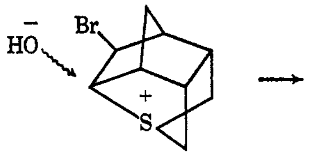
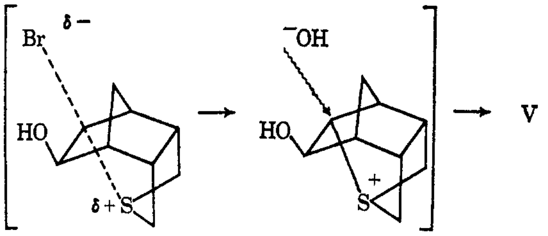
(2) a positive periodic acid test, and (3) an independent synthesis from I with permanganate oxidation. The glycol was characterized by oxidation to its sulfone.

In the transformation IV → V, the initiating step is undoubtedly the nucleophilic attack of hydroxyl ion from the less encumbered (*exo*) side of the sulfonium ion. Formation of the specifically *cis* glycol (V), rather than *trans*, suggests a sulfonium ion (VII) which suffers a second displacement by hydroxyl from the *exo* side and not an epoxide intermediate derived from an incipient *cis* bromohydrin or the hydroxy sulfonium ion (VII). The intermediacy of VII would also preserve the *endo* stereochemistry of the molecule.



IV



VII

Finally, no product indicative of nucleophilic displacement at other methylenes adjacent to sulfur (C_1 and C_3) was observed.

Experimental Section[6]

2-Thia-1,2-dihydro-*endo*-dicyclopentadiene (I) was prepared by the method previously described.[3]

Reaction of 2-Thia-1,2-dihydro-*endo*-dicyclopentadiene and Bromine. Preparation of Bromosulfonium Bromide (IV).—To 1.52 g (0.010 mole) of unsaturated *endo*-sulfide in 6 ml of dry chloroform cooled in an ice bath was added dropwise with stirring 1.76 g (0.011 mole) of bromine in 4 ml of dry chloroform. When addition was complete, dry ether was added and the precipitate was separated by vacuum filtration. After solution of the solid in hot absolute methanol and then precipitation with ether, there was obtained 2.59 g (83%) of the colorless salt, mp 117–118°.

Anal. Calcd for $C_9H_{12}Br_2S$: C, 34.62; H, 3.85. Found: C, 34.62; H, 3.84.

Reaction of Bromosulfonium Bromide (IV) with Lithium Carbonate. Preparation of *exo,cis*-2-Thiatetrahydro-*endo*-dicyclopentadiene-9,10-diol (V).—A mixture of 2 g (0.006 mole) of IV, 1.15 g (0.016 mole) of lithium carbonate, 5 ml of absolute methanol, and 11 ml of water was refluxed for 2 days according to the method of Roberts.[7] The reaction mixture was then extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The solvents were removed under vacuum and the residue was recrystallized from absolute methanol-heptane, mp 102–106°. This substance gave a positive test for a *cis*-vicinal diol.[8]

Anal. Calcd for $C_9H_{14}O_2S$: C, 58.06; H, 7.53. Found: C, 58.33; H, 7.74.

A sulfone was prepared, mp 180–181°, from absolute methanol-heptane after being chilled in a Dry Ice–acetone bath. This material also gave a positive test for a *cis*-vicinal diol.

Anal. Calcd for $C_9H_{14}O_4S$: C, 49.54; H, 6.42. Found: C, 49.31; H, 6.26.

Reaction of 2-Thia-1,2-dihydro-*endo*-dicyclopentadiene (I) with Potassium Permanganate.—A procedure similar to the method of Kwart and Vosburgh[9] was employed. A solution of 4.21 g (0.027 mole) of potassium permanganate in 7 ml of water and 70 ml of reagent grade acetone was added slowly with stirring to a solution of 2.7 g (0.018 mole) of *endo*-sulfide I in 4 ml of reagent grade acetone previously cooled to −20° in a Dry Ice–acetone bath. When addition was complete, the reaction was allowed to come gradually to 0°. Manganese dioxide was removed by filtration. The resulting solution was saturated with Dry Ice, and potassium carbonate was separated by filtration. The solution was treated with Norit and solvent was removed by slow evaporation at room temperature. An oily residue was obtained. Treatment with boiling acetone dissolved the glycol which was precipitated by the addition of heptane and chilling in a Dry Ice-acetone bath, mp 102–106°, mmp with V 102–106°.

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[6] Melting points are uncorrected.

[7] J. D. Roberts, E. R. Trumball, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

[8] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 145.

[9] H. Kwart and W. G. Vosburgh, *J. Am. Chem. Soc.*, **76**, 5400 (1954).

9-*t*-Butylanthracene[1]

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The Grignard reaction of anthrone is often used for the preparation of 9-alkylanthracenes.[2,3] Russell found, however, that *t*-butylmagnesium chloride and anthrone yield isobutylene and the magnesium salt of anthrone rather than 9-*t*-butylanthracene.[2] A reexamination of this reaction employing excess *t*-butylmagnesium chloride[4] revealed that 9-*t*-butyl-9-hydroxy-9,10-dihydroanthracene (I) is formed in 28% yield. The spectroscopic properties of I (Experimental part) support this structure. Alcohol I is stable at its melting point and is not dehydrated by mild reagents, *e.g.*, cupric sulfate in refluxing xylene. The compound is degraded to anthracene in acid-catalyzed elimination reactions. However, I is readily converted to 9-*t*-butylanthracene (II) by phosphorus pentoxide in carbon tetrachloride.[5] Hydrocarbon II forms an adduct with maleic anhydride and is oxidized to anthraquinone. These findings and the definitive spectroscopic properties (Experimental Section) establish the structure.

Compounds I and II react with trifluoroacetic acid at −10° to yield 9-*t*-butyl-9-trifluoroacetoxy-9,10-dihydroanthracene (III). This structural assignment is based on the similar spectroscopic properties of I and III and the fact that III is hydrolyzed to I under basic conditions. Ester III is not stable. It slowly decomposes to anthracene during storage at ambient temperature. The decomposition is rapid in the presence of acids.

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[1] This work was supported by a grant (G25190) from the National Science Foundation.

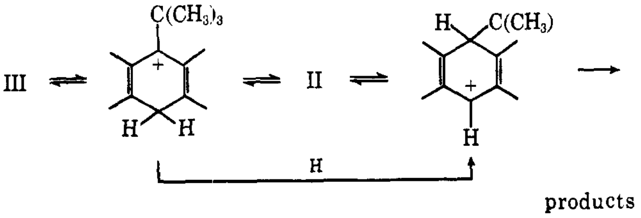
[2] G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958).

[3] R. LaLonde and R. Calas, *Bull. Soc. Chim. France*, 766 (1959).

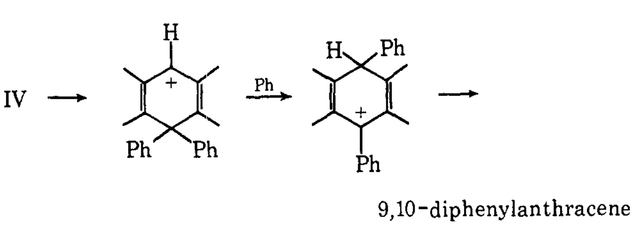
[4] Excess Grignard reagent is necessary. For a discussion of the problem see E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 288–291.

[5] K. G. Flynn and G. Bergson, *Acta Chem. Scand.*, **18**, 2002 (1964).

When I or II is dissolved in trifluoroacetic acid (or a mixed solvent of the acid and carbon tetrachloride or chloroform), ester III is formed rapidly. The unstable ester solvolyzes to yield anthracene and *t*-butyl trifluoroacetate in a subsequent slower reaction. Two distinct mechanisms may be formulated for the conversion of III to anthracene. A conventional path



is through 9-*t*-butylanthracene (II). However, the accessible boat conformation of dihydroanthracene has a favorable stereoelectronic environment for a 1,4-hydride shift.[6] Several observations favor the conventional formulation. An intermediate, $\lambda_{\max}$ 410 mμ, forms and decays during the solvolysis of III in trifluoroacetic acid. The absorbance of the intermediate is much lower under less acidic conditions, *e.g.*, in trifluoroacetic acid–carbon tetrachloride. These observations suggest that the intermediate is *t*-butylanthracenonium ion.[7] When III is solvolyzed in trifluoroacetic acid–carbon tetrachloride, 9-*t*-butylanthracene (II) is detectable by nmr spectroscopy. As the reaction proceeds the concentration of II increases to about 10 mole % and then decreases as the products form. When .III is solvolyzed in trifluoroacetic acid-*d*–carbon tetrachloride, the 10,10 hydrogen atoms of III are completely exchanged in 15 min. The half-life for the reaction under these conditions is about 1 hr. The conventional mechanism requires this rapid exchange because II forms III rapidly. These findings are most compatible with the conventional mechanism, but the 1,4 shift cannot be excluded on their basis. As a further test, we examined the trifluoroacetolysis of 9-hydroxy-10,10-diphenyl-9,10-dihydroanthracene (IV). Several hydrocarbons (unidentified, but apparently alkylation products) form in the solvolysis of of IV in trifluoroacetic acid. However, the characteristic ultraviolet absorptions of 9,10-diphenylanthracene (stable under the reaction conditions) do not appear in the spectra of the products or in the spectra of reaction solutions. Control experiments establish that the concentration of 9,10-diphenylanthracene could not exceed 2%. We infer that 1,4 shifts are unimportant in these dihydroanthracenes and that the conventional mechanism is applicable for the solvolysis of III.



Experimental Section[8]

9-Hydroxy-9-*t*-butyl-9,10-dihydroanthracene (I).—Anthrone (29.1 g, 0.15 mole) was added as a dry powder to *t*-butylmagnesium chloride (0.45 mole) in ether (200 ml) at 0°. After 30 min, benzene (50 ml) was added and the reaction mixture was hydrolyzed with dilute hydrochloric acid at 0°. The organic layer was separated and dried. After the removal of ether, the benzene solution was chromatographed on neutral alumina (eluent, benzene) to separate anthrone from I. Alcohol I (10.7 g, mp 150–150.5°, 28%) was purified by recrystallization from petroleum ether. Alcohol I exhibited an hydroxyl band in the infrared and three ultraviolet absorptions, $\lambda_{\max}^{CHCl_3}$ mμ (log ϵ), at 258 (sh, 2.84), 264 (2.94), and 271.5 (2.90).[9] The nmr spectrum has signals (ppm from TMS in carbon tetrachloride) at δ 7.0–8.0, m (8 H); 3.90, q (J = 19 cps, $\Delta\nu$ = 20.6 cps) (2 H); 1.66, s (1 H); 0.82, s (9 H).[10]

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.84; H, 7.82.

9-*t*-Butylanthracene (II).—Alcohol I (10.0 g, 0.04 mole) was warmed on a steam bath with phosphorus pentoxide (70 g, 0.07 mole) in carbon tetrachloride (150 ml) for 2 hr. The solution was decanted, washed with water, and dried. The solvent was removed *in vacuo* and the residue was chromatographed on neutral alumina (eluent, petroleum ether). Compound II (7.0 g, colorless, fluorescent needles, mp 103.5–105°, 75%) eluted first and was recrystallized from ethanol. The ultraviolet spectrum, $\lambda_{\max}^{EtOH}$ mμ (log ϵ), is typical of a 9-alkylanthracene: 249 (4.81), 256 (5.26), 304 sh, 318 (3.03), 332 (3.42), 348 (3.75), 362 sh, 367 (3.96), 3.82 sh, and 386 (3.95). The nmr spectrum has signals (ppm from TMS in carbon tetrachloride) at δ 8.00–8.50, m (9 H); and 1.92, s (9 H).

Anal. Calcd for $C_{18}H_{18}$: C, 92.11; H, 7.89. Found: C, 92.22; H, 7.83.

Compound II (90 mg, 0.38 mmole) and maleic anhydride (120 mg, 1.2 mmoles) were refluxed in *o*-xylene (5 ml) for 2.5 hr. 9-*t*-Butyl-9,10-ethano-9,10-dihydroanthracene-11,12-*cis*-dicarboxylic anhydride (54 mg, mp 228–231° after sublimation, 24%) was isolated in the usual way. The nmr spectrum has signals (ppm from TMS in chloroform-*d*) at δ 7–8, m (8 H); 4.66, d (2 H); 3.67, m (2 H); and 1.89, s (9 H).

Anal. Calcd for $C_{22}H_{20}O_3$: C, 79.49; H, 6.06. Found: C, 79.60; H, 6.13.

9-Trifluoroacetoxy-9-*t*-butyl-9,10-dihydroanthracene (III).—Hydrocarbon II (200 mg, 0.85 mmole) was dissolved in chloroform (5 ml). Trifluoroacetic acid (1 ml) was added at −10°. After 3 hr, the solution was evaporated to dryness *in vacuo* without warming. The product III (97%) was virtually colorless. Compound III melted at 75–80°, solidified, and remelted at 215° (anthracene). Analytical data were not obtained since anthracene (1–5%) was detectable in the infrared spectra of all the samples prepared in this study. The infrared spectrum of III has an intense band at 1795 cm^{-1}, and several intense bands in the 1125–1250-cm^{-1} region, but no hydroxyl band. Three absorptions, $\lambda_{\max}^{CHCl_3}$ mμ (log ϵ), appear in the ultraviolet spectrum: 256 (3.24), 265 (3.17), and 272.5 (3.08).[9] The nmr spectrum has signals (ppm from TMS in carbon tetrachloride) at δ 7.0–8.0, m (8 H); 3.92, s (2 H); and 1.99, s (9 H).

Compound III (150 mg, 0.43 mmole) was suspended in ethylene glycol (30 ml) with potassium hydroxide (2 g). After 17 days, alcohol I was isolated by filtration. Spectroscopic examination (infrared, nmr) of the crude product indicated contamination by a small amount of anthracene.

Conversion of III to Anthracene.—In a typical experiment, III (20 mg, 0.06 mmole) was dissolved in carbon tetrachloride (0.3 ml) and trifluoroacetic acid (0.1 ml) was added. The reaction was followed by the decay of the resonance of the *t*-butyl hydrogen atoms of III and the growth of the resonance of *t*-butyl trifluoroacetate. The half-life for the disappearance of III is about 30 min at the probe temperature. At short reaction times, the resonances of the *t*-butyl groups of III, II, and *t*-butyl trifluoroacetate were evident. After 1 day, only the resonance of

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(6) M. J. S. Dewar ["Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 295] points out that such shifts are unknown and unlikely.

(7) Spectra of related ions are discussed by G. Dallinga, E. L. Mackor, and A. A. Verrijn Stuart, *Mol. Phys.*, **1**, 123 (1958).

(8) Microanalyses are by Mr. William Saschek. Cary 14, Beckman IR-7, and Varian A-60 and HR-60 spectrometers were employed to record spectroscopic properties.

(9) For comparison, $\lambda_{\max}^{EtOH}$ mμ (log ϵ) for 9,10-dihydroanthracene are 252 (3.33), 264 (3.10), and 271 (3.09): G. M. Badger, M. L. Jones, and R. S. Pierce, *J. Chem. Soc.*, 1700 (1950).

(10) For comparison, the methylene resonance for 9-hydroxy-9-benzyl-9,10-dihydroanthracene is at δ 3.22 (q, J = 19 cps).[5]

t-butyl trifluoroacetate was detectable in the high-field region. The exchange experiment employing trifluoroacetic acid-*d* was carried out under the same conditions; half-life ~1 hr.

The reaction was also followed by ultraviolet spectroscopy with 10^{-4} *M* III in trifluoroacetic acid and in mixed solvents of the acid and carbon tetrachloride. The absorption of anthracene at 325 mμ increased steadily as an intermediate, λ_{max} 410 mμ, first increased and then decayed.

9-Hydroxy-10,10-diphenyl-9,10-dihydroanthracene (IV).—*o*-Benzoylbenzoic acid was converted to 10,10-diphenylanthrone.[11] The ketone was reduced to IV (mp 245–246°; lit.[12] mp 240–241°) with sodium borohydride in monoglyme.[13] Equal volumes of 2×10^{-3} *M* IV in carbon tetrachloride and trifluoroacetic acid were mixed. Aliquots were withdrawn over a 24-hr interval and diluted 1:25 with carbon tetrachloride, and the ultraviolet spectra were recorded. No absorptions were detected in the region (350–390 mμ) where 9,10-diphenylanthracene exhibits three intense bands (log ε >4). Control experiments established that 9,10-diphenylanthracene was stable under the reaction conditions and that yields of 2% were detectable.

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[11] E. de Barnett, J. W. Cook, and I. G. Nixon, *J. Chem. Soc.*, 504 (1927). Phenyllithium replaced phenylmagnesium bromide.

[12] C. Liebermann and S. Lindenbaum, *Ber.*, **38**, 1804 (1905).

[13] H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

Deoxygenation of Pyridine N-Oxides with Sulfur Dioxide

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Received June 27, 1966

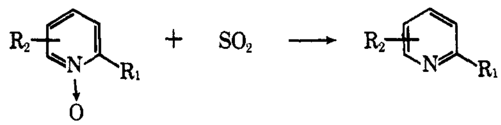
In recent years, synthetic manipulations on the pyridine nucleus have been greatly facilitated through the use of the N-oxide function, as pioneered by Ochiai and co-workers.[2] Consequently, a number of reagents have also been developed for the deoxygenation of pyridine N-oxides.[3]

In a study of the deoxygenation of pyridine N-oxides with various reducing agents, Relyea[3h] and co-workers reported that sulfur dioxide does not reduce pyridine N-oxide. We wish to report herein reaction conditions whereby sulfur dioxide is a useful agent for the deoxygenation of pyridine N-oxides.[4]

The addition of a slow stream of sulfur dioxide to a refluxing solution of the pyridine N-oxides in dioxane or water for a period of 3 hr[5] led to the formation of the corresponding free base in yields ranging from 21 to 78%. The results are summarized in Table I. The products were identified by comparison of their physical constants, chromatographic behavior (tlc), infrared spectra, and derivatives (picrate salts) with those of authentic samples.

TABLE I

DEOXYGENATION OF PYRIDINE N-OXIDES WITH SULFUR DIOXIDE



N-Oxide		Solvent		Free base, mp or bp (mm), °C	Picrate mp, °C
R_1	R_2	Dioxane	Water		
H	H	66		114[j]	166–167[j]
CH_3	H	34		126–127[j]	166–167[j]
H,	4-CH_3	31		141–142[j]	165–166[j]
H,	3-Cl[a]	21		54 (20)[j]	133–134[j]
CH_3	4-OCH_3[b]	62		89 (15)[k]	146–147[k]
CH_3	5-$CO_2C_2H_5$[c]	68	54	67 (0.5)[l]	167–168[l]
CH_3	6-$NHCOCH_3$[d]	65		88–89[d]	
CH_3	4-Cl[e]	41	38	61 (19)[m]	176–177[m]
CH_3	6-CH_3	67	78	142–143[j]	167–168[j]
CH_3	5-CH_3[f]	65		55 (17)[j]	167–169[j]
CH_3	5-C_2H_5[g]	63	74	72 (19)[n]	166–168[n]
CH_3	6-CH_3, 5-NO_2	31		36–38	
CH_3	4-NO_2[h]	NR	NR		
H,	4-$COOCH_3$[i]	NR			

[a] M. P. Cava and B. Weinstein, *J. Org. Chem.*, **23**, 1616 (1958).
[b] E. Ochiai and I. Suzuki, *J. Pharm. Soc. Japan*, **67**, 158 (1947).
[c] F. A. Daniher and B. E. Hackley, Jr., unpublished results.
[d] R. Adams and S. Miyano, *J. Am. Chem. Soc.*, **76**, 2785 (1954).
[e] E. Profft and W. Rolle, *Z. Tech. Hochsch. Chem. Leuna-Nersburg*, **2**, 187 (1959); *Chem. Abstr.*, **55**, 1609*i* (1961).
[f] Y. Arata and K. Achiwa, *Yakugaku Zasshi*, **79**, 108 (1959); *Chem. Abstr.*, **53**, 10211*g* (1959).
[g] J. A. Berson and T. Cohen, *J. Am. Chem. Soc.*, **78**, 416 (1956).
[h] E. Ochiai, K. Arima, and M. Ishikawa, *J. Pharm. Soc. Japan*, **63**, 79 (1943).
[i] R. L. Bixler and C. Niemann, *J. Am. Chem. Soc.*, **80**, 2716 (1958).
[j] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons Inc., New York, N. Y., 1964, p 235.
[k] M. Endo and T. Nakashima, *Yakugaku Zasshi*, **80**, 875 (1960); *Chem. Abstr.*, **54**, 24705*c* (1960).
[l] P. A. Plattner, W. Keller, and A. Boller, *Helv. Chim. Acta*, **37**, 1379 (1954).
[m] T. Kato, *J. Pharm. Soc. Japan*, **75**, 1228 (1955); *Chem. Abstr.*, **50**, 8665*i* (1956).
[n] C. P. Farley and E. L. Eliel, *J. Am. Chem. Soc.*, **78**, 3477 (1956).

Of the 14 pyridine N-oxides employed in this study, only two, 4-nitro-2-picoline N-oxide and methyl isonicotinate N-oxide, were not deoxygenated even under forcing conditions (6 to 12 hr at reflux). The unreactivity of the nitro compound is not unexpected since 4-nitropyridine N-oxide is not deoxygenated by other reducing agents.[3a,d]

Yields of 60 to 78% were obtained with electron-releasing substituents such as alkyl, acetamido, and methoxyl, with the exception of 2- and 4-picoline N-oxide, the yields being 34 and 31%, respectively.

In general, electron-withdrawing groups such as 3- and 4-chloro and 5-nitro gave somewhat lower yields ranging from 21 to 41%. On the other hand, ethyl 6-methylnicotinate N-oxide gave a 68% yield of product in dioxane so that factors other than electronegativity are operative.

The reaction proceeds with the formation of 1 mole of sulfur trioxide. For example, the reduction of 2,6-lutidine N-oxide in water led to the formation of 0.78 mole of 2,6-lutidine and 0.82 mole of sulfur trioxide, determined as sulfate. In many cases in dioxane sol-

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[1] (a) Ash Stevens Inc.; (b) U. S. Army Edgewood Arsenal.

[2] For a summary, see E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

[3] (a) M. Hamana, *J. Pharm. Soc. Japan*, **75**, 121, 135, 139 (1955); (b) K. Takeda and K. Tokuyama, *ibid.*, **75**, 620 (1955); (c) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 3164 (1955); (d) F. Furukawa, *Pharm. Bull. Japan*, **3**, 230 (1955); (e) E. Howard, Jr., and W. F. Olszewski, *J. Am. Chem. Soc.*, **81**, 1483 (1959); (f) E. Hayashi, H. Yamanaka, and K. Shimizu, *Chem. Pharm. Bull.* (Tokyo), **7**, 141 (1959); (g) T. R. Emerson and C. W. Rees, *J. Chem. Soc.*, 1917 (1962); (h) D. I. Relyea, P. O. Tawney, and A. R. Williams, *J. Org. Chem.*, **27**, 477 (1962); (i) E. E. Schweizer and G. J. O'Neill, *ibid.*, **28**, 2460 (1963); (j) W. Hoefling, D. Eilhauer, and G. Reckling, East German Patent 36,422 (1965); *Chem. Abstr.*, **63**, 18047*d* (1965); (k) R. A. Abramovich and K. A. H. Adams; *Can. J. Chem.*, **39**, 2134 (1961).

[4] However, nonaromatic tertiary amine N-oxides have been reduced with SO_2: (a) E. C. Taylor and N. E. Boyer, *J. Org. Chem.*, **24**, 275 (1959); (b) W. Wiewiorowski and P. Baranowski, *Bull. Acad. Polon. Sci.*, **10**, 549 (1962).

[5] The yields reported for ethyl 6-methylnicotinate N-oxide and 3-nitro-2,6-lutidine N-oxide were those obtained at 4 and 6 hr, respectively.