applied above, 170 mg (1.2 mmol) of epoxy ketone 7 was converted in 80% yield to enone 8 which was identical with an authentic sample:[6a] ^{13}C NMR ($CDCl_3$) δ 203.4, 153.5, 131.1, 81.2, 46.0, 43.8, 42.5, 29.0.

Bicyclo[3.3.0]oct-7-en-2-ol Methyl Carbonate (12). Methyl carbonate 12 was prepared from alcohol 1 by a standard procedure: ^{13}C NMR ($CDCl_3$) δ 155.4, 132.7, 127.6, 81.0, 54.4, 53.6, 41.3, 39.2, 30.9, 30.7. Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.67; H, 7.61.

Registry No. 1, 41164-15-2; 2, 10095-78-0; 3, 79068-87-4; 4a, 79068-88-5; 4b, 79068-89-6; 5a, 79068-90-9; 5b, 72397-63-8; 5c, 72397-62-7; 6, 72397-61-6; 7, 79120-22-2; 8, 79068-91-0; 9, 79068-92-1; 10, 79068-93-2; 11, 79120-23-3; 12, 79068-94-3.

Regioselective Reduction of Anhydrides by L-Selectride

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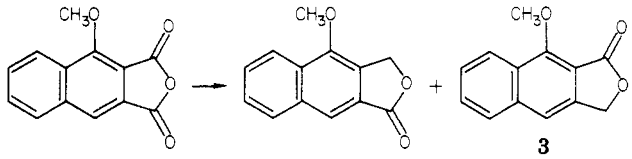
Cyclic anhydrides are useful precursors to lactones via reduction. An older procedure involving zinc/acetic acid appears to be nonselective with unsymmetrical anhydrides[1] and has been largely supplanted by borohydride reduction. With this reagent, the initially formed hydroxy carboxylate product is usually considered to be resistant to further reduction and is converted to lactone by acidification/dehydration. There are intriguing reports[2,3] of selective reduction of the apparently most hindered carbonyl group by $NaBH_4$ and at least one example[4] of selectivity in the opposite sense. Additional examples and a discussion of mechanistic possibilities are found in recent work by Kayser and Morand.[5] A troublesome feature of several examples of reported regioselectivity is the modest yield of isolated lactone.[2-5]

Results and Discussion

We have recently described[6] an approach to 1-alkoxy-2,3-naphthoic anhydride via 1-alkoxyisobenzofuran that should be general for more highly substituted analogues. Similar work has been reported by MacLean and coworkers.[7] Further synthetic utility would be enhanced by selective reduction to one or the other possible lactone. Consequently, we treated naphthoic anhydride 1 with $NaBH_4$ in the expectation that behavior similar to that reported by McCrindle and co-workers[3] for 3-methoxyphthalic anhydride 4a might obtain. The reduction of 1 proved, however, to be essentially devoid of selectivity with this reagent; similar results were obtained with $LiBH_4$. In contrast, L-Selectride provided significant regioselectivity, giving 90% (of total lactone) isomer 3, from hydride attack at the *least* hindered carbonyl. The results are given in Table I.

Table I. Reductions of 1



1 2 3

reagent	% yield (2 + 3)	% 2	% 3
$NaBH_4$	80	58	42
$LiBH_4$	87[a]	55	45
L-Selectride	90	10	90

[a] Corrected for 35% recovered starting material.

The absence of selectivity in the $NaBH_4$ reduction of 1 led us to reexamine the reactions of 4a (R = OCH_3) and 4b (R = CH_3) with this reagent. Contrary to the earlier report[3] for 4a (5a/6a = 87/13), but in close agreement with the low selectivity reported[3] for 4b (5b/6b = 57/43), we find both substrates giving nearly equal mixtures of the two lactones. We suggest that the differences between our observations and those of McCrindle et al. are due to selective loss of material, probably at the hydroxy acid stage, in the earlier work. McCrindle gives overall lactone yields of 52% for 5a,6a, and 77% for 5b,6b. We find that yields are significantly lower for the product from 4a if the evaporation–extraction procedure described in the Experimental Section is not followed.

Lithium triethylborohydride (Superhydride) has recently been shown to give phthalide from phthalic anhydride, in high yield.[8] Application of this reagent to 4a indicates that, like $NaBH_4$, it shows little selectivity; because of cost and workup factors, it offers no advantages over the simpler hydride. L-Selectride reductions of 4a and 4b exhibit regioselection similar to that found in the naphthalene system. The ratio of lactones from 4a does not change significantly when the reduction with L-Selectride is carried out at −78 °C (initial, allowed to warm to ambient), 0 °C, or room temperature.

Although the selectivity observed with this bulky reagent is not exceptionally high, the increase in one isomer can be useful in further synthetic applications, and the product is more easily purified than from the near 50/50 mixtures obtained with $NaBH_4$. Selective reduction of the least hindered carbonyl group is most simply rationalized on steric grounds, although electronic factors may also play a role.

Experimental Section

The preparation of 1-methoxy-2,3-naphthalenedicarboxylic anhydride 1 has been described previously.[6] The procedure of Newman and Kanakarajan[9] was followed to prepare dimethyl 3-methoxyphthalate, mp 76–77 °C, using dimethyl acetylenedicarboxylate and trifluoroacetic acid as catalyst. This ester was hydrolyzed, and the diacid dehydrated in refluxing acetic anhydride to give 4a, mp 162–163 °C (lit.[10] mp 160–161 °C). The anhydride 4b was a commercial sample purified by sublimation and recrystallization from hexane, mp 117.5–119 °C (lit.[11] mp 116–117 °C).

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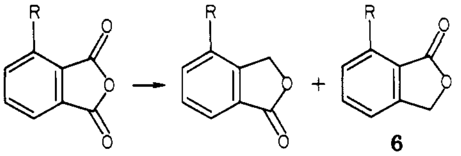
Table II. Reductions of 4



R	reagent	% yield (**5** + **6**)	% **5**	% **6**
OCH_3 (**4a**)	$NaBH_4$	80-93[a]	53 ± 3	47 ± 3
	$LiBH(Et)_3$	76	50	50
	L-Selectride	83	10	90
CH_3 (**4b**)	$NaBH_4$[b]	95	56	44
	L-Selectride	91	15	85

[a] Several reductions were carried out with $NaBH_4$.
[b] Excess $NaBH_4$ must be avoided in this case, as it leads to overreduction to diol, in a reaction that shows some selectivity, diminishing the percentage of **5b** relative to **6b**. The value shown in the table was obtained by using the stoichiometric amount of hydride.

Analyses of lactone mixtures were carried out on the crude products by using ^1H NMR (Varian T-60). The percentage compositions were determined by integration of the sharp singlets due to the methoxy protons in **2**, **3**, **5a**, and **6a**, and the methyl protons of **5b**,**6b** and checked by comparison of the benzylic absorptions where these were distinguishable. The values given in the Tables I and II have the error limits usual to this method of analysis.

Reduction Procedures. Reactions were carried out by using 0.5 g of anhydride, added to a mixture of 1 molar equiv (100% excess) of $NaBH_4$ in 10 mL of THF, and the slurry was refluxed for 2 h. The solvent was removed by rotary evaporation, and 6 N HCl (2.5 mL) was added to decompose excess hydride. The acidic solution was extracted 3 times with small volumes of CH_2Cl_2, and the combined organic phase was dried (Na_2SO_4) and evaporated. Toluene or chlorobenzene (ca. 15 mL) was added, and distilled to effect dehydration; the last traces of solvent were removed by vacuum evaporation, the residue weighed, and a homogeneous sample taken for analysis.

L-Selectride (1 M in THF) reductions were done on the same scale in THF, usually at ambient temperature, for 2 h, using 10% excess of the hydride (a twofold excess of the reagent did not affect yield or composition of products). Approximately 2 mL of 3 N NaOH was added followed by 3 mL of 30% H_2O_2 (vigorous, ice bath needed with dropwise addition). The mixture was acidified with 6 N HCl and rotary evaporated to remove the THF. The remaining slurry/solution was saturated with NaCl and extracted with CH_2Cl_2 as above.

Lactone Identification. Individual isomers were isolated by silica gel chromatography (pentane/CH_2Cl_2) and/or recrystallization and had the following characteristics.

4-Methoxyphthalide: mp 126–128 °C (lit.[12] mp 127 °C); NMR ($CDCl_3$) δ 3.90 (OCH_3), 5.24 (CH_2); IR ($CHCl_3$) 1764 cm^{-1}.

7-Methoxyphthalide: mp 104–106 °C (lit.[13] mp 103.5–105 °C); NMR δ 4.00 (OCH_3), 5.22 (CH_2); IR 1761 cm^{-1}.

4-Methylphthalide: mp 69–70.5 °C (lit.[14] mp 69–70 °C; NMR[15] δ 2.39 (CH_3), 5.27 (CH_2); IR 1760 cm^{-1}.

7-Methylphthalide: mp 87–88 °C (lit.[14] mp 85–87 °C); NMR[15] δ 2.69 (CH_3), 5.27 (CH_2); IR 1752 cm^{-1}.

1-Methoxy-3-(hydroxymethyl)-2-naphthoic Acid γ-Lactone (3): mp 137–139 °C (lit.[16] mp 138 °C); NMR δ 4.33 (s, 3, OCH_3), 5.30 (d, J = 1.3 Hz, 2, CH_2, irradiation of this peak causes sharpening of some signals in the aromatic region), 7.35–8.45 (m, 5, arom); IR ($CHCl_3$) 1761 cm^{-1} (lit.[16] 1757 cm^{-1}); mol wt 214.0627 (calcd 214.0630). We note that our NMR and IR data do not coincide with the values given by Kraus et al.[17]

4-Methoxy-3-(hydroxymethyl)-2-naphthoic Acid γ-Lactone (2): mp 164–166 °C (lit.[16] mp 168 °C); NMR δ 4.13 (s, 3, OCH_3), 5.65 (s, 2, CH_2), 7.5–8.4 (m, 5, arom); IR 1756 cm^{-1}.

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Registry No. 1, 60678-31-1; **2**, 79069-93-5; **3**, 33295-75-9; **4a**, 14963-96-3; **4b**, 4792-30-7; **5a**, 4792-33-0; **5b**, 2211-83-8; **6a**, 28281-58-5; **6b**, 2211-84-9.

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Synthesis and Reactions of 11,12-Dinitro-9,10-dihydro-9,10-ethenoanthracene[1]

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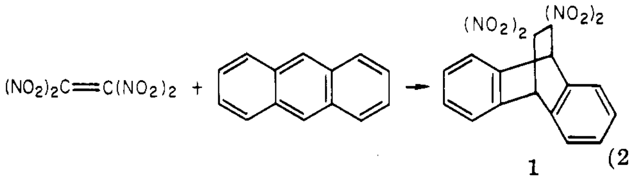
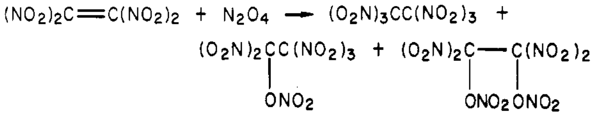
We reported recently[2] that hexanitroethane undergoes elimination of dinitrogen tetraoxide in refluxing benzene (eq 1). When this reaction was carried out in the presence of a diene or an anthracene derivative, the corresponding Diels–Alder adduct derived from tetranitroethylene was isolated; anthracene gave 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene (**1**). In the absence of such a trapping agent, hexanitroethane gives simple gaseous decomposition products.[3] The reaction of the ambident NO_2 radical with olefins is known to give both C–N and C–O products,[4] and readdition to tetranitroethylene by the latter mode would give unstable products.

$$(NO_2)_3CC(NO_2)_3 \rightarrow [(NO_2)_2C{=}C(NO_2)_2] + N_2O_4 \qquad (1)$$



1 (2)



$$(NO_2)_2C{=}C(NO_2)_2 + N_2O_4 \rightarrow (O_2N)_3CC(NO_2)_3 + \underset{ONO_2}{(O_2N)_2C}C(NO_2)_3 + \underset{ONO_2}{(O_2N)_2C}{-}\underset{ONO_2}{C}(NO_2)_2 \qquad (3)$$

It appears, therefore, that if tetranitroethylene is to be isolated directly, contact with N_2O_4 must be avoided. The Diels–Alder reaction is generally reversible, and the retro-Diels–Alder reaction has been found to be useful in synthesis.[5] With this objective we investigated the vacuum pyrolysis of the tetranitroethylene adduct of anthracene (**1**).

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[1] This work was supported by the U.S. Army Research Office.

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