was filtered into either an H_3PO_4–EtOH or HCl–EtOH solution of 10 mmol of 2,4-dinitrophenylhydrazine. The derivative was filtered, dried, weighed, and recrystallized from an appropriate solvent. Yields are given in Tables I, II, and III.

Reaction of Et_3SiH with Benzoyl Chloride.—Into a 25-ml erlenmeyer flask containing 100 mg of 10% Pd–C and 6.0 ml (50 mmol) of PhCOCl was added 8.0 ml (50 mmol) of Et_3SiH. The mixture heated to 60° and some gas was evolved. After standing overnight (18 hr), the mixture was filtered and then distilled at atmospheric pressure on a $\frac{3}{8}$ × 24 in. spinning-band column. The first fraction was pure Et_3SiCl, and a total of 5.0 g (66%) of the chlorosilane, bp 142.5–147°, was isolated. The mixture was then distilled at reduced pressure to give 1.6 g (31%) of PhCHO, bp 60.5–65° (16 mm).

Reaction of Et_3SiH with Butyryl Chloride.—The procedure is similar to the preceding reaction except that the reaction mixture was filtered after 15 min. Upon distillation the first fractions, bp 89–135°, were mixtures of n-C_3H_7COCl (0.6 g), Et_3SiH (1.0 g), and n-C_3H_7CHO (0.1 g) [all estimated by infrared (ir) spectrum]. The next fractions were 5.4 g (88%, correcting for recovered Et_3SiH) of Et_3SiCl, bp 143–147°. No other material except a trace of butyric acid distilled up to a pot temperature of 205°.

Reaction of Et_3SiH with Octanoyl Chloride.—Into a 25-ml erlenmeyer flask were placed 100 mg of 10% Pd–C, 4.25 ml (25 mmol) of octanoyl chloride, and 4.8 ml (30 mmol) of Et_3SiH. After some bubbling, the temperature of the flask rose to ~100° (2 min), and it was cooled in a water bath. After 1 hr, the reaction mixture was filtered into a separatory funnel containing 20 ml of ether, 20 ml of water, and 0.21 g of $NaHCO_3$. The contents were shaken, and then the ether layer was washed with water several times over the course of 2 hr until neutral. The organic layer was dried over anhy Na_2SO_4 and then distilled under vacuum. The first fraction isolated was n-octanal, 1.63 g (51%), bp 31° (0.6 mm), $n^{23.5}\text{D}$ 1.4234.

Low Temperature Reactions.—Into a flask containing 50 mg 10% Pd–C was added 10 mmol of acid chloride. While stirring (magnetic) the mixture was cooled to $\sim -70°$ with a Dry Ice–acetone bath. Ten millimoles of Et_3SiH (in the case of aroyl chlorides the Et_3SiH was added first, owing to solidification of the acid chloride) was then added and the system was stirred for 1 hr. At the end of this time, the mixture was allowed to warm slowly (1 hr) to +10° in the acetone bath. It was allowed to stir for 15 min at room temperature and then worked up with 2,4-DNPH as above. The results are given in Table IV.

Registry No.—Triethylsilane, 617-86-7; benzoyl chloride, 98-88-4; butyryl chloride, 141-75-3; octanoyl chloride, 111-64-8.

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Activation of Manganese Dioxide by Azeotropic Removal of Water

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Manganese dioxide, once known as a relatively selective oxidant of allylic alcohols, is now viewed as a less discriminate, condition-dependent oxidizing agent. Numerous functionalities can be oxidized by various types of manganese dioxide used over a wide range of time, temperature, and solvent polarity.[1] Whereas oxidations with manganese dioxide are generally simple to perform, the reproducible preparation of the activated reagent is often difficult and time consuming. The preparation and properties of manganese dioxide activated by an expeditious and reproducible procedure are reported herein.

Precipitated manganese dioxide was prepared from solutions of manganous sulfate, sodium hydroxide, and potassium permanganate according to a modified Attenburrow procedure.[2] Following the filtration and washing steps, the wet filter cake, containing about 40–60% water, was stored in a closed bottle. Portions of the wet material were activated conveniently, as needed, by the simple expedient of azeotropic distillation of the excess water with benzene, thereby circumventing the lengthy drying and grinding procedures usually employed for activation of precipitated manganese dioxide. With adequate rates of stirring (to break up lumps) and heating, the azeotropic activation is complete in about 1 hr, leaving a dense, brownish black, rapidly sedimenting precipitate having the appearance of irregular agglomerates under the microscope. In the presence of substrate, however, the agglomerates are quickly dispersed in benzene to a blackish brown suspension of fine, slowly sedimenting particles. Reagent activated by the azeotropic method can be used directly or stored under benzene; the benzene may be replaced with another solvent by successive decantations and washings; or the reagent may be collected by filtration for storage and/or use in other solvents. Both wet filter cake and the activated reagent under benzene have been stored unchanged for more than 1 year.

Inspection of the data in Table I shows that the reagent prepared by the azeotropic method is a typical activated manganese dioxide. No effort was made to optimize yields and conditions, or to evaluate activity and substrate specificity in comparison with activated manganese dioxide prepared *via* standard procedures.[3]

Azeotropic procedures have been employed by Pratt[2,4] as a useful device for following the rates of manganese dioxide oxidations in which the by-product water is distilled into a Dean–Stark trap. The reagent used for these studies, however, had already been activated in the conventional way in a prior step.[5]

The structure of activated manganese dioxide remains an enigma.[3,6,7] Gritter, *et al.*,[3] have noted an important role for cationic impurities, and Evans[6] and Henbest[8] have pointed to the critical role for water of hydration. In the present procedure, the azeotroping serves to remove occluded (not firmly bound) water and, presumably, water adsorbed to oxidatively active

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[1] For leading references, see L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," 1st ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 637.

[2] E. F. Pratt and S. P. Suskind, *J. Org. Chem.*, **28**, 638 (1963).

[3] Some differences in activity for various preparations of activated manganese dioxide have been demonstrated in the study of R. J. Gritter, G. D. Dupre, and T. J. Wallace, *Nature*, **202**, 179 (1964).

[4] E. F. Pratt and J. F. Van de Castle, *J. Org. Chem.*, **26**, 2973 (1961); E. F. Pratt and T. P. McGovern, *ibid.*, **29**, 1540 (1964).

[5] The activation procedures employed in the studies of Pratt[2,4] included a combination of some of the following steps prior to azeotroping: drying at 125° for various periods of time, grinding to pass a 60-mesh screen, redrying at 125°, equilibration with atmospheric moisture, and storing at −20° in closed containers.

[6] R. M. Evans, *Quart. Rev.* (London), **13**, 61 (1959), and references cited therein.

[7] W. F. Pickering, *Rev. Pure Appl. Chem.*, **16**, 185 (1966), and references cited therein.

[8] H. B. Henbest, E. R. H. Jones, and T. C. Owen, *J. Chem. Soc.*, 4909 (1957); and H. B. Henbest and A. Thomas, *ibid.*, 3032 (1957).

TABLE I

CHARACTERIZATION OF AZEOTROPICALLY ACTIVATED MANGANESE DIOXIDE[a]

Starting material	Product	Yield, %	Time, hr
$C_6H_5CH_2OH$	C_6H_5CHO	70[b]	1.0
$C_6H_5CHOHCH_3$	$C_6H_5COCH_3$	70[b]	0.5
$C_6H_5CH{=}CHCH_2OH$	$C_6H_5CH{=}CHCHO$	70[b]	1.0
$C_6H_5CHOHCOC_6H_5$	$C_6H_5COCOC_6H_5$	50	16
$C_6H_5CHOHCHOHC_6H_5$ (*meso*)	C_6H_5CHO	60[b]	1.0
$(C_6H_5)_2COHCOH(C_6H_5)_2$	$(C_6H_5)_2CO$	65[b]	16
$C_6H_5CHOHCH_2NH_2$	C_6H_5CHO	55[b]	3.0
$C_6H_5CHOHCOOC_2H_5$	$C_6H_5COCOOC_2H_5$	65[b]	1.0
$(C_6H_5)_2COHCOOH$	$(C_6H_5)_2CO$	45[b]	16
Hydroquinone	Quinone	65	1.0
Geraniol	Citral	80[c,d]	2.0
$C_6H_5CH_2CH_2OH$	Recovered starting material	80[c]	0.5

[a] Oxidations were performed with 1.0 g of substrate and 10.5 g (25 g of wet) of manganese dioxide in 125 ml of benzene at room temperature with stirring, except as noted. See Experimental Section for details. [b] As the 2,4-dinitrophenylhydrazone. [c] By gas chromatography. [d] Geraniol (2 g) as substrate.

adsorption sites on the surface. The azeotropically activated material contains 7% water as compared to an excess moisture content of 4–8% reported for material prepared by the Attenburrow procedure.[6] Continued azeotroping, past the point of complete activation, does not remove the firmly bound water of hydration, and so there is no danger of deactivating the activated hydrate by this azeotropic procedure.

On the assumption that the activation of precipitated manganese dioxide involves, as the critical step, the liberation of active sites on the surface by desorption of adsorbed water, it was reasoned that activation might also be effected by azeotroping at a lower temperature and, perhaps, even by the simple expedient of extractive dehydration by means of solvents having an avidity for water. The results of preliminary experiments indicate that some degree of azeotropic activation can indeed be achieved using ethyl ether, carbon tetrachloride, chloroform, and propionitrile. These are qualitative results, only, and no data was sought regarding the relative oxidizing power of the reagents prepared in this way *vs.* that using the benzene procedure. The results of extractive activation by ethyl ether or acetonitrile, summarized in Table II, indicate that significant activation can also be achieved with appropriate dehydrating solvents.

TABLE II

EXTRACTIVE ACTIVATION *vs.* THE BENZENE AZEOTROPIC PROCEDURE[a]

Method of activation	Oxidizing power[b]
A. Standard benzene azeotrope	1.5 mequiv of [O] per g of reagent[c]
B. 25 g of wet MnO_2 extracted with ten 200-ml portions of ethyl ether	0.47 mequiv of [O] per g of reagent
C. 25 g of wet MnO_2 extracted with five 200-ml portions of acetonitrile	0.87 mequiv of [O] per g of reagent

[a] Manganese dioxide (25 g of wet) was activated by azeotropic distillation with benzene or by repetitive extractions with ethyl ether or acetonitrile. Oxidations were performed with 3.0 g of benzyl alcohol for 1 hr. See Experimental Section for details. [b] Oxidizing power was calculated from the amount of benzaldehyde-2,4-dinitrophenylhydrazone which could be prepared after the 1-hr oxidation, based on 10.5 g of activated reagent. [c] This value compares favorably with the value of 1.25–1.35 mequiv of [O] per g of MnO_2 reported by Henbest, *et al.*,[8] for oxidation of allylic alcohols.

The foregoing results not only demonstrate an efficient azeotropic procedure for activating precipitated manganese dioxide, but point to the possibility that useful procedures may be devised for production of manganese dioxides of intermediate degrees of activity for application to substrates requiring greater selectivity than heretofore available by conventional methods for preparation of the active reagent.

The observation that some degree of activation may be achieved simply by washing the wet precipitate with an appropriate dry solvent is consistent with the early hypothesis[9] that the initial step in the manganese dioxide oxidation is adsorption of substrate. An ensuing publication will present evidence that the rate-determining step in the manganese dioxide oxidation of benzylic alcohols is C–H bond cleavage.

Experimental Section

Preparation of Activated Manganese Dioxide.—Active manganese dioxide was prepared by a modified Attenburrow procedure.[2] After the final water wash the filter cake was left on the funnel with suction for about 24 hr. Surface cracks were closed with a flat spatula to facilitate washing and water removal. The hydsated filter cake was cut into chunks and stored in closed bottles. Activation of small quantities was effected as required by the following procedure. Into a 250-ml flask fitted with a Dean–Stark trap, condenser, and magnetic stirrer were added 150 ml of benzene and 25 g of the hydrated precipitated manganese dioxide (large chunks were crumbled on Glassine paper prior to addition). Water (14.5 ml) was removed by vigorous azeotropic distillation with stirring over about 1 hr, or until separation of water was complete. Reagent activated in this way was brownish black and dense, as contrasted to the blackish brown and finely dispersed appearance after addition of substrates for oxidation. Wet filter cake has been stored for more than 2 years without change. Activated reagent has been stored in stoppered flasks under benzene for 1 year without loss of activity. In a second run, the wet filter cake was pressed on the funnel until the water content, determined by azeotroping, was about 40%. This material, upon azeotropic activation, had the same oxidizing power on a dry-weight basis as the material used in Table II.

Oxidations, Table I.—Substrates were added at room temperature under nitrogen to stirred mixtures of 10.5 g (from 25 g of wet) of activated manganese dioxide (above) in 125 ml of benzene. The flasks were stoppered and the mixtures stirred for the designated times. The reaction mixtures were filtered through Celite and the filter cakes were washed with three portions of fresh solvent. Benzene was removed from the combined filtrates and washings under reduced pressure. Products of oxidation were identified directly or as the 2,4-dinitrophenylhydrazones.

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[9] S. Ball, T. W. Goodwin, and R. A. Morton, *Biochem. J.*, **42**, 516 (1948).

Activations, Table II.—In preliminary experiments, 2.5-g samples of wet manganese dioxide were azeotropically activated using ethyl ether, carbon tetrachloride, chloroform, or propionitrile. After a suitable azeotroping period, as judged by the appearance of the manganese dioxide, excess benzyl alcohol was added, with stirring for about 0.5 hr. Following filtration and solvent removal, benzaldehyde was detected by conversion to the 2,4-dinitrophenylhydrazone. In each case a substantial amount of the derivative formed, indicating some degree of activation. The wet catalyst, unactivated, gave no detectable benzaldehyde under these conditions.

The extractive activations with ethyl ether and acetonitrile were performed as follows. Wet manganese dioxide (25-g samples) was stirred vigorously with ten 200-ml portions or five 200-ml portions of ether or acetonitrile, respectively. Stirring was continued for about 5 min for each portion of fresh solvent. Spent solvent was decanted prior to addition of fresh solvent. To the activated materials, in benzene solvent, were then added 3-g samples of benzyl alcohol. After 1 hr, the yield of benzaldehyde, as the 2,4-dinitrophenylhydrazone, was determined. Oxidizing power was determined in comparison with benzene-azeotroped material, on the basis of 10.5 g of active material in each case.

Registry No.—Manganese dioxide, 1313-13-9.

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Catalytic Decomposition and Chemical Reduction of Diaryliodonium Salts. Reactions Involving Ligand Transfer[1]

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Copper(I) salts have been shown to be extremely efficient catalysts for the decomposition of diaryliodonium salts.[2] A study of the reaction of iodonium salts with metal salts more strongly reducing than copper(I), *i.e.*, titanium(III) and chromium(II), has been initiated, and the copper-catalyzed reaction has been further investigated.

Titanium(III) chloride was found to be an efficient catalyst for the decomposition of diphenyliodonium chloride (Table I). The reaction in water proceeds to completion with 0.06 equiv of titanium(III) chloride, yielding only iodobenzene and chlorobenzene without consuming titanium(III). The same reaction in methanol, however, went only 39% to completion, with complete consumption of catalyst (Table I). The main products were iodobenzene and benzene, along with small quantities of chlorobenzene and biphenyl.

Polarographic studies[3] of iodonium salts had previously revealed that diphenyliodonium cations may accept one electron ($E_{1/2} = -0.2$ V *vs.* sce) forming diphenyliodine, which is unstable and rapidly decomposes to iodobenzene and phenyl free radicals. Further, the reactions of diphenyliodonium salts have been intensively studied, and on the basis of several factors (product distribution, steric effects, dehydrogenation of solvent, effect of oxygen, polymerization of styrene) an initial step of electron transfer from carbanion to iodonium ion has been proposed.[4a,5] In the light of these earlier conclusions and in light of the above results with titanium(III) chloride, a mechanism to explain this catalysis is now proposed.

The reaction is formulated as initiated by an electron transfer from a titanium(III) species[6] to yield unstable diphenyliodine and a titanium(IV) species.[6] In turn, diphenyliodine decomposes to iodobenzene and a phenyl free radical,[3] whose fate is determined by the solvent and other reactants. In water the phenyl radicals react exclusively with a titanium(IV) species, forming chlorobenzene and regenerating titanium(III) by a ligand-radical transfer process.[7] In methanol, however, the predominant path is hydrogen abstraction from solvent; regeneration of titanium(III) is therefore much less efficient. The reaction in water, in the presence of acrylonitrile, yielded polyacrylonitrile. Polymerization did not take place under identical conditions in the absence of iodonium salt. This observation is in accord with the postulated existence of phenyl free radical intermediates. Product distribution studies of the titanium(III)-catalyzed decomposition of unsymmetrical 4-methoxydiphenyliodonium chloride in water showed the ratio of cleavages of C_6H_5–I/$CH_3OC_6H_4$–I to be 1.4. This insensitivity of carbon–iodine bond cleavage to polar substituents on the phenyl ring has been taken to indicate nonpolar bond fission.[4,8] The yield of chlorobenzene, from reactions run in methanol, was independent of acid and chloride ion concentrations but did depend on the Ti(IV)/Ti(III) ratio (Table I). Addition of $TiCl_4$ to methanol results in the formation of $TiCl_2(OMe)_2$.[9] The resulting increased concentration of titanium(IV)-bound chloride, which can undergo ligand-radical transfer to a phenyl radical, is reflected in significantly increased yields of chlorobenzene. As expected, anisole was not detected since methoxide does not readily undergo ligand-radical transfer.[7a] To the knowledge of the authors ligand-radical transfer processes involving titanium salts have not previously been described.

Chromium(II) chloride, a more powerful reducing agent than titanium(III), yielded mainly iodobenzene

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[1] This paper is largely based on part II of a dissertation submitted by P. Bodlaender in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry), 1967.

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[5] (a) F. M. Beringer and P. S. Forgione, *Tetrahedron*, **19**, 739 (1963); (b) F. M. Beringer and S. A. Galton, *J. Org. Chem.*, **28**, 3417 (1963).

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