bromate and independent of both the concentration and chemical nature of the reducing agent.[1] This peculiar behavior is observed only after a rather ill-defined induction period and in solutions containing a large excess of reducing agent. When bromate is in considerable excess over cerium(III), Kasperek and Bruice[2] report a very different behavior in which the induction period is followed by a sudden burst of reaction that slows greatly long before the equilibrium concentration of cerium(IV) is approached.

The possible complications of this system are further illustrated by the following potentials for different stages of reduction of bromate based on values in Latimer,[3] on the free energy of formation of bromite ion by Lee and Lister,[4] and on the observation of Buxton and Dainton[5] that $BrO_2\cdot$ is unstable with respect to disproportionation.

$$BrO_3^- + 2H^+ + e^- = BrO_2\cdot + H_2O \qquad E^0 < 1.24\ V$$
$$BrO_3^- + 3H^+ + 2e^- = HBrO_2 + H_2O \qquad E^0 = 1.24\ V$$
$$BrO_3^- + 5H^+ + 4e^- = HOBr + 2H_2O \qquad E^0 = 1.49\ V$$
$$BrO_3^- + 6H^+ + 5e^- = {}^1/_2Br_2 + 3H_2O \qquad E^0 = 1.51\ V$$

Since Latimer[3] reports that in 1 M sulfuric acid $E^0 = 1.44$ V for the reaction $Ce^{4+} + e^- = Ce^{3+}$, it is apparent that cerium(III) can reduce bromate if the overall process involves four or five electrons but that the one- and two-electron processes are thermodynamically unfavorable.

These difficult restrictions can be satisfied by the following mechanism.

$$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2\cdot + H_2O \qquad (1)$$
$$BrO_2\cdot + Ce^{3+} + H^+ \rightleftharpoons HBrO_2 + Ce^{4+} \qquad (2)$$
$$BrO_2\cdot + Ce^{4+} + H_2O \longrightarrow BrO_3^- + Ce^{3+} + 2H^+ \qquad (3)$$
$$2HBrO_2 \longrightarrow BrO_3^- + HOBr + H^+ \qquad (4)$$

Thompson[1] worked at high concentrations of cerium(III) where step 2 essentially suppressed steps -1 and 3. Then steps 1 and 2 accomplish process A which produces $HBrO_2$ autocatalytically according to the kinetics of eq 5. Although process A has a somewhat unfavorable $\Delta G°$, the almost irreversible step 4 competes effectively with eq -2 in the initial stages of reaction. The overall process is then described by thermodynamically favored process B.

$$BrO_3^- + 2Ce^{3+} + 3H^+ \longrightarrow HBrO_2 + 2Ce^{4+} + H_2O \qquad (A)$$

$$d[HBrO_2]_A/dt = k_1[BrO_3^-][HBrO_2][H^+] \qquad (5)$$

$$BrO_3^- + 4Ce^{3+} + 5H^+ \longrightarrow HOBr + 4Ce^{4+} + 2H_2O \qquad (B)$$

If rates of formation and destruction of $HBrO_2$ are equal, the steady state of eq 6 is established. We

$$[HBrO_2] = (k_1/2k_4)[BrO_3^-][H^+] \qquad (6)$$

have found that establishment of this steady state can be inhibited by traces of bromide ion, and oxidation of cerium(III) commences only after the bromide has been consumed during the induction period. The reaction then proceeds by kinetic eq 7 in exact agreement with the observations of Thompson.[1] The rate is clearly independent of the chemical nature of the one-electron reducing agent in step 2 just as is observed. This interpretation can be combined with the kinetic data of Buxton and Dainton[5] to indicate that $E^0 = 1.14$ V for the one-electron reduction of acid bromate ion, thereby supporting the observation that only moderately strong one-electron reducing agents will react directly with bromate ion.

$$-d[BrO_3^-]/dt = (k_1^2/4k_4)[BrO_3^-]^2[H^+]^2 \qquad (7)$$

Kasperek and Bruice[2] worked at low concentrations of cerium(III) where reversibility of step 2 needed to be considered and where $k_3[Ce^{4+}]$ rapidly became significant with respect to $k_2[Ce^{3+}][H^+]$. If step -1 is still neglected, and if steady-state treatments are applied to the concentrations of $HBrO_2$ and of $BrO_2\cdot$, the kinetic equation becomes 8. This equation explains

$$\frac{-d[BrO_3^-]}{dt} = \frac{1}{4k_4}\{(k_1k_2[BrO_3^-][Ce^{3+}][H^+]^2 - k_1k_3[BrO_3^-][Ce^{4+}][H^+] - k_{-2}k_3[Ce^{4+}]^2)/(k_2[Ce^{3+}][H^+] + k_3[Ce^{4+}])\}^2 \qquad (8)$$

why Kasperek and Bruice[2] observed a very pronounced diminution in rate long before equilibrium was approached. It also explains the observation of Thompson[1] that the stronger reductant Np(V) obeys the simple kinetics of eq 7 until reaction has gone much further than with the very weak reductant Ce(III).

A more complete discussion of the thermodynamic and kinetic features of these complex systems and a mechanistic explanation of the oscillations when malonic acid is also present[6] will be published later.

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Stereospecific Elaboration of the A Ring of Gibberellic Acid by Partial Synthesis

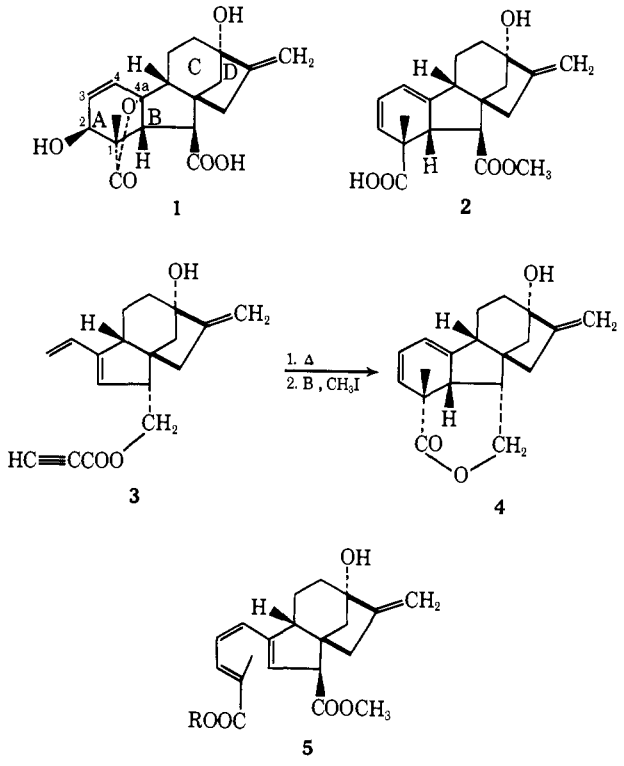
Sir:

Chemists in far-flung laboratories have undertaken the formidable task of reproducing gibberellic acid (gibberellin A_3) (**1**) and related structures by chemical synthesis. The result of their efforts to date has been an almost unprecedented outpouring of ingenious synthetic designs and highly original new synthetic methods.[1] We report herein an efficient reaction se-

(1) Among these outstanding investigations there may be cited contributions emanating from the schools of (a) H. J. E. Loewenthal [*e.g.*, *Tetrahedron Lett.*, 5333 (1966)]; (b) K. Mori and M. Matsui [*e.g.*, *ibid.*, 2183 (1968)]; (c) F. E. Ziegler [*e.g.*, *ibid.*, 2201 (1971)]; (d) R. A. Raphael [*e.g.*, *J. Chem. Soc.*, 3958 (1961)]; (e) W. Nagata [*e.g.*, *J. Amer. Chem. Soc.*, 92, 3202 (1970)]; (f) G. Stork [*ibid.*, 87, 1148 (1965)]; (g) S. Masamune [*ibid.*, 86, 288 (1964)]; (h) H. O. House [*e.g.*, *J. Org. Chem.*, 34, 2209 (1969)]; (i) L. J. Dolby [*e.g.*, *ibid.*, 36, 1277 (1971)];

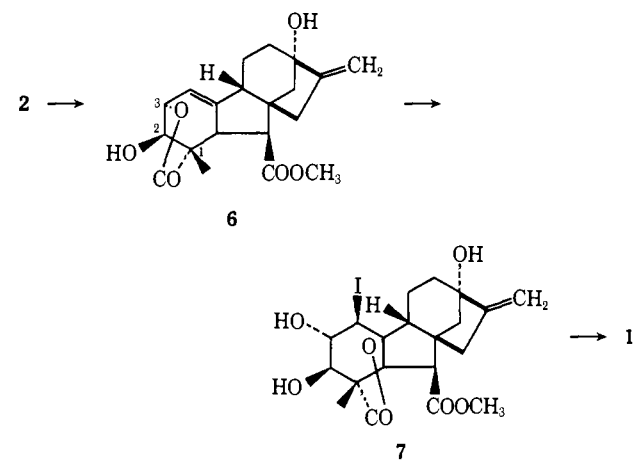
quence by which the A ring unit of gibberellic acid with its highly sensitive and dense arrangement of functionality can be recreated stereospecifically. Knowledge of these processes should expedite the realization of a stereospecific total synthesis.

The tetracyclic structure **2** is an attractive intermediate for the synthesis of gibberellic acid, being accessible in principle by a number of routes which are subject to stereochemical control. For example, **2** might be produced *via* **3** and **4** using an internal Diels–Alder reaction *or via* **5** by thermal cyclization.



Toward the objective of a partial synthesis of **2**, methyl gibberellate was converted to the 2-monotosylate, mp 165° dec,[2] by treatment with 2 equiv of *p*-tosyl chloride in pyridine (3.5 ml/g of methyl gibberellate) at +5° for 30.8 hr. The reaction product was homogeneous by tlc (thin layer chromatographic) analysis on silica gel after recrystallization from methylene chloride–hexane in the cold (93% yield). Exposure of the tosylate to dry sodium bromide in hexamethylphosphoric triamide (freshly distilled from calcium hydride) at 22° for 4.75 hr yielded a mixture of epimeric 4-bromides ($\Delta^{2,3}$) which was directly treated with excess activated[3] zinc (30 mesh) in ethanol to afford the triene acid **2**,[2] ultraviolet max (95% ethanol) 272 nm (ϵ 5200) (88% overall from methyl gibberellate), as a solid foam which could be converted to a crystalline silver salt (colorless prisms from ethyl acetate–hexane) and which was homogeneous by tlc analysis. This acid was reconverted to gibberellic acid by the pathway described below.

The unsaturated acid **2** was selectively oxidized with 1.3 equiv of *m*-chloroperbenzoic acid in methylene chloride at −20 to −25° (75 ml of CH_2Cl_2/g of **2**) until tlc analysis indicated that less than 2% of **2** was unchanged (*ca.* 2.7 hr) to afford 76% of the dihyroxy γ-lactone ester **6**,[2] identical with the compound obtained by base-catalyzed trans lactonization of methyl gibberellate, as previously described, and assigned structure **6**.[4] Saponification of the γ-lactone function in **6**



was effected by exposure to a fourfold excess of a 5:3 mixture of 0.1 *N* aqueous sodium hydroxide–ethanol at 25° for 4 hr, and the resulting monoacid monoester was treated with 1.1 equiv of iodine in a mixture of aqueous sodium bicarbonate–tetrahydrofuran (THF)–methylene chloride to form the crystalline iodo lactone **7**,[2] mp 125° dec (60%). This substance was converted to methyl gibberellate (in 90% yield from **7**) in one flask by the following sequence: (1) trifluoroacetylation with 6 equiv of trifluoroacetic anhydride and excess pyridine in THF at 0° for 1 hr, (2) addition of excess zinc dust at 0° and stirring for 1 hr at 0° to effect elimination, and (3) detrifluoroacetylation by addition of 10% aqueous sodium bicarbonate and stirring at 25° for 14 hr. The methyl gibberellate so obtained was chromatographically homogeneous and identical in all respects with an authentic specimen. Finally, the conversion of methyl gibberellate to gibberellic acid itself, **1**, was accomplished in high yield by the elegant method of Johnson and Bartlett.[5]

An investigation aimed at the total synthesis of the key intermediates **3** and **4** and also **5** is now in progress.

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