exo-exo-1,4:5,8- and exo-endo-1,4:5,8-diepoxy-1,2,3,4,4a,5,6,7,8,8a-decahydronaphthalenes (4 and 5) were prepared by catalytic hydrogenation of the 2:3 mixture of exoexo-1,4:5,8- and exo-endo-1,4:5,8-diepoxy-1,4,4a,5,8,8a-hexahydronaphthalenes, syntheses of which will be reported in a forthcoming⁷ paper. Typically, the procedure was as follows. A solution of 0.08 g (4.9 10⁻⁴ mol) in 10 mL of EtOAc containing 0.03 g of 5% palladium-on-carbon was hydrogenated in a Parr apparatus at room temperature for 12 h. The catalyst was removed by filtration through a Florisil column. Evaporation of the filtrate gave 0.066 g of the 2:3 mixture of 4 and 5. The crude product was separated by HPLC, employing the conditions indicated previously to give 0.026 g of 4 (mp 72-74 °C; ¹H NMR δ 1.2–1.7 (m, 8 H), 1.87 (s, 2 H), 4.4 (m, 4 H); ¹³C NMR δ 29.68, 52.77, 79.00; mass spectrum m/e 166. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.29; H, 8.43. Found: C, 72.19; H, 8.36) and 0.040 g of 5 (mp 58-60 °C; ¹H NMR δ 1.21-1.88 (m, 8 H), 2.2 (m, 2 H), 4.2-4.5 (m, 4 H); ¹⁸C NMR δ 26.30, 29.80, 53.27, 74.21, 78.72; mass spectrum m/e 166. Anal. Calcd for C₁₀H₁₄O₂: C, 72.29; H 8.43. Found: C, 72.38; H, 8.31).

exo-exo-1,4:9,10- and exo-endo-1,4:9,10-Diepoxy-1,2,3,4,4a,9,9a,10-octahydroanthracene. The same hydrogenation procedure as described previously was followed. Compound 7 was obtained by hydrogenation of exo-exo-1,4:9,10-diepoxy-1,4,4a,9,9a,10-hexahydroanthracene (0.072 g, 3.4×10^{-4} mol) and subsequent purification of the crude hydrogenation product by HPLC in 94% yield: mp 163-165 °C; ¹H NMR δ 1.2-1.73 (m, 4 H), 1.90 (s, 2 H), 4.6 (m, 2 H), 5.28 (s, 2 H), 7.1 (m, 4 H); ¹³C NMR δ 29.74, 51.13, 78.39, 81.72, 118.91, 126.47, 146.11; mass spectrum m/e 214. Anal. Calcd for C₁₄H₁₄O₂: C, 78.48; H, 6.58. Found: C, 78.34; H, 6.64. Similarly, 8 was prepared (by starting with pure exo-endo-1,4:9,10-diepoxy-1,4,4a,9,9a,10-hexahydroanthracene) in 92% yield: mp 164-166 °C; ¹H NMR δ 1.51-1.96 (m, 4 H), 2.38 (m, 2 H), 4.5 (m, 2 H), 5.01 (s, 2 H); ¹³C NMR δ 26.58, 52.54, 77.60, 78.16, 119.19, 126.36, 147.18; mass spectrum m/e 214. Anal. Calcd for C₁₄H₁₄O₂: C, 78.48; H, 6.58. Found: C, 78.37; H, 6.67.

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Decomposition of Cyclobutanecarbonyl m-Chlorobenzoyl Peroxide on Silica. Formation of Esters without the Intervention of Carboxyinversion Compounds

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Introduction

Many diacyl peroxides can give both radical pairs and ion pairs on thermolysis. For peroxides of this type, a change to a more polar medium, particularly the surface of silica,¹ increases the decomposition rate and usually increases the proportion of ionic products. Typical ionic products are carboxyinversion compounds 2, esters 3, and carbenium ions trapped by reaction with a nucleophilic solvent.²⁻⁵

Table I						
medium	Т, ⁰С	concn	$10^{5} k, s^{-1}$			
dry silicaª	26	2.4	120			
silica/CCl ₄ slurry	26	1.0 ^b	230			
CHCi ₃	55	0.04 M	25.6			
CCI4	55	0.04 M	3.0			

^a Placed on the surface with pentane, the solvent removed on a rotary evaporator, and degassed, first point at about 11 min. ^b Wt % of the silica.

Table II. Recovery of Alkyl Groups (mol %)^e

structure	form			
	estera	alcohol ^b	alcohol	alcohold
cyclobutyl	11.8	3.5	3.0	6.5
cyclopropylmethyl	45.5	4.8	4.8	9.6
3-butenyl	19.5	2.3	2.0	4.3

^am-Chlorobenzoates. ^bAlcohol from the slurry solvent plus ether wash. ^cAdditional alcohol recovered after refluxing the washed silica with ether and water. ^dSum of b and c. ^eTotal alkyl group recovery, 97.2. Total m-chlorobenzoate 96, including 19.4 as the acid.

Cyclobutanecarbonyl *m*-chlorobenzoyl peroxide is particularly interesting. Previous studies in fluid solvents suggest that one of the intermediates on the way to the carboxyinversion product is a cluster consisting of an *unbonded* carbenium ion, an unbonded CO_2 molecule, and the *m*-chlorobenzoate counter ion. The evidence for this is the formation of carboxyinversion products **2b** and **2c** in which the alkyl moiety has undergone a carbenium ion rearrangement⁴ and the presence of exchanged OOC moiety in the carboxyinversion product when the reaction is carried out in supercritical CO_2 as the solvent.⁶



The behavior of this peroxide adsorbed on silica was of interest both because this medium has been shown to be especially favorable to the various ionic modes of reaction and because the surface can sometimes trap carbenium ions or change migration aptitudes in the rearranging carbenium ion.⁷

Results

Kinetics. As expected, the decomposition of cyclobutanecarbonyl *m*-chlorobenzoyl peroxide (1) on silica is very fast. The first-order rate constant (Table I) for the reaction at 26 °C, on silica without solvent or in a CCl₄ silica slurry, is of the order of 10^{-3} s⁻¹, while the rates in CHCl₃ or CCl₄ solution are an order of magnitude lower even at 55 °C, a much higher temperature.

Products. The products and their yields are given in Table II. None of the carboxyinversion compounds 2a-c could be detected in the final product mixtures, but experiments with 2a and 2b showed that these compounds decompose on the surface. The products from experiments with 2a and 2b were CO_2 and the corresponding ester 3 with the alkyl group *unrearranged*, indicating that the

Flowers, G. C.; Leffler, J. E. J. Org. Chem. 1985, 50, 4406.
 Leffler, J. E. J. Am. Chem. Soc. 1950, 72, 67.

⁽³⁾ Walling, C.; Waits, H. P.; Milovanovic, J.; Pappiaonnou, C. G. J. Am. Chem. Soc. 1970, 92, 4927.

⁽⁴⁾ Taylor, K. G.; Govindan, C. K.; Kaelin, M. S. J. Am. Chem. Soc. 1979, 101, 2091.

⁽⁵⁾ Walling, C.; Sloan, J. P. J. Am. Chem. Soc. 1979, 101, 7679.
(6) Sigman, M. E.; Barbas, J. T.; Leffler, J. E. J. Org. Chem. 1987, 52, 1754.

⁽⁷⁾ Leffler, J. E.; Barbas, J. T. J. Am. Chem. Soc. 1981, 103, 7768.

decomposition of these compounds does not involve carbenium ion formation. The behavior of 2c was not investigated.

Since some of the ester 3a might have been formed by the decomposition of the carboxyinversion compound, the solvent and washings from the decomposition of 1 in slurries were examined by means of IR in the carbonyl region as soon as possible, about 5 min into the run. Bands from the peroxide and the esters were seen, but none from carboxyinversion compounds. Experiments with slurries containing 2a and 2b showed that bands from 2a could still be seen at 5 min (but not at 12 min) and that bands from 2b could still be seen at 19 min (but not at 39 min).

About 77% of the carbenium ions are trapped as the esters 3a-c. Those that escape reaction with the *m*chlorobenzoate gegenion react with surface water or silanol groups. Alcohols 4a-c were recovered from the silica in two parts, first, from the solvent plus ether washing of the silica, and, second, after refluxing the silica with wet ether to hydrolyze any surface silvl ethers. The total yield of alcohols, 20.4%, is much less than the 49% trapped nucleophilically by acetonitrile when 1 is decomposed in that solvent.4

Experimental Section

Cyclobutanecarbonyl m-chlorobenzoyl peroxide was prepared by the method of Taylor.⁴ It was crystallized several times from hexane at -20 to -18 °C. IR (CH₂Cl₂): C=O stretch at 1800 and 1770 cm⁻¹, C—O at 1230 cm⁻¹. Iodometric titer 99.1%.

Silica. The silica was Fisher S-679, similar to that described previously,⁸ dried overnight at 130 °C.

Cyclobutyl m-Chlorobenzoyl Carbonate and Cyclopropylmethyl m-Chlorobenzoyl Carbonate. The carbonic ester anhydrides 2a,b have been prepared and characterized previously by Taylor et al.⁴ To avoid the use of phosgene, we used a modification of the method used by Michejda and Tarbell in their synthesis of *p*-nitrobenzoic *tert*-butylcarbonic anhydride.⁹

Cyclobutyl m-Chlorobenzoyl Carbonate. To 197 mg of NaH (50% assay), washed twice with low-boiling petroleum ether to remove oil, was added 8 mL of THF distilled over benzophenone ketyl. Then 0.296 g of cyclobutanol was added. After the evolution of H_2 subsided, dry CO₂ was bubbled in for 10-15 min. The solution became warm and then cooled to give a gelatinous mixture. To this was added dropwise 718 mg of m-chlorobenzoyl chloride in THF, with stirring for 10 min. The solvent was removed on a rotary evaporator and replaced with low-boiling petroleum ether; this solution was then washed with water and the solvent again removed. The residual oil was dissolved in about 40 mL of low-boiling petroleum ether and cooled to -20 °C, and a white precipitate (m-chlorobenzoic acid) was discarded. The solvent was again removed, leaving an oil. IR (CH₂Cl₂): carbonyl 1810 cm⁻¹ (strong), 1755 (weaker), C-H 2990 (center, weak to moderate), 1590 (weak), 1435 (weak), 1270 (weak), 1210 (strong), 1140 (weak), 1065 (weak). NMR (CDCl₃): δ 2.6-2.0 (m, 6 H), 5.1 (quintet, 1 H), 8.0–7.2 (m, 4 H).

Cyclopropylmethyl m-chlorobenzoyl carbonate was prepared similarly. IR (CH_2Cl_2) : 1810 cm⁻¹ (strong), 1755 (weaker). NMR (CDCl₃): 0.7-0.3 (m, 4 H), 1.3 (m, 1 H), 4.2 (d, 2 H), 8-7.2 (m, 4 H).

Kinetics. The peroxide was decomposed both in slurries and on the silica after removal of the solvent.

Aliquots for a typical slurry run were prepared by using 5.0 g of the silica, to which were added 10 mL of CCl₄, and then, with stirring, 4 mL of a 0.038 M CCl, solution of peroxide 1. The timer was started midway in the addition of the peroxide. After 5, 8, or 10 min, 4 mL of saturated KI and 50 mL of carbonated glacial acetic acid were added, and the mixture was stirred for 2 min and heated on a steam bath for 3 min while adding pellets of dry ice. Then 50 mL of carbonated water was added and the sample titrated with thiosulfate.

Product Isolation and Analysis. Products were isolated from runs in which the peroxide was decomposed in a CCl₄ slurry and then extracted with ether. The mixture of reaction products, CCL, and ether was then analyzed with a GC/MS, using a Supelcowax-10 capillary column. Authentic samples were run under the same conditions for comparison.

Additional amounts of the alcohols were isolated from the silica by refluxing it with a mixture of 10 mL of H₂O and 50 mL of ether for 12 h and then extracting with ether and drying the extract over Na₂SO₄.

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Novel One-Step Syntheses of Cryptands and **Bis(aza-12-crown-4 ethers)**

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A novel and convenient one-step method to prepare cryptands (1–5, see Scheme I) from readily available α,ω diiodides and α, ω -diamines is reported herein. The cryptands are excellent complexing agents^{1,2} so that a more convenient method for their syntheses is very important. Bis(aza-12-crown-4) compounds 6-8 composed of two identical aza-crowns connected by a di- or trioxaalkane and formed by the reaction of one α, ω -diiodide with each primary amine function of the starting α, ω -diamine (see Scheme I) were isolated as byproducts in some cases. The most convenient syntheses of the cryptands are cyclization reactions from two linear reactants. These cyclic reactions can be $1:1,^{3-7}$ $2:1,^{8-13}$ or $3:2^{7,14-19}$ cyclizations between

- (2) Dietrich, B.; Guilhem, J.; Lehn, J.-M.; Pascard, C.; Sonveaux, E. Helv. Chim. Acta 1984, 67, 91.
- (3) Sun, Y.; Martell, A. E. J. Am. Chem. Soc. 1989, 111, 8023.
 (4) McMurry, T. J.; Hosseini, M. W.; Garrett, T. M.; Hahn, F. E.;
- Reyes, Z. E.; Raymond, K. N. J. Am. Chem. Soc. 1987, 109, 7196. (5) Motekaitis, R. J.; Martell, A. E.; Murase, I. Inorg. Chem. 1986, 25,
- 938 (6) Dietrich, B.; Hosseini, M. W.; Lehn, J.-M.; Sessions, R. B. Helv.
- Chim. Acta 1985, 68, 289. (7) Potvin, P. G.; Wang, M. H. Can. J. Chem. 1988, 66, 2914. (8) Rodriguez-Ubis, J. C.; Alpha, B.; Plancherel, D.; Lehn, J.-M. Helv.
- Chim. Acta 1984, 67, 2264.
- (9) Caron, A.; Guilhem, J.; Riche, R.; Pascard, C.; Alpha, B.; Lehn, J.-M.; Rodriquez-Ubis, J. C. Helv. Chim. Acta 1985, 68, 1577.
 (10) Alpha, B.; Anklam, E.; Descheuanx, R.; Lehn, J.-M.; Pietrasz-kiewicz, M. Helv. Chim. Acta 1988, 71, 1042.
 (11) Lehn, J. M.; de Vains, J. B. R. Tetrahedron Lett. 1989, 30, 2209.
- (12) Pietraszkiewicz, M.; Gasiorowski, R.; Kozbial, M. J. Inclusion Phenom. 1989, 7, 309.
- Kulstad, S.; Malmsten, L. A. Tetrahedron Lett. 1980, 21, 643.
 Newkome, G. R.; Majestic, V. K.; Fronczek, F. R. Tetrahedron Lett. 1981, 22, 3035.
- (15) Krakowiak, K. E.; Bradshaw, J. S.; Izatt, R. M. J. Heterocycl.
- Chem. 1990, 27, 1011.
 (16) McMurry, T. J.; Rodgers, S. J.; Raymond, K. N. J. Am. Chem.
 Soc. 1987, 109, 3451.
 (17) McDowell, D.; Nelson, J. Tetrahedron 1988, 29, 385.

⁽¹⁾ Hamilton, A. D. Crown Ethers and Cryptands. In Comprehensive Heterocyclic Chemistry; Lwowski, W., Ed; Pergamon Press: Oxford, 1984; Vol. 7, pp 731-761.