The Oxidation of Some Carcinogenic Arylhydroxylamines to Nitroso Derivatives with Manganese Dioxide

Activated manganese dioxide was reported to convert N-phenylhydroxylamine to nitrosobenzene in 40% yield[1], and 6-hydroxylaminopurine to 6-nitrosopurine in 21% yield[2]. Water was used as a reaction media in both reports and required reaction times of up to 3 h.

We wish to report that by substituting sufficient chloroform to completely effect solution of the arylhydroxylamines for water, that they are converted to their nitroso derivatives in a few minutes in very high yield with activated manganese dioxide. The rapid rate of the reaction almost completely eliminates the formation of azoxy compounds by further reaction of the unreacted arylhydroxylamine and nitroso product[3] and/or further oxidation to the nitro compounds[4]. Therefore, the yield and purity of the nitroso compound is dependent on the purity of the arylhydroxylamine.

The 'activated' manganese dioxide reagent was prepared according to ATTENBURROW et al.[5]. The arylhydroxylamines[6] were prepared from the corresponding nitro compounds by the general procedure of WILLSTÄTTER and KUBLI[7]: N, 1-naphthylhydroxylamine m.p. 78–79° dec. lit.[7] m.p. 78°, N, 2-naphthylhydroxylamine m.p. 127° dec. lit.[8] m.p. 126°, N, 2-fluorenyl-hydroxylamine[9], N, 4-biphenylhydroxylamine m.p. 151–153° dec. lit.[10] m.p. 153°, N, 3-dibenzofuranylhydroxylamine[11] and N, phenylhydroxylamine[12].

The general experimental procedure is as follows. To freshly prepared arylhydroxylamine in sufficient chloroform to effect complete solution at 0 °C was added 2 equivalents of activated manganese dioxide at once. The resulting suspension was stirred vigorously under nitrogen for 15 min. Thin layer chromatography[13] of the reaction mixture at 2 min intervals revealed that all of the arylhydroxylamines studied were completely oxidized in from 5–10 min. The manganese oxide was removed by filtration through a bed of Celite and rinsed with a few ml of chloroform[14]. The filtrate and washings were concentrated under reduced pressure and the compounds purified by column chromatography on silica gel[15] or aluminum oxide[16]. The first bright emerald green band was collected, the solvent removed in vacuo to yield 90–98% nitroso compound homogenous on thin-layer chromatography. The following nitroso compounds were prepared: 1-nitrosonaphthalene m.p. 84–85° lit.[7] m.p. 85–86°, 2-nitrosonaphthalene m.p. 62–63° lit.[14] m.p. 62–64°, 4-nitrosobiphenyl m.p. 74–75° lit.[10] m.p. 73–74°, 2-nitrosofluorene m.p. 77–78° lit.[17] 77–79°, nitrosobenzene m.p. 68° lit.[18] 67° and 3-nitrosodibenzofuran m.p. 111°. The identities of the nitroso compounds were confirmed by comparison of their physical properties, IR- and UV-spectra and Rf values with those of authentic samples prepared by the oxidation of the corresponding N-arylhydroxylamines in chloroform with a molar equivalent of diethylazodicarboxylate[15] and by the $KMNO_4$ oxidation of the ammonium salts of the corresponding N-nitroso-arylhydroxylamines[8, 14]. Satisfactory C, H, and N analyses were obtained for the new compound 3-nitrosodibenzofuran[19, 20].

Zusammenfassung. Oxidation von N, 1-Naphthyl-, N, 2-Naphthyl-, N, 2-Fluorenyl-, N, 4-Biphenyl-, N, 3-Dibenzofuranyl, und N, Phenylhydroxylamin mit Mangandioxyd ergibt nach kurzer Reaktionszeit entsprechende Nitrosoderivate bei hoher Ausbeute.

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Zur Bestimmung der Elastizitätsgrenze von Bindegewebsstrukturen in vitro

Ein ideal elastischer Körper verformt sich unter der Einwirkung äusserer Kräfte und gewinnt seine ursprüngliche Gestalt nach Aufhören der einwirkenden Kräfte zurück. Diese Vorgänge sind im vorausgesetzten Idealfall unabhängig von der Zeit. Die Elastizitätsgrenze lässt sich angeben als diejenige Kraft, Spannung, Länge oder Dehnung, um die ein Körper maximal beansprucht oder verformt werden kann, ohne dass eine bleibende Deformation nach Entlastung zurückbleibt. Da es keine absolute Elastizitätsgrenze gibt, definiert man eine technische Elastizitätsgrenze, indem man bestimmte Vereinbarungen über statthafte prozentuale Restdehnungen trifft. Dieses Verfahren ist bei den meisten biologischen Geweben nicht ohne weiteres anwendbar, da sie elastische, visköse und plastische Anteile kombiniert enthalten, ihre initiale Länge (SMITH[1], FUNG[2, 3]) oft nicht den in vivo