CH_2Cl_2, and dried (Na_2SO_4), and 330 mg (23%) of **18** was crystallized directly from this solution by addition of an equivalent volume of ethyl ether and refrigeration. Two recrystallizations from CH_2Cl_2/Et_2O (1:1) afforded crystals suitable for X-ray structure determination: ^1H NMR ($CDCl_3$) δ 8.01 (d, J = 8 Hz, 1 H), 7.32–7.63 (m, 7 H), 5.83 (d, J = 13.5 Hz, 1 H), 4.56 (m, 2 H), 4.05 (d, J = 13.5 Hz, 1 H), 3.97 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 169.34, 157.01, 147.68, 138.50, 133.78, 132.48, 131.73, 131.11, 130.71, 130.49, 129.79, 128.75, 127.97, 125.28, 105.19, 66.11, 44.01, 37.21; IR (neat) 1750, 1724, 1640 cm^{-1}.

4-Carbobenzoxy-1-(ethoxymethylene)-2-ketopiperazine (11). 2-Ketopiperazine[16] (1.97 g, 19.67 mmol) and Na_2CO_3 (18 g) were dissolved in a mixture of 50 mL of water and 100 mL of ethyl acetate. The bilayer solution was then vigorously stirred during the dropwise addition of benzyl chloroformate (4.0 g, 23.4 mmol). After the mixture was stirred at ambient temperature for 16 h, the organic layer was separated, dried (Na_2SO_4), and evaporated in vacuo to give 4.51 g (98%) of 4-carbobenzoxy-2-ketopiperazine as a white solid: mp 118–119 °C; ^1H NMR ($CDCl_3$) δ 7.36 (m, 5 H), 6.75 (br s, 1 H), 5.16 (s, 2 H), 4.16 (s, 2 H), 3.70 (t, J = 5.5 Hz, 2 H), 3.39 (m, 2 H). The solid (2.77 g, 11.82 mmol) was added in portions to a stirred suspension of NaH (12.75 mmol) in 75 mL of dry THF under argon. After gas evolution stopped, the reaction was cooled in an ice bath and chloromethyl ethyl ether (1.29 g, 13.64 mmol) in 25 mL of dry THF was added dropwise to the stirred solution. After 18 h at ambient temperature, the reaction was diluted with 25 mL of water and stirred for an additional 0.5 h. The organic layer was separated and evaporated in vacuo, and the residue was purified by flash chromatography, eluting with ethyl acetate/hexane (1:1) to give 3.02 g (87%) of **11** as a pale yellow oil: ^1H NMR ($CDCl_3$) δ 7.35 (m, 5 H), 5.16 (s, 2 H), 4.88 (s, 2 H), 4.20 (s, 2 H), 3.74 (t, J = 7 Hz, 2 H), 3.50 (m, 4 H), 1.21 (t, J = 7 Hz, 3 H). The oil was dried under vacuum (0.25 mmHg) for 24 h and used without further purification.

3-Chloro-9-(ethoxymethyl)-10,11-dihydro-5-phenyl-7*H*,13*H*-pyrazino[1′,2′:3,4]imidazo[1,5-*a*][1,4]benzodiazepine-8,13(9*H*)-dione (19) was prepared from **3** (0.96 g, 1.96 mmol), glycinate **11** (0.82 g, 2.80 mmol), and LDA (3.0 mmol) in THF by the given general procedure. Crude product was purified by flash chromatography, eluting with ethyl acetate/hexane (1:1) followed by 100% ethyl acetate to give 320 mg (37%) of **19** as a tan foam. An analytical sample was dried under vacuum (0.25 mmHg) for 48 h: ^1H NMR ($CDCl_3$) δ 8.01 (d, J = 8 Hz, 1 H), 7.30–7.60 (m, 7 H), 5.93 (d, J = 13.5 Hz, 1 H), 4.95 (s, 2 H), 4.03 (d, J = 13.5 Hz, 1 H), 3.96 (m, 1 H), 3.88 (m, 1 H), 3.68 (t, J = 5.5 Hz, 2 H), 3.55 (q, J = 8 Hz, 2 H), 1.20 (t, J = Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 169.53, 158.43, 148.48, 139.13, 133.34, 131.72, 131.32, 131.03, 130.75, 130.66, 130.17, 129.33, 128.28, 125.61, 109.38, 74.65, 64.13, 44.41, 43.98, 37.93, 14 95. Anal. Calcd for $C_{23}H_{21}N_4O_3Cl$: C, 63.28; H, 4.85; N, 12.82. Found: C, 63.04; H, 4.80; N, 12.63.

Acknowledgment. We thank The BOC Group Technical Center for analytical support and Dr. Ashok Krishnaswami for useful discussions and the 2D-NOESY spectra.

Registry No. **3**, 59318-11-5; **5**, 133473-87-7; **6**, 78605-23-9; **7**, 626-35-7; **8**, 62448-39-9; **9**, 133473-88-8; **10**, 133473-89-9; **11**, 133473-90-2; **12**, 133495-09-7; **13**, 117047-25-3; **14**, 133473-91-3; **15**, 63176-90-9; **16**, 133473-92-4; **18**, 133473-93-5; **19**, 133473-94-6; 7-chloro-1,3-dihydro-5-phenyl-2*H*-1,4-benzodiazepin-2-one, 1088-11-5; 2-oxazolidone, 497-25-6; methyl bromoacetate, 96-32-2; 2-ketopiperazine, 5625-67-2; benzyl chloroformate, 501-53-1; 4-carbobenzoxy-2-ketopiperazine, 78818-15-2; chloromethyl ethyl ether, 3188-13-4.

Supplementary Material Available: X-ray structure drawings and tables listing final atomic positional parameters, atomic thermal parameters, and bond distances and angles for compounds **5** and **18** (16 pages). Ordering information is given on any current masthead page.

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Long-Range Interaction between Lone-Pair Orbitals in Diepoxynaphthalene Derivatives

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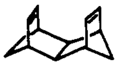
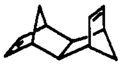
Interactions between π-subunits in "norbornylogues" **1–3** has been extensively studied both spectroscopically[1,2] and theoretically.[2,3]



1



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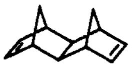
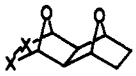


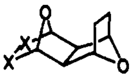
3

PE spectroscopic investigations have unequivocally shown that the two π-levels are split the most in **1** due to cooperative action of through-space (TS)[4] and through-bond (TB)[4] coupling mechanisms. In **2** and **3**, where the TS mode of interaction is negligible due to geometric constraints, the π-orbital splitting is still sizable as a consequence of TB-mediated coupling. Seeking further information with respect to the ability of the norbornylogue skeleton to act as a σ-bond relay, comparative studies with structurally related compounds like **4–6** were a tempting extension.



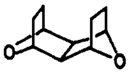
4 X-X = CH_2-CH_2

7 X-X = Ph



5 X-X = CH_2-CH_2

8 X-X = Ph



6

In this paper, we present the results of PES investigations of the newly prepared **4** and **5** and their benzo-annelated analogues **7** and **8**. In all compounds considered here, ionization out of the p-type lone pair orbitals[5] associated with oxygen atoms at etheric bridges is expected to occur bellow 10 eV,[6] thus enabling their clear distinction from the higher laying σ-type bands.

The target compounds **4** and **5** were obtained by catalytic hydrogenation of *exo,exo*-1,4:5,8- and *exo,endo*-1,4:5,8-diepoxy-1,4,4a,5,8,8a-hexahydronaphthalenes. The latter compounds were accessible through a four-step procedure starting with cycloaddition of furan to dimethyl acetylenedicarboxylate.[7,8] Similarly, **7** and **8** were attained by catalytic hydrogenation of *exo,exo*-1,4:9,10- and *exo,-endo*-1,4:9,10-diepoxy-1,4,4a,9,9a,10-hexahydroanthracene,[9] respectively.

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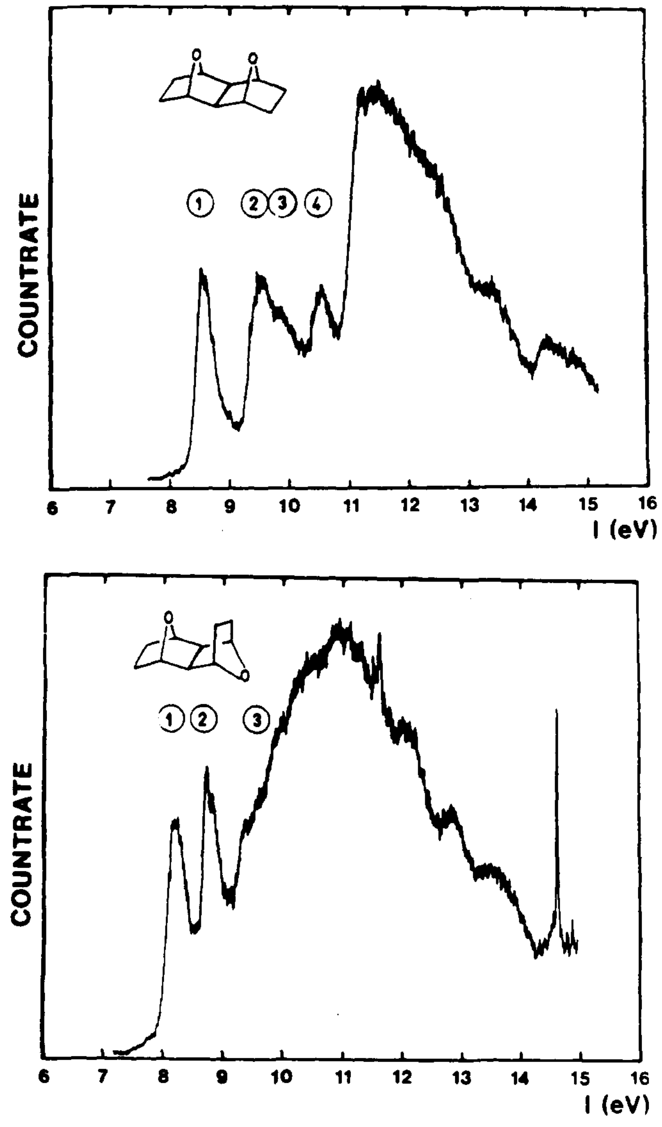

Figure 1. He I PE spectra of 4 and 5.

Table I. Comparison between the Recorded Vertical Ionization Energies ($I_{v,j}$'s) of 4, 5, 7, and 8 and the Calculated Orbital Energies (ϵ_j). All Values in eV.

compd	band	$I_{v,j}$	assignment	$-\epsilon_j$ (AM1)	$-\epsilon_j$ (STO-3G)[a]
4	1	8.87	n_- ($9b_1$)	10.50	8.41
	2	9.80	n_+ ($11a_1$)	10.94	9.15
	3	10.2 (sh)	σ ($6a_2$)	10.99	9.99
	4	10.95	σ ($10a_1$)	11.67	10.00
5	1	9.20	n_- (20a′)	10.67	8.78
	2	9.74	n_+ (19a′)	10.78	9.00
	3	10.45	σ (13a′)	10.86	9.94
7	1	8.68	Ph_S (25a′)	9.45	
	2	9.0	n_- (24a′)	10.58	
	3	9.20 (sh)	Ph_A (16a″)	9.81	
	4	9.96	n_+ (23a′)	11.10	
	5	10.95	σ (22a′)	11.27	
8	1	8.65	Ph_S (25a′)	9.51	
	2 }	9.3	Ph_A (16a″)	9.88	
	3 }		n_- (24a′)	10.71	
	4	9.93	n_+ (23a′)	11.09	
	5	10.6	σ (22a′)	11.16	

[a] Calculations performed on AM1-optimized geometries.

The PE spectra of 4 and 5 are shown in Figure 1, while Figure 2 displays the low-energy region of the PE spectra for 7 and 8. The measured vertical ionization energies are collected in Table I. Assuming the validity of Koopmans' approximation,[10] the ionization energies are assigned to molecular orbital energies. To calculate the orbital energies, we employed semiempirical AM1 procedure assuming C_{2v} and C_s symmetry for 4 and 5–7, respectively. The salient features of the optimized geometry for the compound 4 taken as a representative example are shown

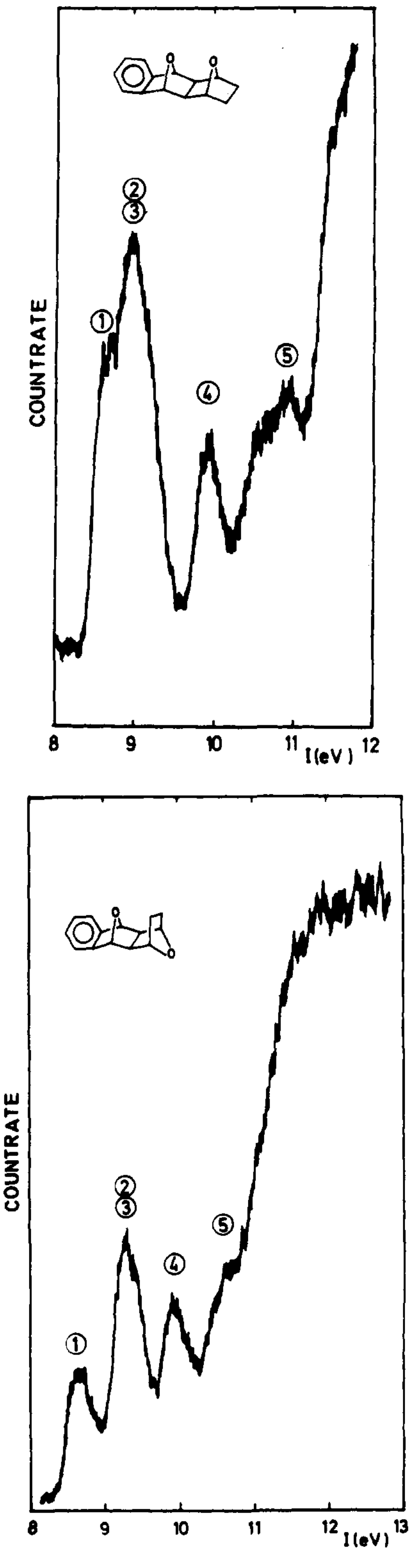

Figure 2. Low-energy region of the He I PE spectra for 7 and 8.

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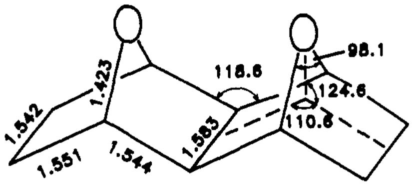
Chart I. Selected Bond Distances (Å) and Bond Angles (deg) for 4 As Calculated by AM1 Procedure



C_{2v}

ΔH_f = -248.8 kJ/mol

in Chart I. It should be pointed out that the calculated structures correspond to absolute minima on the potential surfaces. In addition, for molecules 4 and 5 ab initio STO-3G[12] calculations are performed on the basis of AM1-optimized geometries.

Peak assignments are for the most part straightforward. For instance, starting with 4 and 5 we may safely assign the first ionization band (8.87 eV in 4 and 9.20 eV in 5) to the ionization from the out-of-phase (n_-) linear combination of the p-type oxygen lone pair orbitals and the second ionization band (9.80 eV in 4 and 9.74 eV in 5) to the ionization out of their in-phase (n_+) linear combination. The n_-,n_+ splitting energy drops from 0.97 eV in the former to 0.54 eV in the latter molecule. This is exactly what would be expected on the basis of closer spatial proximity of the oxygen atoms in 4. Bands three and four in the PE spectrum of 4 are assigned to ionization processes from high-lying σ MOs of a_2 and a_1 symmetry, respectively. This conjecture is corroborated by the corresponding band shapes as well as by a comparison of the PE spectral data for 4 and its dimethano congener.[2]

In the case of 7 and 8, we expect four ionization events in the outer valence region, two of predominant n-character and two related to ionization from e_{1g}-symmetry π-orbitals of the benzene moiety, Ph_S and Ph_A, respectively. From the $I_{v,j}$'s of 1,4-epoxy-1,2,3,4-tetrahydronaphthalene,[15] we estimate the latter bands to appear at approximately 8.7 and 9.3 eV, respectively. Let us also mention that a Ph_S,Ph_A energy gap of similar magnitude is also observed in the PE spectra of the dimethano analogues of 7 and 8.[16]

As evidenced by Figure 2, the lowest energy parts of the PE spectra of 7 and 8 feature three ionization events with intensity ratio 1:2:1. We also note that the first and the third peak occupy approximately the same positions in the two spectra, while the position of the second peak is markedly lower in the PE spectrum of 7. Since the energy difference between Ph_S- and Ph_A-related bands is expected to be of the same order of magnitude, the encountered difference should be ascribed to the shift of the ionization event related to ionization from the n_- linear combination. Starting from this assumption, we propose assignment of bands as listed in Table I.

Finally, scrutiny of the data displayed in Table I, shows that the AM1 procedure overestimates the value of the ionization energy associated with the n-type MO's by more than 1 eV.[17] Furthermore, experimentally observed splitting energies between either n_-,n_+ or Ph_S,Ph_A MOs appear to be heavily underestimated. In the case of 7 and 8, this leads to the ordering of the Ph_A and n_- levels in contradiction with the empirical considerations presented previously. STO-3G-calculated splitting energies appear to be somewhat more reliable, but they are still significantly smaller than the experimental values.

Concluding Remarks

The present work indicates that the p-type lone pair orbitals of oxygen atoms incorporated at the bridging positions of fused oxy norbornanes interact strongly irrespective of their conformational arrangement. Significantly larger n,n splitting energies in the exo-exo isomers relative to those found in their exo-endo congeners are compatible with close spatial proximity of the oxygen atoms in the former isomers. It is noteworthy that the splitting between the n-levels in the exo-exo isomers 4 and 7 is found to be slightly weaker (by 0.3 eV) than the splitting between the π-levels in the corresponding norbornylogue 1. Furthermore, the latter value corresponds exactly to the difference in stabilization of the out-of-phase (0.79 eV) and in-phase (0.46 eV) linear combinations encountered, e.g., on passing from 1 to 4. The observed feature can be rationalized in terms of two effects: (i) enhanced through-bond coupling between the in-phase linear combination and the σ-frame in epoxides and (ii) less efficient overlap (i.e., through-space) interaction between 2p(O) lone pair orbitals, as compared to that between the double bond π-orbitals. The origin of the latter effect is a consequence of smaller extention of the lone pair orbitals.

On the other hand, the splitting energies encountered in exo-endo series are roughly equal (0.54 eV in 5 vs 0.44 eV in 2). This implies that the difference in the extent of through-bond interaction between the two series (vide supra) is counterbalanced by other effects, such as, for instance, symmetry-allowed laticyclic conjugation between the bridging groups.[20]

Experimental Section

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX90 FT in $CDCl_3$ with tetramethylsilane as internal standard. Mass spectra were obtained on a Varian CH-7 spectrometer. The PE spectra of 4 and 5 were measured on a PS-18 (Perkin-Elmer Ltd., Beaconsfield) and those of 7 and 8 on a UVG3 Vacuum Generators photoelectron spectrometer. The light source was a He($I\alpha$) lamp. The PE spectra of 4 and 5 were measured at 37 °C and room temperature, respectively, while 7 and 8 had to be heated to 120 °C. The spectra were calibrated with argon and xenon, and a resolution of ~20 meV on the argon line was obtained. High-performance liquid chromatography was performed with a Waters Associates apparatus on a μ-Porasil column with 20% ethyl acetate in hexane as eluent. Calculations were done on a Conwex CP120 computer at the University Computing Center in Zagreb.

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***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 *exo*-*exo*-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 forthcoming[7] 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; ^{1}H NMR δ 1.2–1.7 (m, 8 H), 1.87 (s, 2 H), 4.4 (m, 4 H); ^{13}C 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; ^{1}H NMR δ 1.21–1.88 (m, 8 H), 2.2 (m, 2 H), 4.2–4.5 (m, 4 H); ^{13}C NMR δ 26.30, 29.80, 53.27, 74.21, 78.72; mass spectrum *m/e* 166. Anal. Calcd for $C_{10}H_{14}O_2$: 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; ^{1}H 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); ^{13}C NMR δ 29.74, 51.13, 78.39, 81.72, 118.91, 126.47, 146.11; mass spectrum *m/e* 214. Anal. Calcd for $C_{14}H_{14}O_2$: 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; ^{1}H NMR δ 1.51–1.96 (m, 4 H), 2.38 (m, 2 H), 4.5 (m, 2 H), 5.01 (s, 2 H); ^{13}C NMR δ 26.58, 52.54, 77.60, 78.16, 119.19, 126.36, 147.18; mass spectrum *m/e* 214. Anal. Calcd for $C_{14}H_{14}O_2$: 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	T, °C	concn	10^5 *k*, s^{-1}
dry silica[a]	26	2.4[b]	120
silica/CCl_4 slurry	26	1.0[b]	230
$CHCl_3$	55	0.04 M	25.6
CCl_4	55	0.04 M	3.0

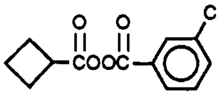
[a] Placed on the surface with pentane, the solvent removed on a rotary evaporator, and degassed, first point at about 11 min. [b] Wt % of the silica.

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

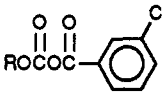
	form			
structure	ester[a]	alcohol[b]	alcohol[c]	alcohol[d]
cyclobutyl	11.8	3.5	3.0	6.5
cyclopropylmethyl	45.5	4.8	4.8	9.6
3-butenyl	19.5	2.3	2.0	4.3

[a] *m*-Chlorobenzoates. [b] Alcohol from the slurry solvent plus ether wash. [c] Additional alcohol recovered after refluxing the washed silica with ether and water. [d] Sum of *b* and *c*. [e] Total alkyl group recovery, 97.2. Total *m*-chlorobenzoate 96, including 19.4 as the acid.

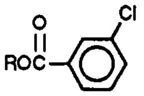
Cyclobutanecarbonyl *m*-chlorobenzoyl peroxide is particularly interesting. Previous studies in fluid solvents suggest that one of the intermediates on the way to the carboxyinversion product is a cluster consisting of an *unbonded* carbenium ion, an unbonded CO_2 molecule, and the *m*-chlorobenzoate 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 rearrangement[4] 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]



1



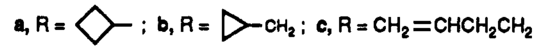
2



3

ROH

4



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 CCl_4 silica slurry, is of the order of 10^{-3} s^{-1}, while the rates in $CHCl_3$ or CCl_4 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

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