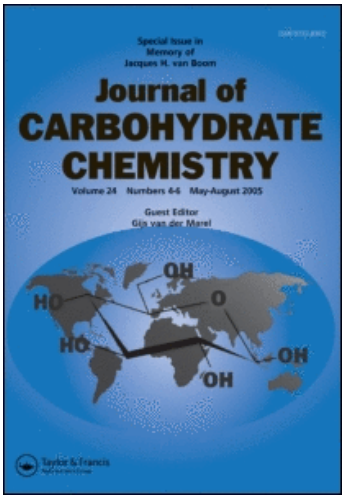

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Reactions of Vicinal Ditriflates with Benzoate and Nitrite Anions

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REACTIONS OF VICINAL DITRIFLATES WITH BENZOATE AND NITRITE ANIONS

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ABSTRACT

The four possible methyl 2,6-dideoxy-ß-D-hexopyranosides were converted into the corresponding vicinal ditriflates **1-4** and these compounds (**1-4**) were reacted with tetrabutylammonium benzoate and with tetrabutylammonium nitrite. In most cases two S_N2 substitution reactions were observed. These reactions usually were accompanied by additional processes in which, after the first displacement occurred, the newly introduced substituent group participated in departure of the remaining triflyloxy group. Probable mechanisms for these participation reactions are discussed.

INTRODUCTION

Even though nucleophilic displacement of triflyloxy groups from carbohydrates is a well established synthetic process, examples in which two triflyloxy groups are displaced from the same molecule are not common. For most of the ditriflates which have been investigated, the two triflyloxy groups actually are well separated from each other (e.g., in different rings of an oligosaccharide[1-5] or on non-neighboring carbon atoms[6-10]) and thus the reactions of these molecules differ little from those of monotriflates. Even for those molecules in which the triflyloxy groups are adjacent, no

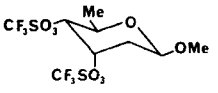
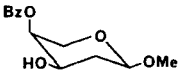
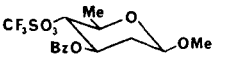
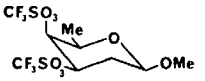
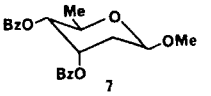
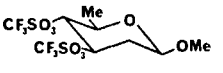
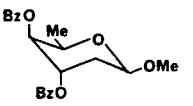
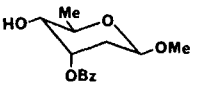
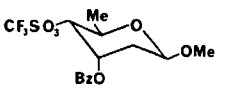
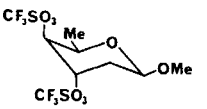
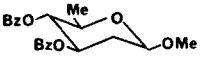
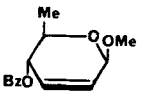
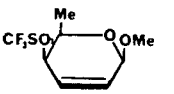
special reactivity has been reported; rather, simple displacement[11] or Tipson-Cohen[12,13] reaction have been observed.

A preliminary report[14] from this laboratory described the reactions of four ditriflates (**1-4**) with tetrabutylammonium benzoate. Tetrabutylammonium benzoate was selected because it is only a moderately effective nucleophile; thus, its use created opportunities for reactions which might not be able to compete with bimolecular displacement by more powerful nucleophiles. The ditriflates **1-4** were chosen specifically to study the possible synergistic interaction between adjacent triflyloxy groups. Compounds **1-4** contain all possible stereochemical arrangements between two neighboring substituent groups, a situation which maximizes the number of potential reaction pathways. This preliminary study now has been expanded to include the reactions of compounds **1-4** with tetrabutylammonium nitrite, a much more effective nucleophile than tetrabutylammonium benzoate. In this paper the reactions of these ditriflates with both nucleophiles are described and the situations are discussed in which neighboring triflyloxy groups participate in reactions other than simple bimolecular substitution.

RESULTS AND DISCUSSION

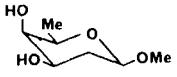
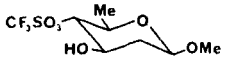
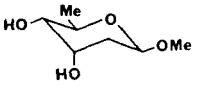
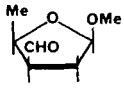
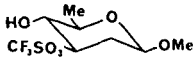
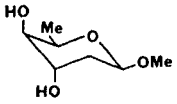
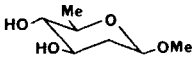
When the ditriflates **1-4** were stirred with tetrabutylammonium benzoate at room temperature in a mixture of toluene and water, only compounds **1** and **4** reacted (Table I). For ditriflates **2** and **3**, heating under reflux was required for reaction (Table I). In contrast, all four compounds (**1-4**) reacted at room temperature with excess tetrabutylammonium nitrite (Table II). Interestingly, for none of the ditriflates did direct displacement of both triflyloxy groups occur for both nucleophiles; that is, in each of the compounds investigated, a reaction other than bimolecular S_N2 substitution was observed. These "other reactions" were attributable to the presence of two adjacent triflyloxy groups in the same molecule.

TABLE I. REACTIONS OF DITRIFLATES 1-4 WITH TETRABUTYLAMMONIUM BENZOATE

STARTING MATERIAL	DIBENZOATE	OTHER PRODUCT	INTERMEDIATE
 1	NONE	 5 81 %	 6
 2	 7 89 %	NONE	NONE
 3	 8 63 %	 9 22 %	 10
 4	 11 26 %	 12 64 %	 13

Although double displacement does occur when three (**2-4**) of the four ditriflates react with tetrabutylammonium benzoate, only for compound **2** is a dibenzoate the sole product. For the remaining ditriflates (**1**, **3**, and **4**) significant, other reactions take place. Reaction of **1** produces the monotriflate **6**, which then experiences internal displacement by the benzoyl

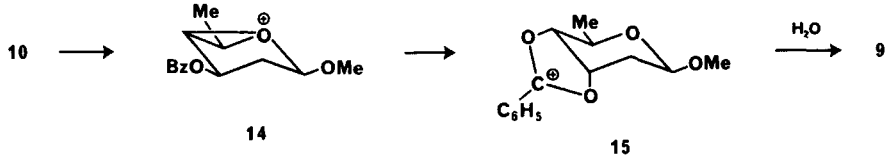
TABLE II. REACTIONS OF 1-4 WITH TETRABUTYLAMMONIUM NITRITE

STARTING MATERIAL	DIDEOXY SUGAR	OTHER PRODUCT	PROPOSED INTERMEDIATE
1	 15 % 16	 75 % 20	 22
2	 85 % 17	 15 % 21	 23
3	 85 % 18	NONE	NONE
4	 95 % 19	NONE	NONE

group leading to **5**.[15] (Compound **6** was detected in the reaction mixture during treatment of **1** with tetrabutylammonium benzoate and has been shown to produce **5** under the reaction conditions.) In a similar manner, monotriflate **10** was shown to be an intermediate in the formation of **9** from the ditriflate **3**. (Subjecting **10** to the reaction conditions produced **9**

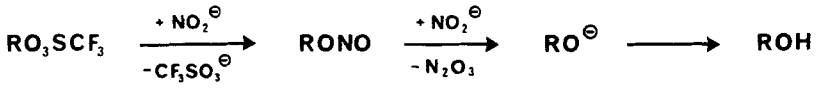
as well as the dibenzoate **8**.) For the monotriflate **10** a competition exists between direct displacement by benzoate ion (to give **8**) and internal substitution involving the ring oxygen (to afford **9**) (Scheme I). Internal displacement of the 4-triflyloxy group in **10** by the ring oxygen leads to the intermediate **15**, a cation that has been shown to be involved in the formation of **9**.[15,16] Finally, compound **12** arises from the ditriflate **4** via the intermediate monotriflate **13**. In the reaction of **4**, elimination competes effectively with substitution because the axial triflyloxy groups at C-3 and C-4 in the ditriflate **4** make difficult the approach of a nucleophile to either of these carbon atoms.

Scheme I



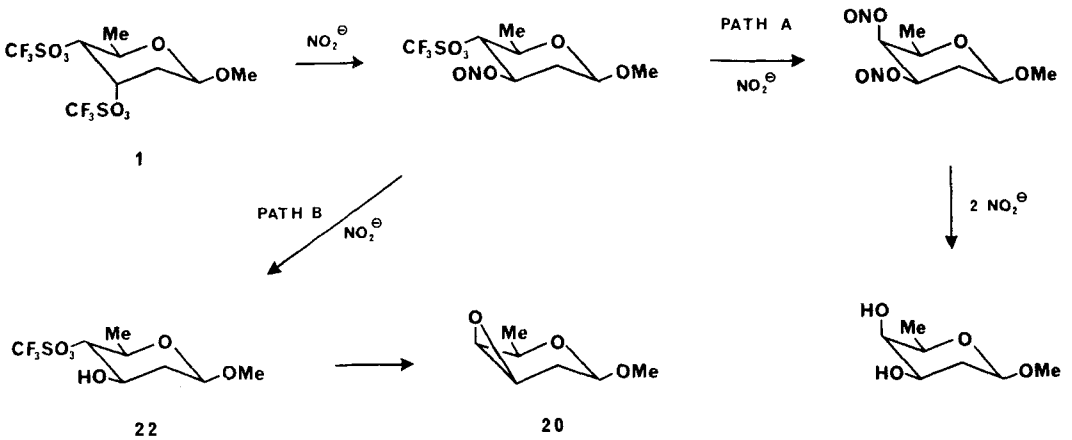
Reaction of the ditriflates **1-4** with nitrite ion proceeded at room temperature to give, in each case, the methyl 2,6-dideoxy-β-D-hexopyanoside arising from two S_N2 substitution reactions (compounds **16-19**, respectively) (Table II). (Triflate displacement by nitrite to produce the corresponding hydroxy compound (Scheme II) was first reported by Dax and coworkers[17,18] and has since been used by other investigators.[2,19-21]) In the cases of the ditriflates **3** and **4**, the dideoxy sugars **18** and **19** were the only products formed. The ditriflates **1** and **2** produced, in addition to dideoxy sugars, the anhydro sugar **20** and the ring contraction product **21**, respectively. The formation of compounds **20** and **21** provided indirect evidence that hydroxy triflates **22** and **23** were intermediates in these reactions. Ring contraction of **23** to give **21** previously has been observed[23] and formation of the anhydro sugar **20** by internal sulfonate (methanesulfonate) displacement also has been reported.[24]

Scheme II

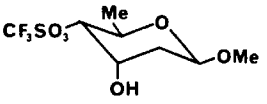


Since the initial reaction of each ditriflate with nitrite ion is to form a nitrous acid ester (Scheme II), the intermediacy of hydroxy triflates in these reactions provides information about the point of attack of the second nitrite anion on the nitrous acid ester. If reaction is to displace the remaining triflyloxy group (as pictured in path A of Scheme III using ditriflate **1** as an example), then a dideoxy sugar will be the ultimate product. On the other hand, if reaction takes place at the nitrous acid ester group, a hydroxy triflate will be formed (path B, Scheme III). A reasonably close competition must exist between these two reactions for compounds **1** and **2**; in fact, reaction of nitrite ion with the nitrous acid ester portion of the molecule is favored over triflate displacement in **1** since the major product is the anhydro sugar **20** derived from the hydroxy triflate **22**.

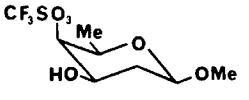
Scheme III



Ditriflates **3** and **4** also may produce intermediate hydroxytriflates upon reaction with nitrite ion; however, the cis relationship between the hydroxyl and triflyloxy groups in such intermediates (e.g., **24** and **25**) makes them less reactive than **22** and **23** since stereochemistry prevents reactions such as internal triflate displacement. As a consequence, a second S_N2 substitution by nitrite ion takes place leading to the dideoxy sugars **18** and **19**, respectively.



24



25

From the reactions shown in Tables I and II, it is clear that vicinal ditriflates do experience processes that take place as a result of the presence of neighboring triflyloxy groups in these molecules. These reactions are attributable to anchimeric assistance in the displacement of the second triflyloxy group by the substituent introduced when the initial triflate displacement occurs.

As a final observation, the reactions of compounds **1-4** provide additional examples supporting the observation that axial triflyloxy groups are displaced more easily than equatorial ones.[16,22] Additional information about group reactivity can be derived from reaction of **3** with benzoate anion, which shows that the equatorial triflyloxy group at C_3 is displaced more easily than that at C_4. In the reaction of **4** with benzoate ion, the axial triflyloxy group at C_3 is more reactive than the axial C_4 group but a decision about ease of displacement cannot be made because this process involves elimination rather than substitution. From the information provided by compounds **1-4**, the order of triflyloxy group reactivity in these systems is $^3_{axial}$, $^4_{axial} > {}^3_{equatorial} > {}^4_{equatorial}$.

EXPERIMENTAL

General Procedures. Column chromatography was conducted using a 2.5 x 15 cm column of 240-400 mesh silica gel (Baker) developed with 1:10 ethyl acetate - hexane. TLC was done using Whatmann silica gel 60A plates developed with 1:10 ethyl acetate - hexane. NMR spectra were determined using a Brucker AC300F spectrometer with deuterochloroform as the solvent. Chemical shifts are relative to tetramethylsilane (δ = 0.0). Optical rotations were determined at 578 nm for solutions in ethyl acetate at 22 ^{0}C using a Perkin-Elmer model 241 spectrometer.

General Procedure for Ditriflate Synthesis. The methyl 2,6-dideoxy-ß-D-hexopyranoside (0.20 g, 1.2 mmol) was dissolved in 15 mL of dichloromethane which contained 1.0 mL (13 mmol) of pyridine. This solution was stirred and cooled to -40 ^{0}C (dry ice - acetonitrile) and a solution of 1.4 g (5.0 mmol) of triflic anhydride was added in a dropwise manner. The reaction mixture was held at -40 to -50 ^{0}C for 90 min and then allowed to warm to room temperature over a period of one h. The solvent was removed under reduced pressure and the residue chromatographed in the standard fashion. The ditriflates **1-4** began to decompose when left at room temperature for more than a few h; consequently, they typically were used immediately after isolation. No elemental analysis of these ditriflates was attempted.

General Procedure for Reaction of Ditriflates with Tetrabutylammonium Benzoate. The ditriflate (200 mg, 0.46 mmol) was dissolved in 10 mL of toluene containing 0.50 g (1.56 mmol) of tetrabutylammonium benzoate and 1 mL of water. After stirring the reaction mixture for 14 h (sufficient for reaction of compounds **1** and **4**) or heating it under reflux for one h (necessary for compounds **2** and **3**) and then cooling to room temperature, the layers were separated and the aqueous layer was extracted with toluene (2 x 5 mL). The solvent was distilled from the combined organic extracts under reduced pressure and the residue was chromatographed in the standard fashion.

General Procedure for Reaction of Ditriflates with Tetrabutylammonium Nitrite. The ditriflate (200 mg, 0.46 mmol) was dissolved in 10 mL of toluene containing 0.85 g (290 mmol) of tetrabutylammonium nitrite and 1 mL of water. After stirring the reaction mixture for 14 h, the solvent was distilled under reduced pressure and the residue was chromatographed in the standard fashion.

Methyl 2,6-Dideoxy-3,4-di-*O*-trifluoromethylsulfonyl-ß-D-*ribo*-hexopyranoside (1). Methyl 2,6-dideoxy-ß-D-*ribo*-hexopyranoside gave by the standard synthesis and isolation procedure 0.37 g (1.10 mmol, 84%) of **1**, $[\alpha] = +1.7^0$ (c = 1.14); $R_f = 0.33$. ^1H NMR: δ 1.42 (H_6, $J_{5,6}$ = 6.4 Hz), 2.45 (H_{2e}, $J_{1,2e}$ = 2.2 Hz, $J_{2e,2a}$ = 14.8 Hz, $J_{2e,3}$ = 5.1 Hz), 2.08 (H_{2a}, $J_{1,2a}$ = 8.3 Hz, $J_{2a,3}$ = 2.7 Hz), 4.17 (H_5, $J_{4,5}$ = 8.4 Hz), 3.50 (OMe), 4.79 (H_1), 5.47 (H_3, $J_{3,4}$ = 2.4 Hz), 4.67 (H_4). ^{13}C NMR: δ 17.39 (C_6), 36.10 (C_2), 56.48 (OMe), 67.77 (C_5), 83.21 (C_4), 81.97 (C_3), 97.76 (C_1), 118.17 (CF_3, $J_{C,F}$ = 317 Hz).

Methyl 2,6-Dideoxy-3,4-di-*O*-trifluoromethylsulfonyl-ß-D-*lyxo*-hexopyranoside (2). Methyl 2,6-dideoxy-ß-D-*lyxo*-hexopyranoside gave by the standard synthesis and isolation procedure 0.47 g (1.10 mmol, 90%) of **2**, $[\alpha] = +76^0$ (c = 0.58); R_f = 0.15. ^1H NMR: δ 1.44 (H_6, $J_{5,6}$ = 6.5 Hz), 2.32 (H_{2e}, $J_{1,2e}$ = 2.2 Hz, $J_{2e,2a}$ = 12.4 Hz, $J_{2e,3}$ = 5.3 Hz), 2.13 (H_{2a}, $J_{1,2a}$ = 9.5 Hz, $J_{2a,3}$ = 12.4 Hz), 3.75 (H_5, $J_{4,5}$ = 0 Hz), 3.53 (OMe), 4.88 (H_1), 5.05 (H_3, $J_{3,4}$ = 9.2 Hz), 5.02 (H_4). ^{13}C NMR: δ 16.50 (C_6), 32.38 (C_2), 56.81 (OMe), 68.24 (C_5), 82.19 (C_4), 80.44 (C_3), 99.50 (C_1), 118.99 (CF_3, $J_{C,F}$ = 317 Hz).

Methyl 2,6-Dideoxy-3,4-di-*O*-trifluoromethylsulfonyl-ß-D-*arabino*-hexopyranoside (3). Methyl 2,6-dideoxy-ß-D-*arabino*-hexopyranoside gave by the standard synthesis and isolation procedure 0.23 g (0.60 mmol, 50%) of **3**, $[\alpha] = +24^0$ (c = 0.53); R_f = 0.25. ^1H NMR: δ 1.48 (H_6, $J_{5,6}$ = 6.2 Hz), 2.68 (H_{2e}, $J_{1,2e}$ = 2.0 Hz, $J_{2e,2a}$ = 12.3 Hz, $J_{2e,3}$ = 5.6 Hz), 2.05 (H_{2a}, $J_{1,2a}$ = 9.5 Hz, $J_{2a,3}$ = 12.2 Hz), 3.64 (H_5, $J_{4,5}$ = 9.2 Hz), 3.51 (OMe), 4.49 (H_1), 5.03 (H_3, $J_{3,4}$ = 9.2 Hz), 4.62 (H_4). ^{13}C NMR: δ 17.48 (C_6), 37.41 (C_2), 56.90 (OMe), 69.08 (C_5), 84.61 (C_4), 81.95 (C_3), 99.02 (C_1), 118.99 (CF_3, $J_{C,F}$ = 317 Hz).

Methyl 2,6-Dideoxy-3,4-di-*O*-trifluoromethylsulfonyl-ß-D-*xylo*-hexopyranoside (4). Methyl 2,6-dideoxy-ß-**D**-*xylo*-hexopyranoside gave by the standard synthesis and isolation procedure 0.40 g (0.92 mmol, 77%) of **4**, $[\alpha] = +15^0$ ($c = 0.10$); $R_f = 0.15$. ^1H NMR: δ 1.42 (H_6, $J_{5,6} = 6.5$ Hz), 2.31 (H_{2e}, $J_{1,2e} = 2.6$ Hz, $J_{2e,2a} = 15.3$ Hz, $J_{2e,3} = 3.1$ Hz), 2.20 (H_{2a}, $J_{1,2a} = 8.5$ Hz, $J_{2a,3} = 3.4$ Hz), 4.24 (H_5) 3.34 (OMe), 4.71 (H_1), 5.73 (H_3, $J_{3,4} = 3.8$ Hz), 5.39 (H_4). ^{13}C NMR: δ 16.00 (C_6), 32.16 (C_2), 56.39 (OMe), 67.37 (C_5), 79.48 (C_4), 80.90 (C_3), 97.60 (C_1), 118.99 (CF_3, $J_{C,F} = 317$ Hz).

Reaction of 1 with Tetrabutylammonium Benzoate. Reaction of **1** with tetrabutylammonium benzoate according to the general procedure gave 104 mg (0.39 mmol, 81%) of methyl 4-*O*-benzoyl-2,6-dideoxy-ß-**D**-*lyxo*-hexopyranoside (**5**), identical in NMR spectra to a previously prepared sample.[23]

Reaction of 2 with Tetrabutylammonium Benzoate. Reaction of **2** with tetrabutylammonium benzoate according to the general procedure gave 152 mg (0.41 mmol, 89%) of 3,4-di-*O*-benzoyl-2,6-dideoxy-ß-**D**-*ribo*-hexopyranoside (**7**), identical in NMR spectra with an independently synthesized sample.[24]

Reaction of 3 with Tetrabutylammonium Benzoate. Reaction of **3** with tetrabutylammonium benzoate according to the general procedure gave 107 mg (0.29 mmol, 63%) of 3,4-di-*O*-benzoyl-2,6-dideoxy-ß-**D**-*xylo*-hexopyranoside (**8**) and 27 mg (0.10 mmol, 22%) of methyl 3-*O*-benzoyl-2,6-dideoxy-ß-**D**-*ribo*-hexopyranoside (**9**), identical in NMR spectra with samples prepared by literature procedures.[25]

Reaction of 4 with Tetrabutylammonium Benzoate. Reaction of **4** with tetrabutylammonium benzoate according to the general procedure gave 44 mg (0.12 mmol, 26%) of 3,4-di-*O*-benzoyl-2,6-dideoxy-ß-**D**-*arabino*-hexopyranoside (**11**), identical in NMR spectra with a sample prepared by a literature procedure,[26] and 78 mg (0.29 mmol, 64%) of methyl 4-*O*-benzoyl-2,3,6-trideoxy-ß-**D**-*erythro*-hex-2-enopyranoside (**12**), $R_f = 0.47$ (3:1 hexane-ethyl acetate). ^1H NMR ($CDCl_3$): δ 1.39 (H_6, $J_{5,6} = 6.7$ Hz), 3.50 (OMe), 4.01 H_5 ($J_{4,5} = 6.7$ Hz), 5.13 (H_1), 5.36 (H_4),

5.95 (H_3, $J_{3,4}$ = 0.6 Hz), 6.02 (H_2, $J_{1,2}$ = 1.4 Hz, $J_{2,3}$ = 10.3 Hz). ^{13}C NMR: δ 18.02 (C_6), 54.98 (OMe), 70.18 (C_5), 71.45 (C_4), 97.06 (C_1), 128.28 (C_3), 130.33 (C_2).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 68.01; H, 6.61.

Reaction of 1 with Tetrabutylammonium Nitrite. Compound **1** reacted with tetrabutylammonium nitrite according to the standard procedure to give, after chromatography according to the standard procedure, 12 mg (0.07 mmol, 15%) of methyl 2,6-dideoxy-ß-D-*lyxo*-hexopyranoside (**16**), identical to the material used in the synthesis of **2**. Chromatography also yielded 57 mg (0.35 mmol, 75%) of methyl 3,4-anhydro-2,6-dideoxy-ß-D-*lyxo*-hexopryanoside (**20**), identical in NMR spectra with a previously prepared sample.[27,28]

Reaction of 2 with Tetrabutylammonium Nitrite. Reaction of **2** with tetrabutylammonium nitrite according to the general procedure gave, after chromatography according to the standard procedure, 65 mg (0.40 mmol, 85%) of methyl 2,6-dideoxy-ß-D-*ribo*-hexopyranoside (**17**), identical with the material used in the synthesis of **1**. Also isolated was 15 mg (0.11 mmol, 15%) of **21**, identical in NMR spectra with an independently prepared sample.[27]

Reaction of 3 with Tetrabutylammonium Nitrite. Compound **3** was reacted with tetrabutylammonium nitrite according to the general procedure to give 66 mg (0.40 mmol, 85%) of methyl 2,6-dideoxy-ß-D-*xylo*-hexopyranoside (**18**), identical with the starting material for the synthesis of **4**.

Reaction of 4 with Tetrabutylammonium Nitrite. Compound **4** reacted with tetrabutylammonium nitrite according to the general procedure to give 72 mg (0.44 mmol, 95%) of methyl 2,6-dideoxy-ß-D-*arabino*-hexopyranoside (**19**), identical with the starting material for the synthesis of **3**.

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