°C; ^{1}H NMR ($(CD_3)_2SO$) δ 3.5 (d, 1 H), 4.2 (m, 1 H), 5.8 (m, 2 H), 7.5–8.6 (m, 8 H); IR (KBr) 3340 (br), 3040, 2920, 1620, 1430, 1320, 1260, 1170, 1060, 900, 880, 840, 800, 770, 750, 740,cm^{-1}; MS (70 eV), *m/e* (relative abundance) 94 (5), 189 (28), 191 (38), 192 (28), 202 (80), 203 (30), 219 (18), 220 (100), 221 (19). Anal. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 87.04; H, 5.69.

Aceanthrylene (1). Compound **6** (0.22 g, 1 mmol) was refluxed for 24 h with a magnetically stirred mixture of 100 mL of benzene and 3.0 g of Al_2O_3 (neutral activity, grade 1) in a 250-mL round-bottom flask equipped with a reflux condenser and a Dean–Stark trap. The orange solution was filtered and the benzene removed by vacuum rotary evaporation. The orange solid was recrystallized from *n*-hexane to yield 0.1 g, 50% of aceanthrylene. Sublimation at 90 °C (0.8 mm) yielded analytically pure **1**: mp 95.0–96.0 °C; UV $\lambda_{max}^{heptane}$ 560 nm (ε 10), 455 (590), 422 (1440), 399 (1970), 378 (2320), 360 (3760), 343 (2160), 250 (40 200), 235 (33 700); ^{1}H NMR ($CDCl_3$) δ 7.0 (d, 1 H, J = 5.0 Hz), 7.3–8.2 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 124.1, 124.6, 125.4, 125.6, 126.7, 127.2, 127.4, 127.6 127.9, 128.0, 129.3, 130.2, 134.3, 135.1, 137.0, 140.3; IR (KBr) 3050, 1600 (w), 1480, 1075, 880, 850, 770, 750, 735, 715 cm^{-1}; MS (70 eV, *m/e* (relative abundance) 57 (12), 88 (8), 178 (78), 200 (22), 202 (100). Anal. Calcd for $C_{16}H_{10}$: C, 95.01; H, 4.99. Found: C, 94.86; H, 5.18.

Aceanthrene (7). A mixture of aceanthrylene (54 mg, 0.2m mmol) and 1 mL of hydrazine in 10 mL of ethanol was magnetically stirred while exposed to the atmosphere and 100 mg of 10% Pd/C was added all at once. After 5 h the catalyst was removed by filtration and the fluorescent yellow solution vacuum rotary evaporated. The pale yellow residue was recrystallized from acetone to yield 49 mg (90%) of aceanthrene: mp 113–114 °C (lit.[11] mp 113–114 °C); ^{1}H NMR ($CDCl_3$) δ 3.7 (m, 4 H), 7.2–8.4 (m, 8 H).

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Registry No. 1, 202-03-9; 3, 6373-11-1; *cis*-4, 90047-28-2; *trans*-4, 90047-31-7; 5, 90047-29-3; 6, 90047-30-6; 7, 641-48-5; oxalyl chloride, 79-37-8; anthracene, 120-12-7.

The Reaction Path of Aqueous Sodium Hydroxide Induced Ring Opening of 4-Bromo-3,4-diphenyl-2-isoxazolin-2-one

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In 1979 an interesting paper on the ring-opening reactions of 3,4-disubstituted-4-bromo-2-isoxazolin-5-ones was published.[1] A noteworthy result was the formation of benzil from 4-bromo-3,4-diphenyl-2-isoxazolin-5-one (**1**).

During the course of a study on the oxidation of 3,4-disubstituted-2-isoxazolin-5-ones,[2] we showed that the mechanism proposed by the above authors for the formation of benzil was not correct. In fact, 4-hydroxy-3,4-diphenyl-2-isoxazolin-5-one (**4b**) forms benzonitrile and benzoylformic acid rather than benzil and carbon dioxide by alkaline treatment followed by acidification.

The aim of this report is to clarify the mechanism of the aqueous sodium hydroxide induced ring opening of 4-bromo-3,4-diphenyl-2-isoxazolin-5-one (**1**).

The reaction path given in Scheme I is proposed for this reaction. The initial formation of an α,β-unsaturated nitroso derivative was previously hypothesized for the ring opening of 3-methyl-4-benzyl-4-bromo-2-isoxazolin-5-one.[1]

The following experimental evidence supports this hypothesis. (i) In aqueous alkaline solution, bromoisoxazolone **1** forms a green solution, which rapidly turns colorless; the benzil precursor is a carboxylic acid salt, and benzil is formed only after acidification and decarboxylation. In fact, carbon dioxide formation is observed, and the nitrogen is present in the final solution as an ammonium salt.

(ii) Treatment of a methanol solution of the bromoisoxazolone **1** with a methanol solution of sodium methoxide affords the methyl ester of 2,3-diphenyl-2-methoxy-3-(hydroxyimino)propanoic acid (**3a**). In this case as well, addition of the methoxide solution initially leads to a green coloration. Hydrolysis of the ester **3a** with aqueous sodium hydroxide, followed by acidification, leads to benzil formation (Scheme II).

The stereochemistry of the hydroxyimine function of ester **3a** is anti with respect to the tertiary carbon atom, as shown in Scheme II. In fact, irradiation of ester **3a** in acetone (Pyrex, high-pressure Hg lamp) leads to the formation of 3,4-diphenyl-4-methoxy-2-isoxazolin-5-one (**4a**). This compound was identified on the basis of analytical and spectroscopic data (see Experimental Section).

The essential role played by the stereochemistry of the hydroxyimine function formed when a 3,4,4-trisubstituted-2-isoxazolin-2-one ring is opened under alkaline conditions is shown by the fact that 3,4-diphenyl-4-methoxy-2-isoxazolin-5-one (**4a**) dissolves in aqueous alkaline solution and is re-formed on acidification.

In the case of bromoisoxazolone **1**, alkaline treatment followed by acidification leads to the exclusive formation of benzil. The 3,4-diphenyl-4-hydroxy-2-isoxazolin-5-one (**4b**) could not be detected (TLC) in the reaction mixture. This supports the hypothesis that ring opening initially leads to the formation of an α,β-unsaturated nitroso derivative that undergoes conjguate addition of the solvent nucleophile (H_2O, MeOH). The preferential addition of the nucleophile to the unsaturated nitroso derivative in a transoid conformation to give oxime in the anti configuration has been previously reported in the literature.[3]

(iii) In the case of the methyl ester of 2,3-diphenyl-2-hydroxy-3-(hydroxyimino)propanoic acid (**3b**)[4] as well, alkaline hydrolysis followed by acidification leads to benzil formation. The stereochemistry of the hydroxyimine function of the ester **3b** is anti with respect to the tertiary carbon. Irradiation under the condition reported above of ester **3b** gave 3,4-diphenyl-4-hydroxy-2-isoxazolin-5-one (**4b**), identified by comparison with an authentic sample[2] (Scheme III).

In conclusion, the particular reactivity of the bromoisoxazolone **1** seems to be related to the following: (i) the presence of the phenyl ring in the 4-position; since a 1,5 hydrogen shift is not possible, the intermediate α,β-unsaturated nitroso derivative reacts exclusively by conjugate addition of the solvent nucleophile, and, (ii) the stereochemistry of the hydroxyimine function formed in this way, which does not allow cyclization to the isoxazolone of the intermediate hydroxyimino acid but rather allows a Neber-type reaction to give a hydroxy azirine, hydrolyzed in acid to benzil.

(1) A. Silveira, Jr., and S. K. Satra, *J. Org. Chem.*, **44**, 873 (1979).
(2) C. Baldoli, E. M. Beccalli, E. Licandro, and A. Marchesini, *Gazz. Chim. Ital.*, 111, 347 (1981).
(3) J. H. Smith, J. H. Heidema, and E. T. Kaiser, *J. Am. Chem. Soc.*, **94**, 9276 (1972); T. L. Gilchrist, *Q. Rev.*, 53 (1983).
(4) H. Le Dao, F. Dayer, L. Duc, H. Rodé-Gowal, and H. Dahn, *Helv. Chim. Acta*, **57**, 2215 (1974).

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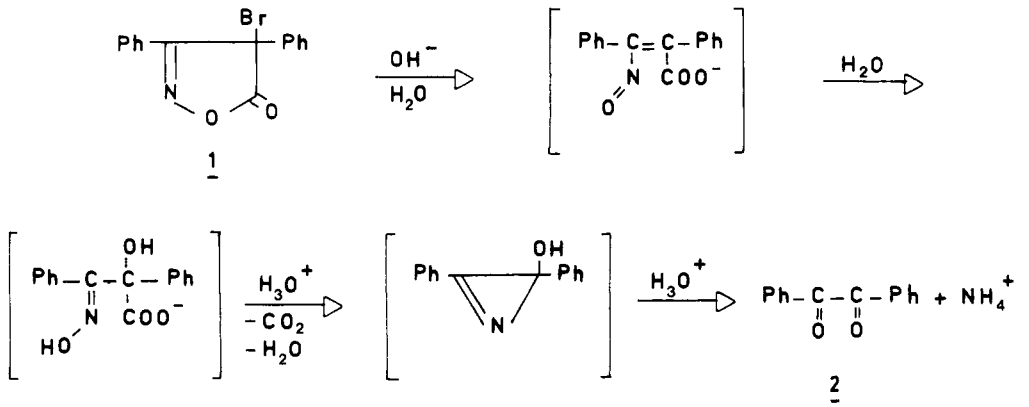
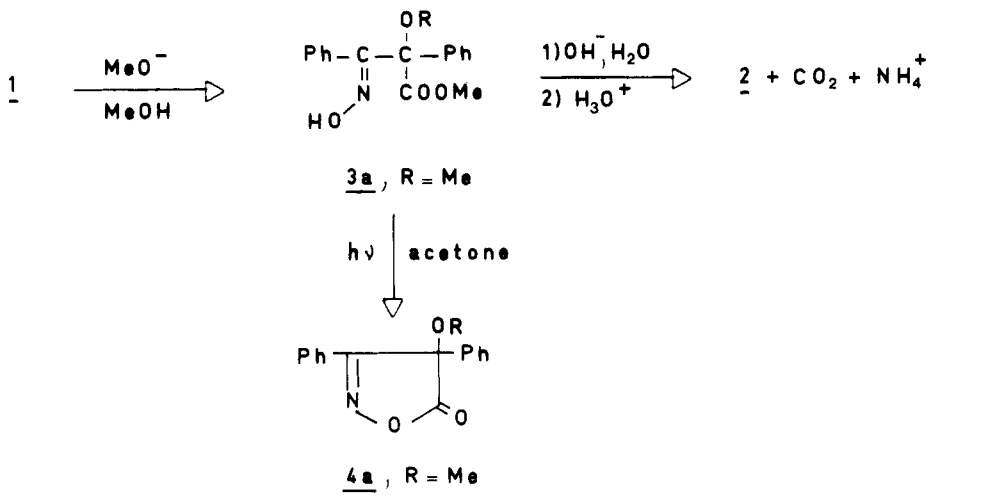
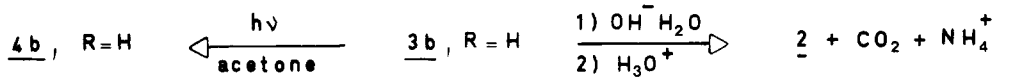
Scheme I



Scheme II



Scheme III



The hypothesis of an azirine intermediate seems reasonable even if it is not suggested by the experimental evidence. However, attempts to capture the intermediate azirine with tetraphenylcyclopentadienone were unsuccessful.

Experimental Section

All melting and boiling points are uncorrected. IR spectra were determined with a Perkin-Elmer 377 instrument. NMR spectra were recorded on a Varian EM-390 spectrometer, in $CDCl_3$ solution with tetramethylsilane as an internal standard. TLC was carried out with Merck Kieselgel F_{254}. Column chromatography was performed on Merck Kieselgel 60, 0.063–0.200 mm. Magnesium sulfate was used as a drying agent. Evaporation was carried out in vacuo (rotary evaporation). Irradiation was carried out with a 125-W HPK Philips high-pressure Hg lamp and a Pyrex filter.

Formation of Methyl 2,3-Diphenyl-2-methoxy-3-(hydroxyimino)propanoate (3a). 4-Bromo-3,4-diphenyl-2-isoxazolin-5-one[1] (1; 2 g) was dissolved in MeOH (50 mL), and then a solution of Na (160 mg) in MeOH (30 mL) was added at room temperature with stirring. The solution became green and then colorless. After 15 min at room temperature, the solvent was evaporated and 9% HCl (50 mL) added. The mixture was extracted with CH_2Cl_2 (2 × 50 mL). Silica gel column chromatography of the residue from the solvent evaporation (eluant hexane–Et_2O, 8:1, v/v) afforded methyl 2,3-diphenyl-2-methoxy-3-(hydroxyimino)propanoate (**3a**; 1.23 g): mp 159–160 °C from CH_2Cl_2–hexane; IR (Nujol) 3420, 1730 cm^{-1}; NMR δ 8.1 (1 H, s), 7.5 (2 H, m), 7.2 (8 H, m), 3.63 (3 H, s), 3.58 (3 H, s). Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.73; N, 4.68. Found: C, 68.55; H, 5.79; N, 4.76.

Alkaline Hydrolysis of Methyl 2,3-Diphenyl-2-methoxy-3-(hydroxyimino)propanoate (3a). Formation of Benzil. Methyl ester **3a** (900 mg) was dissolved in THF (5 mL), and then a solution of NaOH (630 mg) in H_2O (25 mL) was added. The mixture was stirred for 24 h at room temperature, dilute HCl was added (9%, 15 mL), and then the mixture was extracted with CH_2Cl_2 (2 × 30 mL). The yellow organic layer was dried. The residue from the solvent evaporation was purified by silica gel column chromatography (eluant hexane–CH_2Cl_2, 8:1, v/v), affording benzil (440 mg): mp 94–95 °C from benzene–hexane.

3,4-Diphenyl-4-methoxy-2-isoxazolin-5-one (4a). Methyl ester **3a** (500 mg) was dissolved in acetone (80 mL), N_2 was bubbled through the solution for 5 min, and irradiation was carried out for 6 h. After solvent evaporation silica gel column chromatography of the residue (eluant hexane–Et_2O, 5:1, v/v) afforded isoxazolone **4a** (310 mg): mp 101–102 °C from CH_2Cl_2–hexane; IR (Nujol) 1795 cm^{-1}; NMR δ 7.75 (2 H, m), 7.3 (8 H, m), 3.45 (3 H, s). Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.62; H, 4.87; N, 5.26. Unreacted ester **3a** (100 mg) was also obtained.

Alkaline Hydrolysis of Methyl 2,3-Diphenyl-2-hydroxy-3-(hydroxyimino)propanoate (3b). Formation of Benzil. Hydroxyimino ester **3b** (1 g)[4] was dissolved in MeOH (40 mL), and then a solution of NaOH (1 g) in H_2O (5 mL) was added. After 4 h at room temperature, the MeOH was evaporated and the residue diluted with water (30 mL). The colorless solution was treated with dilute HCl (9%, 20mL) and extracted with CH_2Cl_2 (2 × 30 mL). The yellow organic layer was dried. The residue

from the solvent evaporation was purified by silica gel column chromatography (eluant hexane–CH_2Cl_2, 8:1, v/v), affording benzil (385 mg): mp 94–95 °C from benzene–hexane.

3,4-Diphenyl-4-hydroxy-2-isoxazolin-5-one (4b). Methyl 2,3-diphenyl-2-hydroxy-3-(hydroxyimino)propanoate[4] (**3b**; 650 mg) was dissolved in acetone (90 mL), N_2 was bubbled through the solution for 5 min, and irradiation (high-pressure Hg lamp, 125 W, Pyrex filter) was carried out for 5 h. After solvent evaporation, silica gel column chromatography of the residue (eluant hexane–Et_2O, 4:1, v/v) afforded 3,4-diphenyl-4-hydroxy-2-isoxazolin-5-one (215 mg): mp 106–107 °C from Et_2O–pentane, identical with an authentic sample.[2] Unreacted ester **3b** (170 mg) was also recovered.

Registry No. 1, 68708-09-8; **3a**, 89773-82-0; **3b**, 54458-46-7; **4a**, 89773-83-1; **4b**, 80490-41-1.

Communications

A New, Highly Stereoselective Reducing Agent, Potassium 9-(2,3-Dimethyl-2-butoxy)-9-boratabicyclo[3.3.1]nonane

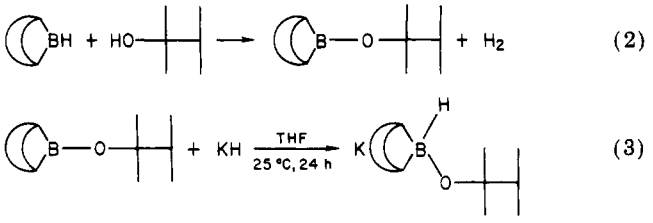
Summary: A new reagent, potassium 9-(2,3-dimethyl-2-butoxy)-9-boratabicyclo[3.3.1]nonane (K9-OThx-9-BBNH), achieves highly stereoselective reductions of cyclic ketones with very simple recovery of the product.

Sir: We have synthesized a new stereoselective reducing agent, potassium 9-(2,3-dimethyl-2-butoxy)-9-boratabicyclo[3.3.1]nonane (K9-OThx-9-BBNH, **1**), and have examined its stereoselectivity toward cyclic ketones. This borohydride reveals an excellent stereoselectivity at 0 °C, comparable to the results previously achieved with lithium tri-*sec*-butylborohydride at that temperature. Moreover, the byproduct 9-BBN derivative is easily removed as an ate complex, greatly simplifying the recovery of the reduction product.

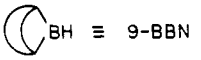
Recently we developed a general method for preparation in high purity of potassium trialkoxyborohydrides containing a wide variety of alkoxy groups from the direct reaction of potassium hydride and the corresponding trialkoxyboranes[1] (eq 1). We were able to extend this

$$KH + (RO)_3B \xrightarrow[\Delta]{THF} K(RO)_3BH \qquad (1)$$

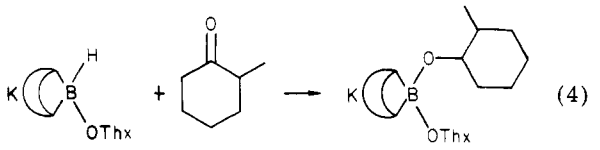
synthesis to the preparation of the borohydrides from B-OR-9-BBN.[2] In the course of this study, we discovered that B-OThx-9-BBN was readily converted into its borohydride, K9-OThx-9-BBNH (eq 2 and 3).[3] The reagent



1



1 is very stable and no disproportionation was observed over more than 1 year when the solution in THF was stored under a positive pressure of nitrogen. This reagent readily reduced ketones at 0 °C and exhibits an excellent stereoselectivity with representative cyclic ketones (eq 4).



98.5% cis

Its stereoselectivity is comparable to the results previously achieved at 0 °C with lithium tri-*sec*-butylborohydride.[4a] However, it still does not approach the exceptionally high stereoselectivity possible with lithium trisiamylborohydride.[4c] The results and comparable data for the other two reagents are summarized in Table I.

Table I. Stereoselective Reduction of Cyclic Ketones with Potassium 9-(2,3-Dimethyl-2-butoxy)-9-boratabicyclo[3.3.1]nonane (K9-OThx-9-BBNH) in Tetrahydrofuran at 0 °C[a,b]

	ratio of less stable isomer, %		
ketone	K9-OThx-9-BBNH	Li-*s*-Bu_3-BH[c]	$LiSia_3$-BH[d]
cyclohexanone			
2-methyl-	98.5	99.3	99.4
3-methyl-	90	85	98
4-methyl-	85.5	80.5	93
4-*tert*-butyl-	87	87.5[d]	96.5
3,3,5-trimethyl-	>99.9	99.8	99
norcamphor	95	99.6	99
camphor	97.5	99.6	>99.9

[a] A 2:1 ratio for reagent:ketone was utilized. [b] The yields of alcohols were quantitative. [c] Data taken from ref 4a. [d] Present study.

In recent years, new developments in the area of stereoselective reduction of cyclic ketones have been exceptionally encouraging.[4] Hindered trialkylborohydrides, such as lithium tri-*sec*-butylborohydride[4a] and lithium trisiamylborohydride,[4c] reduce cyclic ketones containing an α-methyl substitutent to the corresponding alcohols with ≥99% of the less stable isomers. In cases where the alkyl substituent is further removed from the keto group, the stereoselectivity of the reduction is still high, in the 80% to 95% range. Although these trialkylborohydrides are very useful, their byproducts, the trialkylboranes, are often

(1) (a) Brown, H. C.; Nazer, B.; Sikorski, J. A. *Organometallics* **1983**, *2*, 634. (b) Brown, H. C.; Cha, J. S.; Nazer, B. *Inorg. Chem.*, in press.
(2) Research in progress.
(3) Addition of the corresponding potassium alkoxide to 9-BBN did not give these borohydrides in pure form, but the reaction proceeded with disproportionation.

(4) (a) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1972**, *94*, 7159. (b) Krishnamurthy, S. *Aldrichimica Acta* **1974**, *7*, 55. (c) Krishnamurthy, S.; Brown, H. C. *J. Am. Chem. Soc.* **1976**, *98*, 3383. (d) Brown, C. A.; Krishnamurthy, S. *J. Organomet. Chem.* **1978**, *156*, 111. (e) Brown, H. C.; Krishnamurthy, S. *Tetrahedron* **1979**, *35*, 567.

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