mishaps occurred in over 50 reactions with other alkenes.

General Procedure for Data in Table I. 1-Decene (5.0 mmol), manganese(III) acetate hydrate, and sodium azide were refluxed in glacial acetic acid at the concentrations specified until the dark brown color had disappeared (<30 min). The reaction was allowed to cool, poured into 30–60 °C petroleum ether, washed with water (2×) and saturated bicarbonate solution, and dried ($MgSO_4$). Yields for entries 1–8 were determined by GC comparison (dodecane internal standard) with the isolated yield of 68% for entry 9.

Representative Procedure for Diazide Formation. 1-Decene (0.50 g, 4.8 mmol), sodium azide (4.46 g, 72 mmol), manganese(III) acetate (3.86 g, 4.80 mmol, 14.4 mequiv of Mn(III)), and glacial acetic acid (25 mL) were placed in a 50-mL, round-bottomed flask equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet. The mixture was heated to 70–116 °C whereupon the salts dissolved. The heating was continued until the solution lightened from dark brown to clear, or light yellow (10–30 min). The mixture was cooled to room temperature, diluted with water (200 mL), and extracted with 30–60 °C petroleum ether (4 × 25 mL). The combined extracts were washed with saturated bicarbonate solution, dried ($MgSO_4$), and evaporated. The residue was chromatographed (5% EtOAc:Hexane) to yield 1,2-diazidodecane **2** (0.73 g, 3.3 mmol, 68%).

1,2-Diazidodecane (2): IR 2930, 2860, 2100, 1470, 1345, 1270 cm^{-1}; ^1H NMR δ 3.3 (br s, 3 H), 1.7–0.7 (m, 17 H); CI-MS (NH_3 ionization gas) for $C_{10}H_{20}N_6$ (positive) $M - N_3^- + NH_3$ 199, $M - 2N_3^- + NH_2^- + NH_3$ 173, $M - 2\,N_3^- + NH_2^-$ 156, (negative) $M + N_3^-$ 266.

4,5-Diazidooctane (3) Mixture of Diastereomers: IR 2960, 2925, 2870, 2110, 1460, 1260 $cm-^1$; ^1H NMR δ 3.3 (m, 2 H), 1.6–0.8 (m, 14 H); CI-MS (NH_3 ionization gas) for $C_8H_{16}N_6$ (positive) $M + NH_4^+$ 214, $M - N_3^- + NH_3$ 171, $M - N_2 + H^+$ 169, $M - 2N_3^- +NH_2^-$ 128, $M - N_3^- - N_2$ 126, (negative) $M + N_3^-$ 238, $M - N_2$ 168.

4,5-Diazido-5-butylnonane (4): IR 2960, 2930, 2880, 2100, 1470, 1250 cm^{-1}; ^1H NMR δ 3.15 (m, 1 H), 2.2–0.7 (m, 25 H); CI-MS (NH_3 ionization gas) for $C_{13}H_{26}N_6$ (positive) $M + NH_4^+$ 284, $M - N_2 + H^+$ 239, (negative) $M + N_3^-$ 308.

1,2-Diazidocyclohexane[5a,6a] **(5)**: 4:1 trans/cis mixture by GC: IR 2940, 2865, 2100, 1260 cm^{-1}; ^1H NMR δ 3.7–3.0 (m, 2 H), 2.3–0.9 (m, 8 H); CI-MS (NH_3 ionization gas) for $C_6H_{10}N_6$ (positive) $M - N_3^- + NH_3$ 266, $M - N_3^- - N_2 + NH_3$ 113, $M - 2N_3^- + NH_2^-$ 98, $M - N_3^- - N_2$ 96, (negative) $M - N_2 = 138$.

1,2-Diazidocyclooctane[5a] **(6)**: 6:1 trans/cis mixture by GC: IR 2930, 2860, 2100, 1465, 1445, 1255 cm^{-1}; ^1H NMR δ 3.75–3.3 (m, 2 H), 1.9–1.1 (m, 12 H); CI-MS (NH_3 ionization gas) for $C_8H_{14}N_6$ (positive) $M + NH_4^+$ 212, $M - N_2 + NH_4^+$ 184, $M - N_3^- + NH_3$ 169, $M - N_2 + H^+$ 167, $M - 2N_2 + H^+$ 139, $M - 2N_3^- + NH_2$ 126, (negative) $M - N_2$ 166, $M - 2N_2 - H^+$ 137.

Preparation of 1,2-Diaminodecane Diacetamide (7). A 25-mL, two-necked flask equipped with two gas valves and a hydrogen filled balloon was charged with **2** (0.50 g, 2.20 mmol), 10% palladium/carbon (0.25 g), glacial acetic acid (12 mL), and acetic anhyride (3 mL). After stirring at 25 °C for 7 h the mixture was filtered, poured onto water (150 mL), and extracted with chloroform (3 × 50 mL). The combined extracts were washed with saturated sodium bicarbonate (50 mL) and brine (50 mL), dried ($MgSO_4$), and evaporated. Trituration of the oil with diethyl ether/30–60 °C petroleum ether afforded a colorless solid which was filtered and washed with 30–60 °C petroleum ether (0.25 g, 0.98 mmol, 44%): mp 136–138 °C; IR 3290, 3095, 2915, 2850, 1630, 1540, 1370, 1290, 750, 715 cm^{-1}; ^1H NMR δ 6.45 (br, 1 H), 6.0 (br, 1 H), 4.1–3.65 (m, 1 H), 3.4–3.05 (m, 2 H), 1.95 (s, 6 H), 1.8–0.7 (m, 17 H).

Preparation of 1,2-Diaminodecane. A 250-mL pressure vessel was charged with **2** (1.63 g, 7.30 mmol), Lindlar's catalyst (1.63 g), and absolute ethanol (25 mL). After 23 h, at 50 psi H_2 and 25 °C the pressure was relieved and the mixture filtered through diatomaceous earth. The filtrate was diluted with 3 N hydrochloric acid (50 mL) and extracted with diethyl ether (3 × 15 mL). The combined ethereal extracts were washed with 3 N hydrochloric acid (2 × 15 mL) and the combined aqueous layers made basic with potassium hydroxide to pH 11. This solution was extracted with diethyl ether (4 × 25 mL) and the latter combined ethereal extracts washed with saturated sodium bicarbonate, dried (KOH), and evaporated to give the oily diamine (0.92 g, 5.32 mmol, 73% crude).

Benzoyl chloride (2 mL) was slowly added to a mixture of crude diamine (0.35 g, 2.03 mmol) in 10% sodium hydroxide. After 15 min at 25 °C the solution was adjusted to pH 9 and the precipitate filtered. Recrystallization from hot ethanol/water (3:1) afforded a solid (0.79 g, mp 145–148 °C) which was recrystallized from 95% ethanol to give 1,2-diaminodecane dibenzamide **8** (0.48 g, 1.3 mmol, 62%): mp 147–151 °C, lit.[24] mp 160–161 °C; ^1H NMR δ 7.9–7.1 (m, 10 H), 4.5–4.1 (m, 1 H), 3.75–3.4 (m, 2 H), 2.0–0.7 (m, 17 H), NH not observed.

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Registry No. 2, 97644-75-2; (*threo*)-**3**, 97644-76-3; (*erythro*)-**3**, 97654-62-1; **4**, 97644-77-4; (*cis*)-**5**, 10027-79-9; (*trans*)-**5**, 57770-13-5; (*cis*)-**6**, 97644-78-5; (*trans*)-**6**, 97644-79-6; **7**, 97644-80-9; **8**, 97644-81-0; sodium azide, 26628-22-8; manganese(III) acetate, 993-02-2; 1,2-diaminodecane, 13880-30-3; 1-decene, 872-05-9; (*E*)-4-octene, 14850-23-8; 5-butyl-4-nonene, 7367-38-6; cyclohexene, 110-83-8; cyclooctene, 931-88-4.

Some Observations on the Iodination of 2-Naphthol and Its Methyl Ether

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While the bromination of 2-naphthol and its methyl ether were studied many years ago[1] and have served as the basis for an organic synthesis preparation of 6-bromo-2-naphthol,[2] the iodination of 2-naphthol or 2-methoxynaphthalene has received only brief study. Potts[3] iodinated a number of activated aromatic rings with iodine using ethylenediamine as the hydrogen iodide acceptor and reported a 96% yield of 1-iodo-2-naphthol from 2-naphthol. Jones and Richardson[4] in the same year reported a 90% yield of 1-iodo-2-methoxynaphthalene from 2-methoxynaphthalene using iodine, sodium iodide, and dichloroamine Wirth, Konigstein, and Kern[5] subsequently prepared the same compound (76% yield) in developing the use of iodic acid as an oxidizing agent for the hydrogen iodide produced during the reaction.

Recently, we required a reliable supply of 6-iodo-2-methoxynaphthalene. A survey of the literature suggested two potential routes from readily available starting materials. Takagi, Hayama, and Okamoto[6] have published a method for the replacement of bromine in an aryl bromide with iodine. The reaction requires heating the aryl bromide in dimethylformamide with an excess of potassium iodide in the presence of a small amount of nickel bromide and tributylphosphine. The exact role of

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the latter components is unclear, but apparently the rupture of the carbon–bromide bond is facilitated by complexation with the nickel.

The treatment of 6-bromo-2-naphthol in this fashion gave an 68% yield of 6-iodo-2-naphthol. The structure was established by mass spectrometry and NMR. The yield from 6-bromo-2-methoxynaphthalene was 80%. The objections to this method were twofold, however. While commercially available, both 6-bromo-2-naphthol and its methyl ether are expensive. The preparation of the naphthol is well described,[2] but the conversion to the methyl ether by the conventional base–methyl iodide route proceeds only in ca. 70% yield. Furthermore, both compounds (particularly the methyl ether) suffer the disadvantage of being rather strong irritants and lachrymators. Consequently, a second possible pathway was explored.

The monobromination of 2-naphthol yields exclusively the 1-bromo product. Substitution of a second bromine occurs at the 6-position. Both of these observations have been rationalized by Fieser[1a] as consequences of the enol-like character of 2-naphthol with a considerable amount of π-bond fixation between positions 1 and 2. It would seem reasonable that the iodination of either the 1-iodo-2-naphthol or its methyl ether should also occur at position 6. Since it has been known for many years that 1,6-dibromo-2-naphthol undergoes reduction with hydroiodic acid at the 1-position,[7] a route to selectively prepare the 6-iodo-2-methoxy compound suggests itself.

The stoichiometry of the iodination reaction is:

$$5\mathrm{ArH} + 2\mathrm{I_2} + \mathrm{HIO_3} \rightleftarrows 5\mathrm{ArI} + 3\mathrm{H_2O}$$

When 1-iodo-2-methoxynaphthalene in the usual solvent mixture of acetic acid, water, and sulfuric acid was treated with stoichiometric amounts of iodine and iodic acid, it was observed that substantial amounts of 2-methoxynaphthalene and 6-iodo-2-methoxynaphthalene were produced along with a new product shown subsequently to be 1,6-diiodo-2-methoxynaphthalene. The composition of the reaction product was found to be quite variable, reflecting the order of mixing and the time allowed for the experiment. It seemed likely that at least a portion of the difficulty could be attributed to the presence of hydroiodic acid formed during the course of the reaction. In a more controlled experiment, a deficiency of iodine was used, while the amount of iodic acid was increased above the stoichiometric requirement. Samples of this reaction were withdrawn periodically, and it was found that the 1,6-diiodo compound was formed first. However, even with the excess of iodic acid, prolonged heating produced enough hydroiodic acid to yield an appreciable amount of the two reduction products. It was observed that when 2-methoxynaphthalene and iodic acid were heated in the standard solvent iodine was liberated, and 1-iodo-2-methoxynaphthalene was formed. Iodic acid was quite stable when heated in the acid solvent alone.

In another small-scale experiment it was found that the 1-iodo-2-methyl ether was reduced with hydroiodic acid very much faster than the 6-iodo analogue. It was found possible to prepare pure samples of the 1,6-diiodo-2-methoxynaphthalene by iodinating the 6-iodo-2-methoxynaphthalene, suppressing the formation of the various reduction products by employing twice the required amount of iodic acid.

On the basis of these experiences, a synthesis of 6-iodo-2-methoxynaphthalene was evolved as a one-pot process. By use of the required amount of iodine to form the 1,6-diiodo compound with an excess of iodic acid, the 1,6-diiodo compound was generated first. Hydroiodic acid was then added, and the reduction of the iodine from the 1-position was carried out, yielding the desired 6-iodo-2-methoxynaphthalene in 88% yield.

Experimental Section

All melting points were taken on a Kofler Heizbank instrument. Mass spectra were acquired on a Finnigan Model 1020 instrument. Gas chromatography was conducted with a Perkin-Elmer Sigma 3 using a 6-ft, $^1/_8$-in. glass column packed with 3% OV-17. Temperature programming was used throughout on the following schedule: 175 °C, 1 min; 175–250 °C, 15 °C per min; 250 °C, 5 min.

Proton and ^{13}C NMR were carried out on Varian EM-390 and XL-300 instruments as well as on a JEOL FX-60. All spectra were run in deuterochloroform with $\mathrm{Me_4Si}$ as an internal standard. To facilitate the assignment of resonances, both homonuclear and heteronuclear correlation and 2D-J spectroscopy were employed. In the case of 6-iodo-2-methoxynaphthalene, parameters were confirmed by spin simulation.

The standard solvent referred to below was composed of 185 mL of glacial acetic acid, 10 mL of water, and 5 mL of concentrated sulfuric acid.

6-Iodo-2-naphthol. A solution of 2.23 g (0.01 mol) of 6-bromo-2-naphthol and 8.3 g of potassium iodide in 40 mL of dimethylformamide was prepared and brought to reflux. While the mixture was warmed, 0.7 g of nickel bromide and 0.5 mL of tributylphosphine were added. Refluxing was continued overnight. Upon cooling, the mixture was diluted with 100 mL of 1:1 low-boiling petroleum ether and benzene. The mixture was washed with several small portions of water and the solvent removed by rotary evaporation. The residue consisted of 2.0 g of light brown solid, which checked as being ca. 90% product and 10% starting material by GC (yield of product ca. 67%). Crystallization from hexane gave a white product, mp 135–136 °C. Anal. Calcd for $\mathrm{C_{10}H_7OI}$: C, 44.44; H, 2.59. Found: C, 44.67; H, 2.57. MS, *m/e* 270 ($\mathrm{M^+}$, 100), 143 (M − 127, 72); ^{13}C NMR δ 109.57 (C-1), 153.75 (C-2), 118.53 (C-3), 128.85 (C-4), 130.60 (C-4a), 136.39 (C-5), 88.19 (C-6), 134.92 (C-7), 128.01 (C-8), 133.32 (C-8a); ^{1}H NMR 7.14 (m, 2 H), 7.39 (H-3, d, $J_{3,4}$ = 8.8 Hz), 7.61 (m, 2 H), 8.13 (H-5, *d*, $J_{5,7}$ = 1.5 Hz).

6-Iodo-2-methoxynaphthalene. (a) From 6-Bromo-2-methoxynaphthalene. A solution of 40 g (0.14 mol) of 6-bromo-2-methoxynaphthalene was heated in 250 mL of dimethylformamide. While the mixture was warmed, 150 g of potassium iodide, 1.5 g of nickel bromide, and 4 mL of tributylphosphine were added. The mixture was refluxed overnight, cooled, and worked up in a fashion analogous to the above. The yield of crude material was 46 g (80%) of NMR pure product. Crystallization from hexane gave an analytically pure sample, mp 141–142 °C. Anal. Calcd for $\mathrm{C_{11}H_9OI}$: C, 46.48; H, 3.17. Found: C, 46.80; H, 3.28. MS, *m/e* 284 ($\mathrm{M^+}$, 100), 269 (M − 15, 75), 241 (M − 43, 71), 157 (M − 127, 75); ^{1}H NMR δ 7.04 (H-1), 7.11 (H-3), 7.58 (H-4), 8.11 (H-5), 7.63 (H-7), 7.43 (H-8), 3.87 (methoxyl) a [$J_{1,3}$ = 2.7 Hz, $J_{1,4}$ = 0.2 Hz, $J_{3,4}$ = 9.2 Hz, J_{57} = 1.8 Hz, $J_{5,8}$ = 0.2 Hz, $J_{7,8}$ = 8.6 Hz], ^{13}C NMR δ 105.81 (C-1), 158.07 (C-2), 119.46 (C-3), 128.34 (C-4), 130.68 (C-4a), 136.27 (C-5), 88.05 (C-6), 134.76 (C-7), 128.38 (C-8), 133.40 (C-8a), 55.28 (methoxyl).

(b) From 2-Methoxynaphthalene. A mixture of 3.16 g (20 mmol) of 2-methoxynaphthalene in 60 mL of the standard solvent was reacted with 4.06 g (16 mmol) of iodine and 1.76 g (10 mmol) of iodic acid at 65 °C overnight. At this point, 10 mL of 57% hydroiodic acid was added, and heating was continued for 2 h. The solution was poured into 200 mL of water, and the dark brown precipitate was collected by filtration under vacuum. The solid filtrate was slurried with dilute sodium thiosulfate and extracted with two 50-mL portions of methylene chloride. The solvent was removed by rotary evaporation. The dark residue was taken up in benzene and filtered through a plug of alumina to remove the color. Evaporation of the benzene gave 5.54 g of yellow colored solid, which was crystallized from a minimum of hot hexane, yielding 5.0 g (88%) of 6-iodo-2-methoxynaphthalene, mp 141 °C.

1,6-Diiodo-2-methoxynaphthalene. A mixture of 2.84 g (10 mmol) of 6-iodo-2-methoxynaphthalene, 1.01 g (4 mmol) of iodine,

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[7] Quoted in ref 6 as: Armstrong, *Chem. News* **1897**, *74*, 302.

and 0.7 g (4 mmol) iodic acid in 50 mL of the standard solvent was heated at 65 °C for 5 h. The mixture was cooled and mixed with 100 mL of 1:1 petroleum ether–benzene. The whole was then washed with two 50-mL portions of water and one of 10% sodium thiosulfate. The solvent was removed by rotary evaporation, yielding 4.4 g of buff colored residue. Crystallization from hexane gave 2.8 g (68%) of light yellow colored 1,6-diiodo-2-methoxynaphthalene, mp 146–148 °C. Anal. Calcd for $C_{11}H_8OI$: C, 32.20; H, 1.95. Found: C, 32.24; H, 1.94. MS, *m/e* 410 (M^+, 100), 395 (M – 15, 22); ^1H NMR δ 7.17 (H-3, d, $J_{3,4}$ = 9.0 Hz), 7.68–7.71 (H-3 and H-7, m, 2 H, 8.10 (H-5, s), 7.86 (H-8, d, $J_{7,8}$ = 9.2 Hz); ^{13}C NMR δ 87.47 (C-1), 157.17 (C-2), 113.64 (C-3), 129.40 (C-4), 131.31 (C-4a), 136.64 (C-5), 89.34 (C-6), 136.45 (C-7, may be reversed with C-5), 133.07 (C-8), 134.76 (C-8a), 57.20 (methoxyl).

Ancillary Experiments. (a) The Reaction of 1-Iodo-2-methoxynaphthalene with Iodine. A mixture of 1-iodo-2-methoxynaphthalene (4.0 g, 15.7 mmol), 2.3 g (3.66 mmol) iodine, and 0.93 g (5.3 mmol) iodic acid were heated to 80 °C in 60 mL of the standard solvent. Aliquots (15 mL) were withdrawn after 1, 2, and 18 h. Each was poured into 50 mL of 10% sodium thiosulfate solution and filtered after 2 h. The collected solid residues were air-dried and analyzed by GC. The results were as follows: sample 1, starting material; sample 2, ca. 1:1 starting material and 1,6-diiodo-2-methoxynaphthalene; sample 3, 13% 2-methoxynaphthalene, 12% 6-iodo-2-methoxynaphthalene, 30% starting material, and 55% of the 1,6-diiodo-2-methoxynaphthalene.

(b) Reductions with HI. Samples of 1-iodo-2-methoxynaphthalene (0.284 g, 1 mmol) and the corresponding amount of the 6-iodo compound were placed in two test tubes respectively. Each was dissolved in 20 mL of the standard solvent, 2 g of potassium iodide was added, and the respective mixtures were heated to 80 °C for 1 h. These reactions were worked up as in a above. It was noted that the tube with the 1-iodo compound turned dark brown very rapidly, while the tube with the 6-iodo isomer darkened at a much slower rate. GC of the product from the former sample showed 98% 2-methoxynaphthalene and 2% starting material. The 6-iodo isomer appeared to be unreacted despite the color.

(c) Reaction with Iodic Acid. A solution of 3.60 g of 2-methoxynaphthalene in 60 mL of standard solvent was heated to 80 °C and 2.82 g (16 mmol) of iodic acid was added. The solution, which turned dark brown very rapidly, was heated for 18 h. It was then worked up as in a above. GC analysis indicated that it was equal parts of starting material and 1-iodo-2-methoxynaphthalene.

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Pathways in Chromic Acid Oxidations. 3.[1] Kinetics and Mechanism of Oxidation of Malonic Acid

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Pioneering and incisive studies by Westheimer, Wiberg, and Rocek have provided much of our understanding of the pathways in the chromic acid oxidation of organic substrates. The "chromate ester" mechanism of the oxidation of alcohols has been placed on firm grounds.[2,3] Rate-limiting C–H cleavage in the oxidation of 2-propanol[4] and diphenylmethane[5] is evident in the substantial primary kinetic isotope effect ($k_H/k_D \sim 6$). Chromium(VI) is also known to cleave C–C bonds in pinacol[6] and oxalic acid[7] with remarkable facility. In oxidations of cyclobutanol,[8] phenyl *tert*-butyl carbinol,[9] and mandelic acid,[10] where there is a possibility of either C–H and C–C cleavage, C–C cleavage products have been attributed to the highly reactive Cr(IV) and/or Cr(V) intermediates. The mechanism of C–C cleavage in oxalic acid has been investigated in detail. A definitive study has come from Rocek's group[7] in which the second-order term in oxalic acid was interpreted in terms of a one-step three-electron reduction of Cr(VI) to Cr(III). The oxidation of higher homologues have been reported,[11] where the site of oxidation is at the CH_2 rather than at the carboxyl.

Very little work has been done with malonic acid, in spite of the fact that this substrate is atypical in other oxidations. Only two reports[12,13] are available on the Cr(VI) oxidation of malonic acid, and they have been in narrow concentration ranges without any meaningful product analysis. We found that hydroxymalonic acid

$$3CH_2(COOH)_2 + 2Cr(VI) \rightarrow 3CH(OH)(COOH)_2 + 2Cr(III) \quad (1)$$

[HMA] is about 250 times more reactive than malonic acid, and it seemed very unlikely that it would accumulate in stoichiometric amounts. We wish to report in this paper a detailed kinetic and product study of the chromic acid oxidation of malonic acid.

Experimental Section

Malonic acid (Aldrich, mp 136 °C) and hydroxymalonic acid (Sigma, mp 154 °C) were used without further purification. Deuteromalonic acid ($DOOCCD_2COOD$, Sigma, 99+ atom % D) was used as received. Sulfuric acid-d_2 (Sigma, D_2SO_4, 99.5+ atom % D, 98% solution in D_2O) was diluted in D_2O and was used for the determination of kinetic isotope effect. Sodium dichromate dihydrate (Baker analyzed) was used to prepare stock solutions of chromium(VI) and was standardized iodometrically and spectrophotometrically (a = 1560 M^{-1} cm^{-1} at 350 nm). $HClO_4$ (BDH, AnalaR, 70%) was further diluted in doubly distilled water to achieve the required hydrogen ion concentrations. Bromine (BDH; AnalaR) was used for the enolization studies.

Kinetics. (a) Oxidation of Malonic Acid. The kinetics of oxidation were followed under pseudo-first-order conditions, with at least a tenfold excess of malonic acid over chromium(VI), by monitoring the decrease in absorbance at 350 nm in a Cary-15 double-beam recording spectrophotometer, fitted with a thermostated cell holder. Kinetic measurements were carried out at 50 ± 0.2 °C, unless otherwise stated. Pseudo-first-order plots of the log of absorbance (350 nm) vs. time were linear through time courses greater than three half-lives, except for the first few initial points. Absorbance vs. time curves were closely similar to what

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