J = 6 Hz), 1.35 (d, 6 H, J = 6 Hz); IR (CCl_4) 1765 (C=O), 1580 (NO_2) cm^{-1}.

3,4-Bis(methoxycarbonyl)furazan 2-Oxide. A 0.40-g sample of methyl dinitroacetate was stored at room temperature for 1 week. The liquid was dissolved in 20 mL of methylene chloride, washed with two 10-mL portions of 0.2 N sodium hydroxide, and dried over sodium sulfate. Removal of the solvent gave 0.236 g (96%) of 3,4-bis(methoxycarbonyl)furazan 2-oxide, identical with the previously reported[4] material: NMR ($CDCl_3$) δ 3.95 (s, 3 H), 4.00 (s, 3 H); IR (CH_2Cl_2) 1750, 1740 (C=O), 1625 (NO) cm^{-1}.

3,4-Bis(ethoxycarbonyl)furazan 2-oxide was obtained similarly in 92% yield, identified on the basis of reported[8] spectral properties: NMR ($CDCl_3$) δ 4.38, 4.33 (overlapping quartets, J = 7 Hz), 1.40, 1.35 (overlapping triplets, J = 7 Hz); IR (CH_2Cl_2) 1750, 1740 (C=O), 1625 (NO) cm^{-1}.

3,4-Bis(isopropoxycarbonyl)furazan 2-oxide, a liquid, was obtained similarly in 93% yield: NMR ($CDCl_3$) δ 5.23, 5.18 (overlapping septets, J = 6 Hz each), 1.42 1.37 (doublets, J = 6 Hz); IR (CCl_4) 1740 (C=O), 1620 (NO) cm^{-1}.

Anal. Calcd for $C_{10}H_{14}N_2O_6$: C, 46.51; H, 5.46; N, 10.85. Found: C, 46.36; H, 5.37; N, 11.05.

Registry No. Hexanitroethane, 918-37-6; methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0; methyl dinitroacetate, 25160-76-3; ethyl dinitroacetate, 87711-32-8; isopropyl dinitroacetate, 87711-33-9; 3,4-bis(methoxycarbonyl)furazan 2-oxide, 18322-90-2; 3,4-bis(ethoxycarbonyl)furazan 2-oxide, 18417-40-8; 3,4-bis(isopropoxycarbonyl)furazan 2-oxide, 61678-01-1.

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A Simple Synthesis of Pyracylene[1]

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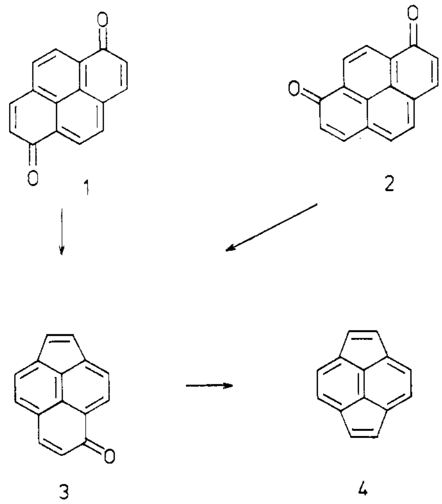
Pyracylene (cyclopent[*fg*]acenaphthylene, 4) is an interesting compound owing to its π-electron system. It is regarded as a [12]annulene perturbed by the internal vinyl cross-link. As a 4n π-system, it is of limited stability. Its synthesis and spectral properties have been described by Trost,[2] however, the synthesis of 4 still remained complicated.



It has been found that cyclic carbonyl compounds eliminate CO upon flow pyrolysis,[3] leading to the corresponding ring-contracted products. If one starts from a six-membered carbonyl system, the corresponding five-membered ring can be obtained.[4] Though flow pyrolysis usually takes place at high temperatures, it can be a suitable method for the synthesis of unstable systems.[3b] There are two six-membered carbonyl systems corresponding to 4: 1,6-pyrenedione (1) and 1,8-pyrenedione (2). Both compounds are accessible easily by oxidation of pyrene.[5]

Flow pyrolysis of 1 and 2 led to a product, which showed in the gas chromatogram–mass spectrum a peak with a molecular weight corresponding to that of 4. The reaction conditions were optimized by using gas chromatography, and subsequently the substance was isolated by careful column chromatography. By comparison of its spectra with the data given by Trost,[2a] it was shown that the substance really was pyracylene (4).

In addition, the primary pyrolysis product, corresponding to the elimination of one CO, 5*H*-cyclopenta[*cd*]phenalen-5-one (3) could be isolated. This substance is a model compound for perturbed [13]annulenones; it was obtained before also only by a multistep synthesis.[6]

After it was shown that both quinones 1 and 2 behaved identical upon pyrolysis and led to the same products, a mixture of 1 and 2, as it was obtained by the oxidation of pyrene, was used. The same results were observed, so it was shown that the expensive separation of the two isomers is unnecessary for this purpose.

Experimental Section

The flow pyrolyses were performed in the apparatus described already,[4b] using a quartz tube (diameter 16 mm, length 250 mm). The pyrolysis zone was filled with a bundle of seven small quartz tubes to increase the contact surface. The reactions were studied in the temperature range of 1000–1200 °C, 1100 °C resulted as the optimum temperature. The pressure measured after the cold trap was 2×10^{-3} mbar; a two-stage rotary pump (displacement swept 40 m^3 h^{-1}) was necessary to maintain the pressure.

The gas chromatographic steel column was 2-m long, 3.2 mm in diameter, and filled with 2.5% OV 17 on Chromosorb G-AW-DMCS 80–100 mesh. The oven temperature started at 150 °C and was programmed at 15°/min to 200 °C. Pyracylene (4) was eluted within 4 min; 1 and 2 remained on the column. A Varian 111 mass spectrometer was used. NMR spectra were run on a Varian T-60 instrument at 50 °C, UV spectra on a Beckman ACTA M VI at 25 °C, and IR spectra on a Perkin-Elmer 521 instrument.

Pyracylene (Cyclopent[*fg*]acenaphthylene, 4) and 5*H*-Cyclopenta[*cd*]phenalen-5-one (3). 1,6-Pyrenedione (1), 1,8-pyrenedione, or a mixture of both, as obtained by the oxidation of pyrene[5] (232 mg, 1 mmol), was sublimed through the pyrolysis tube. The products were condensed on a trap cooled with liquid nitrogen. The pyrolysate was dissolved from the cold trap with cold acetone–cyclohexane (1:1) and evaporated in vacuo to 10 mL (evaporation to dryness has to be avoided because 4 decomposes easily). The products were chromatographed twice on a column of neutral alumina (diameter 2 cm, length 20 cm, activity grade 3). Elution with light petroleum ether and crystallization from CCl_4 gave 46 mg (0.26 mmol, 26%) of slowly decomposing crystals of 4. The NMR (in CCl_4) and the UV (in ethanol) were in accordance with ref 2a; GC–mass spectrum, m/e (relative intensity)

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[1] Presented at the 5th International Symposium on Analytical Pyrolysis, Vail, CO, Sept. 27, 1982. Part 10 of the series "Short Time Pyrolysis and Spectroscopy of Unstable Compounds". Part 9: ref 4b; part 8: ref 4c.

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176 (M^+, 100), 150 (8), 88 (35), 75 (16).

On elution with benzene 5*H*-cyclopenta[*cd*]phenalen-5-one (**3**) (25 mg, 0.12 mmol, 12%) was obtained: mp 158–159 °C (lit.[6] mp 154–156 °C); NMR, UV, and IR according to ref 6; mass spectrum, *m/e* (relative intensity) 204 (M^+, 70), 176 (100), 150 (16), 88 (60), 75 (35).

By further elution with ethyl acetate the starting materials **1** or **2** (76 mg, 0.33 mmol, 33%) could be recovered.

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Registry No. **1**, 1785-51-9; **2**, 2304-85-0; **3**, 23353-92-6; **4**, 187-78-0.

Stereochemistry of Lithium Trimethoxyaluminohydride Reduction of Cyclic Ketones. A Comparison of Its Stereochemical Character with That of Lithium Aluminum Hydride

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Lithium trimethoxyaluminohydride (LTMAH) was assumed[1] to have a greater effective bulk than lithium aluminum hydride (LAH) in their reaction with ketones, presumably owing to the greater steric requirement of the reducing species, $AlH(OCH_3)_3^-$. For instance, hydride reduction of 3,3,5-trimethylcyclohexanone produces a trans/cis alcohol ratio of 79.8:20.2 by LAH; the ratio increases to 95.8:4.2 by LTMAH reduction[1,2] in tetrahydrofuran.[1,2] Likewise, in the hydride reduction of norbornanone,[3] 89% of the endo alcohol was obtained by the use of LAH while 98% of the endo alcohol was obtained by LTMAH. However, in the case of 4-*tert*-butylcyclohexanone,[2,3] the trans/cis alcohol ratio of 88.5:11.5 by LAH is decreased to 61:39 by LTMAH. Here the trend is the same in that the formation of the less stable alcohol (axial or endo alcohol) increases with the replacement of LAH by LTMAH.

These results were generally attributed[2,3] to the greater contribution of steric strain control at the transition states and, hence, a lesser degree of product stability control by the bulkier LTMAH than by LAH.

Through a principle of linear combination of free energies of steric strain and product stability differences, we derived the empirical equation[4]

$$\begin{aligned}\Delta(\Delta G^{\ddagger})_{H} &= \Delta\sigma + \Delta\pi \\ &= \Delta(\Delta G^{\ddagger})_{Me} + 1.4\Delta G^{\circ}\end{aligned}$$

This equation has successfully provided both qualitative and quantitative explanations of the stereochemistry of the hydride reduction of cyclic ketones with LAH.[5] Furthermore, this equation enables one to estimate both steric strain contribution ($\Delta\sigma$) and product stability contribution ($\Delta\pi$) to the energy difference at the transition states, $\Delta(\Delta G^{\ddagger})_H$. In the case of LAH, $\Delta\sigma$ was estimated from the reaction of methyllithium with the same ketone, $\Delta(\Delta G^{\ddagger})_{Me}$ while $\Delta\pi$ was found to be 1.4 ΔG°_H of the two isomeric alcoholic products.

We, therefore, decided to examine the steric strain factor, $\Delta\sigma'$, for the LTMAH reduction of nine cyclic ketones. Unexpectedly, we found that both LAH and LTMAH have about the same steric strain contribution to the energy difference of transition states. The observed stereochemical character of LTMAH is, therefore, best attributed to the diminishing of product stability control.

Results and Discussion

We have chosen nine cyclic ketones ranging from flexible and less hindered substituted cyclohexanes to semirigid and crowded cyclopentanones and to the rigid methyl-substituted norbornanones and studied their reactions with LAH, LTMAH, and methyllithium (MeLi). It was claimed that the stereospecificity of LTMAH becomes particularly effective in the rigid and hindered systems such as 3,3,5-trimethylcyclohexanone[2] and norbornanone;[3] these ketones should provide a clue for estimating the contribution of steric strain and its possible variation from system to system as their steric environment becomes more rigid and congested. A literature method for the preparation of LTMAH in THF[6] was used for this study; the reduction was carried out at 0 °C as reported before. The results are presented in Table I together with the stereochemistries of reactions of these ketones with LAH and with MeLi reported in the literature.[4]

In general, when LAH is replaced by LTMAH, the stereospecificity decreases in the relatively open and flexible system but it becomes larger in the rigid and congested system as reported in the literature.[2,3]

For estimation of $\Delta\sigma'$ and $\Delta\pi'$ for LTMAH reductions of cyclic ketones, the following equation was subjected to linear regression analysis:

$$\Delta(\Delta G^{\ddagger})_{H'} = \Delta\sigma' + \Delta\pi' \tag{1}$$

$$y = ax + b \tag{2}$$

with $x = \Delta(\Delta G^{\ddagger})_{Me}/\Delta G^{\circ}_H$ and $y = \Delta(\Delta G^{\ddagger})_{H'}/\Delta G^{\circ}_H$

Both x and y are calculated from $\Delta(\Delta G^{\ddagger})_{H'}$, $\Delta(\Delta G^{\ddagger})_{Me}$, and ΔG°_H listed in Table I; a best fit for the analysis requires $a = 1.0$ and $b = 0.4$ with a correlation coefficient of 0.9713 (Figure 1). Consequently, a new empirical equation for the LTMAH reduction can now be expressed as

$$\begin{aligned}\Delta(\Delta G^{\ddagger})_{H'} &= \Delta\sigma' + \Delta\pi' \\ &= \Delta(\Delta G^{\ddagger})_{Me} + 0.4\Delta G^{\circ}_H\end{aligned} \tag{3}$$

In the LAH reduction, the corresponding empirical equation[4] is

$$\begin{aligned}\Delta(\Delta G^{\ddagger})_{H} &= \Delta\sigma + \Delta\pi \\ &= \Delta(\Delta G^{\ddagger})_{Me} + 1.4\Delta G^{\circ}_H\end{aligned} \tag{4}$$

Comparison of eq 3 and 4 leads one to conclude that while both LAH and LTMAH have equal steric strain contribution to the transition-state complexes, the transition-state complexes from LAH reduction is under greater influence of product stability difference than is LTMAH reduction. Moreover, Figure 1 shows that irrespective of the steric environment and rigidity of ketones, the effect of steric strain on the transition-state complexes is uniform.

The observed changes in the stereospecificity from the LAH to LTMAH reduction can now be attributed to the diminishing contribution of product stability control, not the enhanced contribution of steric strain from LTMAH.

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