The synthetic strategy employed in preparing the new organometallic nitrosyl radical anions described herein is a simple but effective one. A solvent is chosen in which the reductant and oxidant (i.e. the nitrosyl complex) are both soluble, but the electron-transfer product is not. This facilitates the isolation of the desired ionic compounds as fairly pure solids while avoiding accelerated decomposition rates that they might experience if the products remained in solution. Secondly, the reducing agent becomes a bulky counterion. Other reductants, such as Na or Zn, result in the formation of small counterions that can strongly interact with the nitrosyl ligands[43] and thus destabilize an anionic complex by polarizing the metal–ligand linkage. The syntheses and characterizations of the new radical complexes are of interest in their own right, representing a little explored area of the chemistry of group 6[30] organometallic nitrosyl compounds. The anionic complexes described in this paper join a small family of simple, nitrosyl-containing anions that only in the last five years has begun to grow in number more steadily.[44] Obviously, further work is required to delineate the characteristic chemistry of these anions, particularly their reactivities toward nonoxidizing electrophiles.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and a graduate scholarship to B.W. We are also indebted to Professor F. Geoffrey Herring for his assistance in the acquisition and interpretation of some of the ESR spectra.

Registry No. $CpMo(NO)_2Me$, 57034-48-7; $CpMo(NO)_2Cl$, 12305-00-9; $CpW(NO)_2Me$, 57034-45-4; $CpW(NO)_2BF_4$, 87189-85-3; $CpW(NO)_2Cl$, 53419-14-0; $[Cp_2Co][CpW(NO)_2Me]$, 111469-36-4; Cp_2Co, 1277-43-6; $[Cp_2Co][CpMo(NO)_2Me]$, 111469-38-6; $CpCr(NO)_2Me$, 53522-59-1; $CpFe(\eta^6\text{-}C_6Me_6)$, 70414-92-5; $CpW(NO)_2H$, 69532-01-0; $[Cp_2Co][CpW(NO)_2H]$, 111469-40-0; $[Cp_2Co][CpW(NO)_2D]$, 111469-42-2; $CpW(NO)_2D$, 69532-02-1; $[Cp_2Co][CpW(NO)_2Cl]$, 111469-44-4; $[Cp_2Co][CpMo(NO)_2Cl]$, 111469-46-6; $CpW(NO)_2P(OMe)_3$, 82044-74-4; $P(OMe)_3$, 121-45-9; $[CpW(NO)_2P(OMe)_3]BF_4$, 111469-47-7; $CpW(NO)_2PPh_3$, 82044-73-3; $[CpW(NO)_2PPh_3]$, 87189-86-4; $[Cp_2Co]BF_4$, 52314-53-1; Cp_2Fe, 102-54-5; $[CpCr(NO)_2(CH_3CN)]PF_6$, 74924-59-7; $CpCr(NO)_2Cl$, 12071-51-1; $[CpMo(NO)_2PPh_3]BF_4$, 111469-48-8; $CpMo(NO)_2Et$, 57034-47-6; $CpW(NO)_2Et$, 87189-91-1; $[Cp_2Co][CpMo(NO)_2Et]$, 111409-66-6; $[Cp_2Fe]BF_4$, 1282-37-7.

(43) Pannell, K. H.; Chen, Y.-S.; Belknap, K.; Wu, C. C.; Bernal, I.; Creswick, M. W.; Huang, H. N. *Inorg. Chem.* **1983**, *22*, 418.
(44) Weiner, W. P.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7462.

Reaction of Organoboranes with Olefinic α,β-Unsaturated Nitro Compounds

George W. Kabalka,* Yuan-Zhu Gai, Naganna M. Goudgaon, Rajender S. Varma, and Eugene E. Gooch

Departments of Chemistry and Radiology, University of Tennessee, Knoxville, Tennessee 37996

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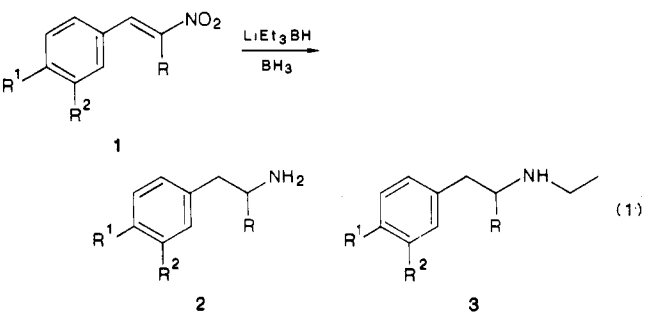
The reaction of lithium triethylborohydride with nitroalkenes in the presence of borane results in the unexpected formation of *N*-ethylamine derivatives. Evidence supports a reaction sequence involving the 1,2-addition of triethylborane to a nitroso intermediate.

Introduction

α,β-Unsaturated nitroalkenes have proven to be versatile synthetic intermediates.[1] They react with a variety of reducing agents to yield nitroalkanes,[2] amines,[3] oximes,[4] ketones,[5] and hydroxylamines.[6] In the course of recent investigations involving the reaction of borohydrides with conjugated nitroalkenes, we noted the consistent formation of *N*-ethylamines as byproducts in reactions utilizing lithium triethylborohydride (eq 1). Interestingly, N-alkylated products were not produced when other alkylborohydrides were used.



(1)

Earlier studies had established that borohydride-catalyzed, borane reductions of conjugated nitroalkenes proceed via *aci*-nitro derivatives which are then further reduced to hydroxylamines and, finally, amines.[7] Alternatively the *aci*-nitro intermediates may be hydrolyzed to carbonyl compounds. The observation that N-ethylation products are formed leads to the conclusion that a Grignard-like addition reaction between an alkylborane and a nitroso intermediate can also occur.[8]

(1) Barrett, A. G. M.; Graboski, G. G. *Chem. Rev.* **1986**, *86*, 751.
(2) Varma, R. S.; Kabalka, G., W. *Synth. Commun.* **1985**, *15*, 443.
(3) Mourad, M. S.; Varma, R. S.; Kabalka, G. W. *Synth. Commun.* **1984**, *14*, 1099.
(4) Varma, R. S.; Varma, M.; Kabalka, G. W. *Synth. Commun.* **1985**, *15*, 1325.
(5) Mourad, M. S.; Varma, R. S.; Kabalka, G. W. *Synthesis* **1985**, 654.
(6) Mourad, M. S.; Varma, R. S.; Kabalka, G. W. *J. Org. Chem.* **1985**, *50*, 133.
(7) Varma, R. S.; Kabalka, G. W. *Synth. Commun.* **1985**, *15*, 843. Varma, R. S.; Kabalka, G. W. *Org. Prep. Proced. Int.* **1985**, *17*, 254.

(8) The formation of *N*- hydroxyldialkylamines via a Grignard-like reaction between a trialkylborane and nitrosoalkane has never been reported. Yashida and his co-workers observed the formation of trace quantities dicyclohexylamine when they reacted nitrosyl chloride with tricyclohexylborane, a product which, logically, could be derived from the corresponding *N*-hydroxyldicyclohexylamine. See: Yoshida, Z.; Ogushi, T.; Manabe, O.; Hiyama, H. *Tetrahedron Lett.* **1965**, 753. Okushi, T.; Manabe, O.; Hiyama, H.; Yoshida, Z. *Kogyo Kagaku Zasshi* **1965**, *68*, 1685.

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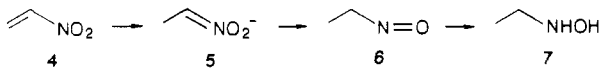
Results and Discussion

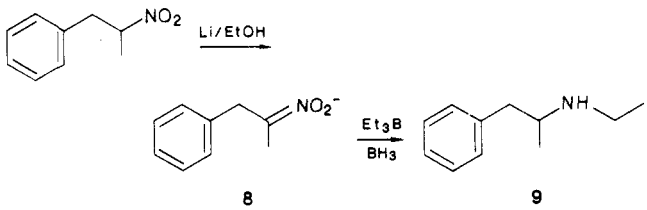
The synthesis of amines via the reduction of α,β-unsaturated nitroalkenes is a consequence of a multistep reaction sequence involving the conjugate addition of hydride and subsequent reduction of the *aci*-nitro intermediate **5** to the product amine via the nitroso and hydroxylamine intermediates **6** and **7**, respectively. It appeared



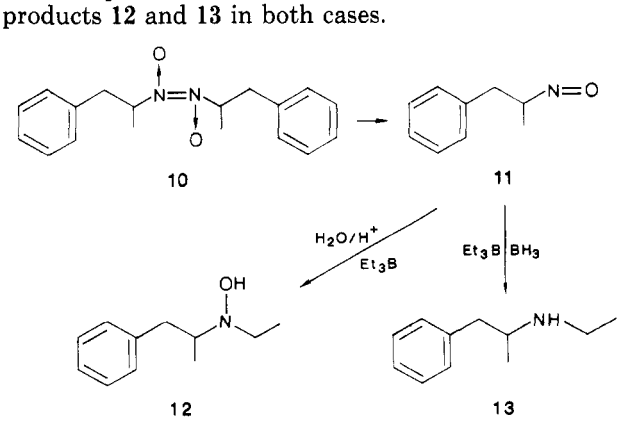
reasonable to assume that the formation of the N-ethylated products **3** occurred via a competative addition of triethylborane (generated as a byproduct during the Michael addition of hydride) to the nitroso intermediate **6**.

Simple trialkylboranes are not known to participate in 1,2-addition reactions with π systems. In fact, it has been reported that trialkylboranes will reduce nitrosoalkanes to the corresponding *N*-hydroxylalkylamines in nonpolar solvents.[9] The reaction is analogous to the reduction of aldehydes by alkyl 9-borabicyclo[3.3.1]nonane.[10] Presumably complexation, and intermolecular reduction, occur more readily in the absence of polar solvents such as tetrahydrofuran since reduction products are not observed in the present study.

To support the postulation that lithium triethylborohydride simply served as a source of triethylborane, the *aci*-nitro derivative **8** of 1-phenyl-2-nitropropane was prepared via the reaction of lithium with the corresponding nitro reagent. The nitronate intermediate was then treated with a mixture of triethylborane and borane. The reaction produced a 50% yield of *N*-ethylamphetamine (**9**). As expected, the yield of the N-ethylated product **9** increased as the ratio of triethylborane to borane was increased.



To confirm that the reaction involved a nitroso intermediate, 1-phenyl-2-nitrosopropane (**11**) was prepared (as a dimer, **10**) and allowed to react with triethylborane in both the presence of borane and the absence of borane. As anticipated, the reaction generated the N-ethylated products **12** and **13** in both cases.



Experiments involving the reaction of potassium tri-*sec*-butylborohydride, more sterically demanding, produced only primary amines, **2**, indicating that the competition between reduction and alkylation of the nitroso group is sensitive to steric effects. Nevertheless the trialkylborohydride reaction has been utilized to prepare a series of N-ethylated amine derivatives (Table I).

Table I. Reduction of Nitroalkenes (1) to *N*-Ethylamines (3)

substituents			% yield[a] of amine	mp, °C (amine hydrochloride)
R	R_1	R_2		
H	H	H	78	141–142
CH_3	H	H	64	183–185
H	Br	H	56	172–174
CH_3	C_2H_5O	C_2H_5O	62	130

[a] Isolated yields.

Experimental Section

Melting points are uncorrected. NMR spectra were recorded on a JEOL-FX 90Q spectrometer and referenced to Me_4Si. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, TN. Glassware was thoroughly oven-dried and cooled under dry nitrogen just before use. THF was dried and distilled over $LiAlH_4$ and stored under dry nitrogen. Commercially available BH_3·THF (1.0 M solution in THF), Et_3B (1.0 M solution in THF), and $LiEt_3BH$ (1.0 M solution in THF) were used and transferred by using oven-dried hypodermic syringes. Amine hydrochloride salts were prepared according to a standard procedure by bubbling anhydrous hydrogen chloride through a solution of the base in absolute ether.[11]

Reduction of Nitroalkene with Lithium Triethylborohydride (Superhydride) and Borane: General Procedure. The reduction of β-methyl-β-nitrostyrene with superhydride ($LiEt_3BH$) and borane (BH_3) is representative. Into a flame-dried, nitrogen-flushed, 100-mL flask, equipped with a septum inlet, magnetic stirring bar, and reflux condenser was added a solution of $LiEt_3BH$ (10.5 mmol, 10.5 mL) via a syringe, followed by the addition of a solution of β-methyl-β-nitrostyrene (7 mmol, 1.4 g in 5 mL of THF). After the addition, the reaction mixture was stirred at room temperature for 1 h. Excess BH_3·THF (28 mmol, 28 mL) was then added and heated at 60–70 °C for 15 h. The mixture was poured into ice water and acidified to pH 2. The mixture was stirred and heated at 60–65 °C for 2 h and then cooled to room temperature. The acidic water layer was washed with ether (3 × 30 mL) and the pH adjusted to 7–8 and washed once again with ether (3 × 30 mL) to remove *N*-hydroxylamphetamine. The pH was then adjusted to 10 and the product extracted into ether (3 × 30 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure to yield 0.73 g (64%) of *N*-ethylamphetamine. The hydrochloride salt was prepared and recrystallized from an ether–ethanol (20:1) mixture: mp of hydrochloride salt 141–142 °C (lit.[12] mp 154–156 °C); ^1H NMR (CD_3SOCD_3) δ 1.11–1.38 (m, 6 H, CH_3), 2.53–3.47 (m, 5 H, $ArCH_2CHNCH_2$), 7.31 (s, 5 H, ArH), 9.42 (br s, 1 H, NH); ^{13}C NMR (CD_3SOCD_3) δ 11.17 (CH_3), 14.99 (CH_3), 38.0 ($ArCH_2$), 39.01 (NCH_2), 53.96 (CH), 126.67, 128.54, 129.19, 137.01 (Ar carbons). Anal. Calcd for $C_{11}H_{17}N$·HCl: C, 66.15; H, 9.08; N, 7.01. Found: C, 66.06; H, 9.20; N, 6.99.

Reduction of *p*-Bromo-β-methyl-β-nitrostyrene. *p*-Bromo-β-methyl-β-nitrostyrene (5 mmol, 1.21 g, dissolved in 5 mL of THF), $LiEt_3BH$ (7.5 mmol, 7.5 mL), and BH_3·THF (20 mmol, 20 mL) were reacted as described in the general procedure to yield 0.68 g of *N*-ethyl-*p*-bromoamphetamine. The hydrochloride salt was prepared and recrystallized from an ether–ethanol mixture: mp 172–174 °C; ^1H NMR (CD_3SOCD_3) δ 1.15–1.32 (m, 6 H, CH_3), 2.59–3.54 (m, 5 H, $ArCH_2CHNCH_2$), 7.41 ($A'_2B'_2$ 4 H, J = 8.1 Hz, ArH), 9.43 (br s, 1 H, NH), ^{13}C NMR (CD_3SOCD_3) δ 14.96 (CH_3), 17.40 (CH_3), 39.17 ($ArCH_2$), 47.84 (NCH_2), 53.69 (CH), 119.89, 131.38, 131.52, 136.39 (Ar carbons). Anal. Calcd for $C_{11}H_{16}BrN$·HCl: C, 47.42; H, 6.15; N, 5.03. Found: C, 47.14; H, 5.88; N, 4.89.

(9) Foot, K. G.; Roberts, B. P. *J. Chem. Soc. C* **1971**, 3475.
(10) Midland, M. M.; Graham, R. S. *Org. Synth.* **1985**, *63*, 57.
(11) Gilsdorf, R. T.; Nord, F. F. *J. Am. Chem. Soc.* **1952**, *74*, 1837.
(12) Leonard, N. T.; Adamcik, J. A.; Jerassi, C. D.; Halpern, O. *J. Am. Chem. Soc.* **1958**, *80*, 4858. Brit. 814,339, 1958 (*Chem. Abstr.* **1958**, *58*, 19972e).

Reduction of β-Nitrostyrene. β-Nitrostyrene (7 mmol, 1.04 g, dissolved in 6 mL of THF), $LiEt_3BH$ (10.5 mmol, 10.5 mL), and BH_3·THF (28 mmol, 28 mL) were reacted as described in the general procedures to yield 0.81 g of *N*-ethylphenethylamine. The hydrochloride salt was recrystallized from ether–ethanol: mp 183–185 °C (lit.[13] 182–184 °C); ^1H NMR (CD_3SOCD_3) δ 1.26 (t, 3 H, J = 7.14 Hz, CH_3), 2.83–3.57 (m, 6 H, $PhCH_2CH_2NCH_2$), 7.31 (s, 5 H, ArH), 9.33 (br s, 1 H, NH); ^{13}C NMR (CD_3SOCD_3) δ 10.98 (CH_3), 31.54 ($ArCH_2$), 41.86 (CH_2), 47.25 ($ArCH_2CH_2$), 126.75, 128.64, 137.44 (Ar carbons). Anal. Calcd for $C_{10}H_{15}N$·HCl: C, 64.70; H, 8.63; N, 7.55. Found: C, 64.50; H, 8.57; N, 7.42.

Reduction of 3,4-Diethoxy-β-methyl-β-nitrostyrene. A solution of the 3,4-diethoxy-β-methyl-β-nitrostyrene (3 mmol, 0.74 g in 4 mL of THF) was reduced to yield 0.47 g of *N*-ethyl-3,4-diethoxyamphetamine. The hydrochloride salt was prepared and recrystallized from ether–ethanol; mp 130 °C; ^1H NMR (CD_3SOCD_3) δ 1.11–1.40 (m, 12 H, CH_3), 2.47–3.48 (m, 5 H, Ar CH_2CHNCH_2), 4.02 (q, 4 H, J = 3 Hz, 2 OCH_2), 6.70–6.96 (m, 3 H, ArH), 9.22 (br s, 1 H, NH); ^{13}C NMR (CD_3SOCD_3) δ 11.17 (CH_3), 14.77 (CH_3), 15.12 (CH_3), 38.0 ($ArCH_2$), 39.0 (NCH_2), 54.07 (CH), 63.74 (OCH_2), 113.48, 114.5, 121.36, 129.27, 146.98, 148.15 (Ar carbons). Anal. Calcd for $C_{15}H_{25}NO_2$·HCl: C, 62.59; H, 9.11; N, 4.87. Found: C, 62.55; H, 9.14; N, 4.77.

Reduction of β-Methylphenethylnitronate with Triethylborane and Borane. (A) Into a flame-dried, nitrogen-flushed, septum-capped, round-bottomed flask fitted with a reflux condenser and a magnetic bar was placed β-methylphenethylnitronate (2 mmol, 342 mg),[14] 6 mL of THF, and triethylborane (1.0 M solution in THF, 4 mmol, 4 mL). The reaction mixture was stirred at room temperature overnight. BH_3·THF (14 mmol, 14 mL of a 1.0 M solution) was then added and the mixture heated at 60–70 °C for 20 h. After cooling, the mixture was poured onto ice water, acidified to about pH 2, and heated at 60–70 °C for 2 h. The water solution was worked up as described earlier to yield 0.14 g of *N*-ethylamphetamine; ^1H NMR and ^{13}C NMR were identical with those of authentic samples.

(B) Into a flame-dried, nitrogen-flushed, septum-capped, round-bottomed flask fitted with a reflux condenser and a magnetic bar was placed β-methylphenethylnitronate (3 mmol, 0.51 g), 8 mL of THF, and Et_3B (1.0 M solution in THF, 6 mmol, 6 mL). The reaction mixture was stirred and heated at 60–70 °C overnight. BH_3·THF (9 mmol, 9 mL of a 1.0 M solution) was then added to the mixture and heated at 60–70 °C overnight. After cooling, the mixture was poured into ice water, acidified to about pH 2, and heated at 60–70 °C for 2 h. The water layer was washed with ether (3 × 30 mL), the pH adjusted to 7–8, then extracted with ether (3 × 30 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield 0.35 g of an oil which was purified by column chromatography (petroleum ether/ether = 3:1) to yield 0.2 g (39%) of *N*-ethyl-*N*-hydroxylamphetamine: mp of the oxalate salt 168–170 °C (lit.[15] mp 161–162 °C); lit.[16] mp 172–173 °C); ^1H NMR ($CDCl_3$) δ 0.92–1.20 (m, 6 H, J = 7.0 Hz, CH_3), 2.45–3.25 (m, 5 H, $ArCH_2CHNCH_2$); ^{13}C NMR ($CDCl_3$) δ 12.72 (CH_3), 14.23 (CH_3), 39.23 (CH_2), 49.28 (NCH_2), 63.53 (NCH), 126.02, 128.38, 129.38, 140.24 (Ar carbons).

Reactions of 1-Phenyl-2-nitrosopropane Dimer with Triethylborane. Into a flame-dried, nitrogen-flushed, 100-mL flask, equipped with a septum inlet, magnetic stirring bar, and reflux condenser was placed 1-phenyl-2-nitrosopropane dimer[17] (1 mmol, 0.30 g), followed by 6 mL of dry THF and Et_3B (2 mmol, 2 mL of a 1.0 M solution). The mixture was stirred at room temperature overnight and then heated at 60–70 °C for 8 h. The solvent was removed to yield an oil which was purified by column chromatography (petroleum ether/ether = 3:1). The reaction yield was 0.22 g (61%) of *N*-ethyl-*N*-hydroxylamphetamine; ^1H NMR, ^{13}C NMR, and SFORD ^{13}C NMR were identical with those of authentic samples.

Reaction of 1-Phenyl-2-nitrosopropane Dimer with Triethylborane and Borane. The nitroso dimer was placed into a flame-dried, nitrogen-flushed, 100-mL flask, equipped with a septum inlet, magnetic stirring bar, and reflux condenser (0.30 g, 1 mmol), followed by 6 mL of THF and Et_3B (2 mmol, 2 mL of a 1.0 M solution). The mixture was stirred at 60–70 °C overnight, and BH_3·THF (8 mmol, 8 mL) was then added. The mixture was again heated overnight at 60–70 °C. After cooling, the mixture was poured into ice water and acidified to pH 2. The solution was stirred and heated at 60–65 °C for 2 h and then cooled to room temperature. The mixture was worked up as described earlier to yield 0.16 g (50%) of *N*-ethylamphetamine which exhibited ^1H and ^{13}C NMR identical with those of authentic samples.

Acknowledgment. This research was supported by the Department of Energy, Grant Number DE-FG05-86ER-60434.

Registry No. $LiEt_3BH$, 22560-16-3; BH_3·THF, 14044-65-6; β-methyl-β-nitrostyrene, 705-60-2; *p*-bromo-β-methyl-β-nitrostyrene, 21892-60-4; β-nitrosostyrene, 102-96-5; 3,4-diethoxy-β-methyl-β-nitrostyrene, 94640-30-9; β-methylphenethylnitronate, 111960-03-3; 1-phenyl-2-nitrosopropane dimer, 55941-35-0; *N*-ethylamphetamine, 457-87-4; *N*-ethylamphetamine hydrochloride, 1858-47-5; *N*-ethyl-β-bromoamphetamine, 111960-04-4; *N*-ethyl-β-bromoamphetamine hydrochloride, 111960-05-5; *N*-ethylphenethylamine, 22002-68-2; *N*-ethylphenethylamine hydrochloride, 61185-89-5; *N*-ethyl-3,4-diethoxyamphetamine, 111960-06-6; *N*-ethyl-3,4-diethoxyamphetamine hydrochloride, 111960-07-7; triethylborane, 97-94-9; *N*-ethyl-*N*-hydroxyamphetamine, 52271-37-1; *N*-ethyl-*N*-hydroxyamphetamine hydrochloride, 111960-08-8.

(13) Shapiro, S. L.; Parrino, V. A.; Freedman, L. *J. Am. Chem. Soc.* **1959**, *81*, 3728.
(14) Feuer, H.; Vartlett, R. S.; Vincent, B. F., Jr.; Anderson, R. S. *J. Org. Chem.* **1965**, *30*, 2880.
(15) Beckett, A. H.; Coults, R. T.; Ogunbona, F. A. *Tetrahedron* **1973**, *29*, 4189.
(16) Gribble, G. W.; Leiby, R. W.; Sheehay, M. N. *Synthesis* **1977**, 856.
(17) Beckett, A. H.; Jones, G. R.; Coutts, R. T. *Tetrahedron* **1976**, *32*, 1267. Paulsen-Sörman, U.; Lundkrist, G.; Khuthier, A. H.; Linkeke, B. *Chem.-Biol. Interact.* **1983**, *47*, 1.