)
4	1 (0.37)	CH_3COBr (0.07)	3 (1.3)	ambient (24)	$CH_3CO_2CH_2(CH_2)_2CH_2Br$ (81)
5	1 (0.92)	2 (0.12)	*trans*-$[Pt(C_2H_4)pyCl_2]$ (1.4)[a]	ambient (24)	$CH_3CO_2CH_2(CH_2)_2CH_2Cl$ (19)
6	1 (0.62)	2 (0.12)	$[Rh_2(C_2H_4)_4Cl_2]$ (1.8)	ambient (24)	$CH_3CO_2CH_2(CH_2)_2CH_2Cl$ (83)
7	2-CH_3THF (0.35)	2 (0.08)	3 (1.3)	ambient (24)	$CH_3CO_2CH_2(CH_2)_2CHClCH_3$ (70)
8	2,5-$(CH_3)_2$THF (0.30)	2 (0.06)	$[Pt(C_2H_4)Cl_2]_2$ 4 (0.61)	ambient (24)	$CH_3CO_2CH(CH_3)(CH_2)_2CHClCH_3$ (81)
9	oxetane (0.19)	2 (0.04)	3 (1.4)	ambient (24)	$CH_3CO_2CH_2CH_2CH_2Cl$ (47)
10	tetrahydropyran (0.34)	2 (0.068)	4 (0.61)	ambient (24)	$CH_3CO_2CH_2(CH_2)_3CH_2Cl$ (57)
11	dioxane (0.55)	2 (0.11)	4 (0.60)	ambient (24)	$CH_3CO_2CH_2CH_2OCH_2CH_2Cl$ (22)

[a] Catalyst precipitates during reaction. [b] Reactions liberate heat initially except for 3, 5, and 11. [c] Satisfactory analytical data were reported for all compounds listed in the table.

Oxetane reacts violently to form the chloro ester in 47% yield (reaction 9) while tetrahydropyran (THP) reacts more slowly to form 5-chloropentyl acetate in 57% yield (reaction 10). In the case of THP, Zeise's dimer must be used as catalyst because of the insolubility of the potassium salt; however, this substitution does not alter the course or rate of the reaction (reactions 7 and 8).

It may also be noted that both 2-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran react readily with acetyl chloride. The former reaction leads to the formation of 4-chloropentyl acetate in good yield (reaction 7). Thus the reaction shows the kind of regioselectivity expected in an S_N1 cleavage reaction; however, similar ring-opening reactions which involve cleavage by acetic anhydride in the presence of $MgBr_2$ have been shown to be S_N2 processes,[4] and therefore the mechanism of this reaction is uncertain.

Finally it should be noted that a similar reaction does not occur with acyclic aliphatic ethers such as diethyl ether or 1,2-dimethoxyethane. Thus certain cyclic polyethers can be cleaved to generate esters (eq 2) which contain an



(2)

acyclic aliphatic ether linkage (reaction 11); however, the yield is low. In addition, tetrahydrofuran does not react with a variety of other electrophiles (such as acetic anhydride, trifluoroacetic anhydride, benzenesulfonyl chloride, and chlorotrimethylsilane) in the presence of **2** to afford cleavage products.

Experimental Section

All reactions were conducted in an atmosphere of prepurified nitrogen.

Tetrahydrofuran was dried and distilled from calcium hydride prior to use. Other ethers were obtained commercially and were dried over magnesium sulfate and distilled before use. Acyl halides and anhydrides were obtained commercially and used without further purification. The catalysts, $K[Pt(C_2H_4)Cl_3]$,[7] $[Pt_2(C_2H_4)_2Cl_4]$,[8] *trans*-$[Pt(C_2H_4)(C_5H_5N)Cl_2]$,[9] and $[Rh_2(C_2H_4)_4Cl_2]$,[10] were prepared by previously reported methods.

^1H NMR spectra were determined by using a Perkin-Elmer Model R12A spectrometer. IR spectra were determined by using a Beckman Model 9 spectrophotometer. Yields and product purity were verified by GLC with a Tracor Model 560 chromatograph equipped with a 0.25 in. o.d. × 6 ft column (5% OV-210 on 100/200-mesh Gas Chrom Q). All products showed satisfactory carbon and hydrogen content as determined by Galbraith Laboratories, Knoxville, TN.

Reaction of Tetrahydrofuran (1) with Acetyl Chloride (2). General Procedure for All Cleavage Reactions. In a typical procedure acetyl chloride (8.83 g, 0.113 mol) was added dropwise to a stirred tetrahydrofuran (40.0 g, 0.560 mol) solution of Zeise's salt (**3**; 500 mg, 1.29 mmol). The mixture became warm, and after 24 h the volatiles were flash distilled in vacuo. Distillation of the residue at reduced pressure yielded 12.1 g (72%) 4-chlorobutyl acetate: bp 85–86 °C (20 torr) [lit.[11] bp 92–93 °C (22.0 torr)]; ^1H NMR ($CDCl_3$) δ 4.15 (t, J = 6 Hz, 2 H, $AcOCH_2$), 3.63 (t, J = 6 Hz, 2 H, CH_2Cl), 2.05 (s, 3 H, CH_3CO), 1.95–1.70 (m, 4 H, CH_2CH_2); IR (neat) 1750 cm^{-1} (carbonyl). In a similar experiment the chloroester was obtained in 75% yield after a 2-h reaction time.

Reaction of 1 with Acetyl Bromide. Reaction of 1 (27.0 g, 0.369 mol) and **3** (500 mg, 1.29 mmol) with acetyl bromide (9.08 g, 0.070 mol) yielded 11.1 g (81%) of 4-bromobutyl acetate: bp 85–88 °C (7.0 torr) [lit.[11] bp 87–93 (15.0 torr)]; ^1H NMR (neat) δ 4.20–3.95 (t, J = 6 Hz, 2 H, $AcOCH_2$), 3.65–3.45 (t, J = 6 Hz, 2 H, CH_2Br), 2.0 (s, 3 H, CH_3CO), 1.95–1.6 (m, 4 H, CH_2CH_2); IR (neat) 1750 cm^{-1} (carbonyl).

Reaction of 1 with Benzoyl Chloride. Reaction of 1 (39.6 g, 0.550 mol) in the presence of **3** (530 mg, 1.37 mmol) with benzoyl chloride (15.8 g, 0.113 mol) yielded 16.9 g (70.6%) of 4-chlorobutyl benzoate: bp 103–109 °C (0.60 torr) [lit.[11] bp 140–142 °C (4.0 torr)]; ^1H NMR (C_6D_6) δ 8.16–7.75, 7.48–7.20 (m, 5 H, C_6H_5), 4.34 (t, J = 6 Hz, 2 H, $PhCOCH_2$), 3.59 (t, J = 6 Hz, 2 H, CH_2CO), 1.92 (m, 4 H, CH_2CH_2).

Reaction of 1 and 2 with *trans*-$[Pt(C_2H_4)(py)Cl_2]$. Reaction of 1 (66.5 g, 0.923 mol) in the presence of *trans*-$[Pt(C_2H_4)(py)Cl_2]$ (500 mg, 1.35 mmol) with **2** (9.66 g, 0.123 mol) yielded 3.45 g (19%) of 4-chlorobutyl acetate: bp 80–82 °C (15.0 torr); ^1H NMR and IR as above.

Reaction of 1 and 2 with $[Rh_2(C_2H_4)_4Cl_2]$. Reaction of 1 (44.4 g, 0.615 mol) in the presence of $[Rh_2(C_2H_4)_4Cl_2]$ (500 mg, 1.80 mmol) with **2** (9.66 g, 0.123 mol) yielded 15.2 g (83%) of 4-chlorobutyl acetate: bp 80–82 °C (15.0 torr); ^1H NMR and IR as above.

Reaction of 2-Methyltetrahydrofuran with 2. Reaction of 2-MeTHF (30.1 g, 0.350 mol) in the presence of **3** (500 mg, 1.29

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mmol) with 2 (6.28 g, 0.080 mol) yielded 8.32 g (70%) of 4-chloropentyl acetate: bp 92–95 °C (15 torr) [lit.[12] bp 82 °C (10 torr)]; ^{1}H NMR (neat) δ 4.05 (m, 3 H, CHCl and $AcOCH_2$), 1.97 (s, 3 H, CH_3CO), 1.90–1.65 (m, 4 H, CH_2CH_2), 1.60–1.40 (d, J = 7 Hz, 3 H, $CClCH_3$); IR 1750 cm^{-1} (carbonyl).

Reaction of 2,5-Dimethyltetrahydrofuran with 2. Reaction of 2,5-Me_2THF (30.0 g, 0.299 mol) in the presence of 4 (360 mg, 0.612 mmol) with 2 (4.71 g, 0.060 mol) yielded 8.63 g (81%) of 5-chloro-2-hexyl acetate: bp 90–93 °C (13 torr) [lit.[11] bp 85–87 °C (15 torr)]; ^{1}H NMR (neat) δ 5.10–4.70 (m, 1 H, AcOCH), 4.30–3.70 (m, 1 H, CHCl), 1.95 (s, 3 H, CH_3CO), 1.85–1.65 (m, 4 H, CH_2CH_2), 1.45–1.30 (d, J = 6 Hz, 3 H, $AcOCCH_3$), 1.15–1.05 (d, J = 6 Hz, 3 H, $CClCH_3$); IR 1730 cm^{-1} (carbonyl).

Reaction of Oxetane with 2. Reaction of oxetane (10.7 g, 0.185 mol) in the presence of 3 (530 mg, 1.37 mmol) with 2 (2.90 g, 0.037 mol) yielded 2.35 g (47%) of 3-chloropropyl acetate: bp 65–68 °C (15 torr) [lit.[13] bp 166–175 °C (760 torr)]; ^{1}H NMR (neat) δ 4.35–4.05 (t, J = 6 Hz, 2 H, $AcOCH_2$), 3.85–3.50 (t, J = 6 Hz, 2 H, CH_2Cl), 2.2–1.95 (m, 5 H, CH_3CO and CH_2); IR 1750 cm^{-1} (carbonyl).

Reaction of Tetrahydropyran with 2. Reaction of THP (29.0 g, 0.340 mol) in the presence of 4 (360 mg, 0.612 mmol) with 2 (5.34 g, 0.068 mol) yielded 6.35 g (57%) of 5-chloropentyl acetate: bp 90–92 °C (10 torr) [lit.[14] bp 104 °C (18 torr)]; ^{1}H NMR (neat) δ 4.25–3.90 (t, J = 6 Hz, 2 H, $AcOCH_2$), 3.65–3.40 (t, J = 6 Hz, 2 H, CH_2Cl), 1.97 (s, 3 H, CH_3CO), 1.85–1.40 (m, 6 H, $CH_2CH_2CH_2$); IR 1750 cm^{-1} (carbonyl).

Reaction of *p*-Dioxane with 2. Reaction of *p*-dioxane (48.4 g, 0.550 mol) in the presence of 4 (350 mg, 0.60 mmol) with 2 (8.63 g, 0.106 mol) yielded 3.90 g (22%) of 2-(2-chloroethoxy)ethyl acetate: bp 93–95 °C (4.0 torr); ^{1}H NMR (C_6D_6) δ 4.20–3.97 (t, 4 H, $AcOCH_2$ and CH_2Cl), 3.50–3.25 (t, 4 H, CH_2OCH_2), 1.8 (s, 3 H, CH_3CO); IR 1750 (carbonyl), 1150 cm^{-1} (ether).

Acknowledgment. This work was supported by the Robert A. Welch Foundation (Grant AI-306).

Registry No. 1, 109-99-9; 2, 75-36-5; 3, 16405-35-9; 4, 12073-36-8; $CH_3CO_2CH_2(CH_2)_2CH_2Cl$, 6962-92-1; $C_6H_5CO_2CH_2(CH_2)_2CH_2Cl$, 946-02-1; $CH_3CO_2CH_2(CH_2)_2CH_2Br$, 4753-59-7; $CH_3CH_2(CH_2)_2CHClCH_3$, 36978-15-1; $CH_3CO_2CH(CH_3)(CH_2)_2CHClCH_3$, 84602-36-8; $CH_3CO_2CH_2CH_2CH_2Cl$, 628-09-1; $CH_3CO_2CH_2(CH_2)_3CH_2Cl$, 20395-28-2; $CH_3CO_2CH_2CH_2OCH_2CH_2Cl$, 14258-40-3; C_6H_5COCl, 98-88-4; CH_3COBr, 506-96-7; *trans*-[$Pt(C_2H_4)py Cl_2$], 12078-66-9; [$Rh_2(C_2H_4)_4Cl_2$], 12122-73-5; 2-CH_3THF, 96-47-9; 2,5-$(CH_3)_2$THF, 1003-38-9; oxetane, 503-30-0; tetrahydropyran, 142-68-7; *p*-dioxane, 123-91-1.

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Novel 1,2-Ester Transposition Reactions

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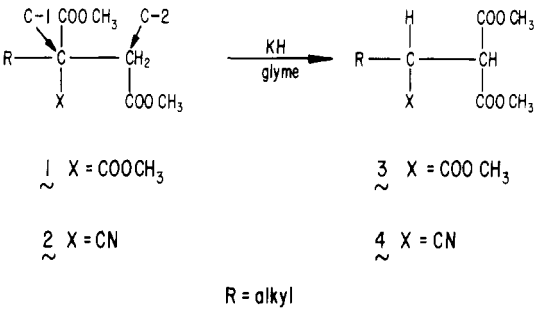
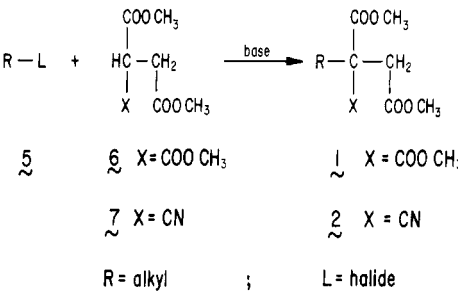
We report a novel 1,2-ester transposition reaction observed during the study of the heavily ester-packed intermediates for synthesis of the experimental anticancer compound Carbethimer (N-137) and its analogues.[1] We have found that in both 1-substituted trimethyl ethane-1,1,2-tricarboxylate **1** and 1-substituted dimethyl cyanoethane-1,2-dicarboxylate **2** systems, treatment with potassium hydride (KH; Scheme I) causes the C-1 ester to migrate cleanly to the adjacent terminal carbon (C-2) to give **3** and **4**, respectively.

(1) J. E. Fields, S. S. Asculai, J. H. Johnson, and R. K. Johnson, *J. Med. Chem.*, **25**, 1060 (1982).

Scheme I



Scheme II



Results and Discussion

The starting materials **1** and **2** for the above rearrangement study were prepared by condensation of the corresponding alkyl halide **5** with trimethyl ethane-1,1,2-tricarboxylate (**6**) or dimethyl 1-cyanoethane-1,2-dicarboxylate (**7**; Scheme II). Treatment of the above alkylation adducts **1** and **2** with KH in 1,2-dimethoxyethane (glyme) leads to this "1,2-ester walk" to the corresponding isomers **3** and **4**. The essentially pure terminal diesters were obtained after acidic workup. We also noticed that this "1,2-ester walk" was extensively inhibited in systems having an additional substituent on C-2. For example, when **8** was subjected to the above condition, the dehydrocyanation and decarbomethoxylation products **9** and **10** were observed[2] (Scheme III).

The structures of the rearranged compounds were established by their ^{1}H NMR and mass spectra. The mass spectroscopic data are very informative. A characteristic pattern of mass fragmentation of the rearranged esters shows the preferential McLafferty rearrangement fragment[3] (e.g., m/e 132 ion), while the spectra of the starting materials indicate the "normal cleavage" ions (e.g., m/e 202 ion; Chart I). Unambiguous structural evidence for this 1,2-ester migration was obtained for the reactions with R = CH_3. The ^{1}H NMR spectra of the rearranged products (i.e., **3** or **4**, R = CH_3) showed three-hydrogen doublets for the methyl absorption, while the ^{1}H NMR spectra of the starting materials (i.e., **1** or **2**, R = CH_3) were three-hydrogen singlets.

To our knowledge this 1,2-ester migration reaction is unprecedented in the literature.[4] A suggested mechanistic

(2) The elimination products were identified by GC/MS analysis. **9**: m/e (relative intensity) 276 (6), 245 (5), 185 (12), 172 (27), 105 (100). High-resolution MS calcd for $C_{16}H_{20}O_4$ (M^+) m/e 276.1362, found m/e 276.1357. **10**: m/e (relative intensity) 218 (27), 159 (88), 129 (55), 117 (100). High-resolution MS calcd for $C_{14}H_{18}O_2$ (M^+) m/e 218.1307, found m/e 218.1299.
(3) F. W. McLafferty, "Interpretation of Mass Spectra", 2nd ed., W. A. Benjamin, New York, 1973, p 58.
(4) An analogous 1,3-ester migration, namely, the "abnormal" Michael addition, was reported by Holder and Lapworth: N. Holder and A. Lapworth, *J. Chem. Soc.*, 2368 (1931). See also: G. A. Swan, *J. Chem. Soc.*, 1939 (1965); E. Bergman and P. Ginsburg, *Org. React.*, **10**, 191–7 (1959).

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