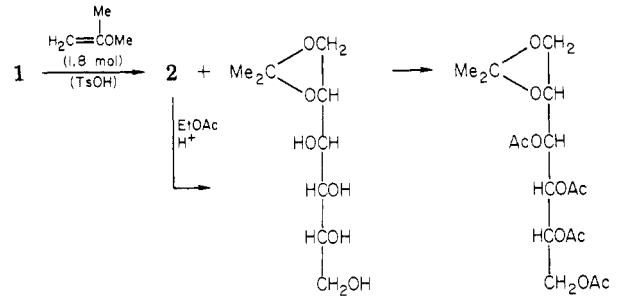
in the molecule. Initial, small-scale experiments have shown[5] that a 5 M excess of 2-ethoxypropene converts 1 into a mixture from which chromatographic resolution gave ~60% of the diacetal plus ~30% of the accompanying 1,2:3,4:5,6 triacetal.

In the optimized procedure reported here, a total amount of 2.4–2.7 molar equiv of 2-methoxypropene reagent is used during a 3-h period at 0 °C; all of the D-mannitol (1) is converted, and the diacetal product 2 crystallizes directly upon evaporation of the solution in 92% isolation yield and pure enough for most further applications.

The monoacetal 3 is readily prepared by conducting the acetonation of 1 with only 1.8 equiv of 2-methoxypropene for 3 h at 0 °C to give mainly 3 plus some diacetal 2.



3 4

Unreacted D-mannitol (1) also present is readily removed as it is insoluble in methanol containing a little ethyl acetate, and addition of more ethyl acetate leads to crystallization of the monoacetal 3. The net yield of 3 is significantly augmented by treating the mother liquors (containing a major proportion of diacetal 2) in ethyl acetate suspension with a trace of *p*-toluenesulfonic acid; this procedure converts 2 into the monoacetal 3 and allows isolation of crystalline monoacetal 3 by direct filtration. The yield of 3 is ~70% in the reaction, not taking into account the amount of starting D-mannitol (1) recovered. The high yield of monoacetal 3 may be ascribed in large measure to its low solubility in ethyl acetate, so that the proportion of 3 in the product mixture crystallizes out almost completely, and the acid-catalyzed deacetalation of the accompanying, ethyl acetate soluble diacetal 2 is arrested by crystallization from the medium at the monoacetal stage.

The monoacetal 3 was characterized directly[7] and as its tetraacetate[7] 4. The literature procedure[7] for 3 is tedious and gives only a 15% yield, and an alternative procedure[8] by way of boronate intermediates is quite complex and still does not readily give good yields.

The monoacetal 3 is of considerable synthetic interest, as its tetraacetate 4 provides access, via deacetonation and glycol cleavage, to *aldehydo*-D-arabinose tetraacetate. The acetylated *aldehydo*-aldoses so widely employed in synthesis are generally prepared in three steps by way of dithioacetal intermediates; the procedural superiority of access to the D-arabinose derivative via compound 4 is readily evident.

Experimental Section

1,2:5,6-Di-*O*-isopropylidene-D-mannitol (2). A solution of D-mannitol (1, 18.2 g, 0.1 mol) in anhydrous *N,N*-dimethylformamide (400 mL) containing 1 g of desiccant (Drierite or Sikkon) is stirred magnetically at 0 °C (ice bath[9]). 2-Methoxypropene (14.4 g, 0.2 mol) is added, followed by a catalytic amount (~0.2 g) of *p*-toluenesulfonic acid, and the mixture is stirred for ~1 h. TLC (silica gel, 1:4 methanol–chloroform) shows some unreacted starting material, which disappears upon addition of more enol ether portionwise over the next 1–2 h (0.4–0.7 equiv in 4–5 portions; total amount 2.4–2.7 equiv of reagent). The mixture is then stirred vigorously with anhydrous sodium carbonate (~5 g) for 1 h and filtered. The filtrate is then evaporated (<1 torr, 40 °C) to afford a crystalline residue of 2. The crystals are washed with a small amount of light petroleum ether, and the mixture is filtered to give 2 (24.1 g, 92%) of acceptable purity (>95% by TLC and NMR) for most further synthetic operations. Pure diacetal 2 may be obtained by recrystallization from dibutyl ether; yield 21.7 g (83%), characterized by comparison (mp, specific rotation) with literature data,[1b] by NMR spectroscopy, and by conversion into the known[8] 3,4-diacetate.

1,2-*O*-Isopropylidene-D-mannitol (3). The foregoing procedure is repeated except that only 1.8 equiv of 2-methoxypropene (10.8 g, 0.15 mol) is used in the reaction with D-mannitol (1, 18.2 g, 0.2 mol) and the reagent is added dropwise. The reaction is stopped after 3 h by addition of anhydrous sodium carbonate. Evaporation of the solution leaves an amorphous residue, TLC of which shows two products, the diacetal 2 and monoacetal 3, totgether with some unreacted 1. The residue is dissolved in anhydrous methanol (~200 mL), ethyl acetate (5–10 mL) is added, and the mixture is kept overnight, whereupon unreacted 1 precipitates out and is filtered off. Further addition of ethyl acetate (50–100 mL) leads to crystallization of the monoacetal 3; yield 5.5 g (30%) of purity >95%. Alternatively, the product mixture may be resolved more completely by column chromatography on silica gel to yield the pure monoacetal 3 as the slower migrating product (6.4 g, 35%).

The yield of monoacetal 3 may be augmented by converting the diacetal 2 in the product mixture into the monoacetal 3. The mixture obtained as described and freed from unreacted D-mannitol is dispersed in suspension in a large volume of ethyl acetate, and a few crystals of *p*-toluenesulfonic acid are added. The mixture is stirred for 1 h, triethylamine (~10 mL) is added, and the suspension is filtered to give the crystalline monoacetal 3 (11.0 g, 60%). Additional 3 may be obtained by evaporating the filtrate (which conains essentially the diacetal 2) and subjecting the recovered material once more in ethyl acetate to the action of a catalytic amount of *p*-toluenesulfonic acid. The monoacetal 3 has mp 161–163 °C, $[\alpha]^{20}_D$ +2.5° (*c* 0.1, water); lit.[8] mp 167 °C, $[\alpha]_D$ +3.5° (in water).

Acetylation of 3 with acetic anhydride–pyridine gives in 91% yield the pure tetraacetate 3: mp 104–106 °C, $[\alpha]^{21}_D$ +29° (*c* 0.1, chloroform); lit.[8] mp 107 °C, $[\alpha]_D$ +28° (in chloroform); ^{1}H NMR ($CDCl_3$) δ 4.9–5.6 m (H-3, -4, -5), 3.7–4.3 (H-1, -1′, -2, -6, -6′), 2.10, 2.07, 2.04, 2.03 (4 s, OAc), 1.37 s, 1.30 s (CMe_2).

Acknowledgment. This work was supported, in part, by Grant GM-11976 from the National Institute of General Medical Sciences, NIH, and by RCP 529 of the Centre National de la Recherche Scientifique.

Registry No. 1, 69-65-8; 2, 1707-77-3; 3, 4306-35-8; 4, 76867-27-1.

(7) L. von Vargha, *Ber.*, 66, 1394–1399 (1933).
(8) C. J. Griffiths and H. Weigel, *Carbohydr. Res.*, 81, 17–21 (1980).
(9) The reaction proceeds more rapidly at room temperature, but exclusive kinetic control may not be operative at the higher temperature.

Sydnone Compounds. 18. Schmidt Reaction of 4-Acetyl-3-arylsydnones

Mou-Yung Yeh and Hsien-Ju Tien*

Department of Chemistry, National Cheng Kung University, Tainan, Taiwan, Republic of China

Tsutomu Nonaka

Department of Electronic Chemistry, Graduate School at Nagatsuta, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, Japan

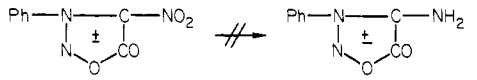
Received October 29, 1982

Although a large number of sydnone derivatives have been synthesized, attempts to prepare 4-aminosydnone or

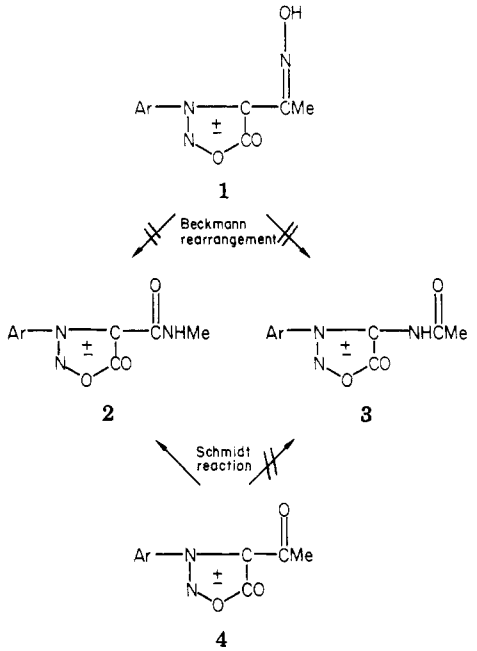
0022-3263/83/1948-1382$01.50/0

its derivatives have not yet been successful. 4-Nitro-3-phenylsydnone, obtained by nitrating 3-phenylsydnone, is the only derivative in which a nitrogen function is attached directly to the sydnone ring.

Kato and Ohta[1] tried unsuccessfully to prepare 4-amino-3-phenylsydnone from methyl 3-phenylsydnone-4-carboxylate via the azide by the Curtius rearrangement. Reduction of 4-nitro-3-phenylsydnone with a variety of reducing agents was attempted in order to obtain the corresponding 4-amino derivative, but all efforts were negative.[2,3]



In present work, we first tried to prepare 4-acetamido-3-phenylsydnone (**3a**) by the Beckmann rearrangement of 4-acetyl-3-phenylsydnone oxime. (**1a**): If the oxime is the anti form, **3a** should be formed, while the syn oxime should give less desirable 3-phenylsydnone-4-*N*-methylcarboxamide (**2a**). The reaction was performed without any confirmation of the geometry of the oxime. The reaction is concentrated sulfuric acid did not occur at temperature below 70 °C, and the starting oxime was recovered. At temperature higher than 70 °C, decomposition of the oxime occurred, and neither **2a** nor **3a** was obtained. The reaction in acetic anhydride proceeded without any decomposition over a wide temperature range (30–140 °C), resulting in the formation of the oxime *O*-acetate. The structure of the *O*-acetate was confirmed by spectroscopic studies and recovery of the original oxime by hydrolysis.



Ar = a, C_6H_5; b, *p*-MeC_6H_4; c, *p*-BrC_6H_4; d, *p*-$MeOC_6H_4$; e, *p*-$EtOC_6H_4$

The Schmidt reaction of 4-acetyl-3-arylsydnones (**4**) was then examined; the reaction should be expected to give **2**, **3**, or their mixture. For this reaction some new derivatives of **4** were prepared by methods reported in our earlier papers[4,5] (Table I). Infrared spectra of **4** indicated two carbonyl stretching bands in ranges of 1780–1792 cm^{-1} and 1655–1658 cm^{-1} assigned to the carbonyl groups of the sydnone ring and the acetyl substituent, respectively.[6]

Table I. Properties of New 4-Acetyl-3-arylsydnones (4)[a]

compd	yield,[b] %	mp, °C	mass spectrum (M^+, *m/e*)	IR (KBr), cm^{-1}
4c	72	168–170	282 284	1790 1655
4d	64	97–98	234	1780 1658
4e	61	120–121	248	1792 1660

[a] Satisfactory analytical data (±0.4% for C, H, N, Br) were reported for all compounds listed in the table. [b] After purification.

The 4-acetylsydnones (**4a–e**) were reacted with a small excess of sodium azide in aqueous sulfuric acid. 3-Arylsydnone-4-*N*-methylcarboxamides (**2a–e**) were obtained in good yields, as shown in Table II, but neither 4-acetamidosydnones (**3**) nor any other solid products could be detected.

The structure of **2** could be confirmed from analytical and spectral data. The mass spectra of **2** gave the molecular peaks. The infrared spectra indicated ν_{N-H} absorption bands at 3340–3352 cm^{-1}, and $\nu_{C=O}$ bands at 1740–1746 cm^{-1} and 1655–1670 cm^{-1} assigned to the carbonyl groups of the ring and the amido group, respectively.[6] The ^1H NMR spectrum showed a broad signal for the NH proton (overlapping the phenyl multiples) and a doublet for the CH_3 group. Addition of D_2O removed the former signal and changed the CH_3 doublet to a singlet, behavior consistent with **2** but not **3**.

For structural confirmation, **2a** was prepared by the reaction of 3-phenyl-4-sydnonecarboxylic acid chloride with methylamine and identified with the sample formed in the Schmidt reaction.

In the Schmidt reaction of **4**, neither unreacted **4** nor any solid products other than **2** could be separated from the reaction mixture. This may be suggest that **3** decomposed to degraded fragments under the reaction condition, even if it once formed by migration of the sydnonyl group.

Experimental Section

Beckmann Rearrangement of 4-Acetyl-3-phenylsydnone Oxime (1a). A solution of 2.19 g (0.010 mol) of **1a**[7] in 10 mL of acetic anhydride was heated at 140 °C for 3 h. After cooling, the reaction mixture was poured into cold water to decompose acetic anhydride. Recrystallization of the resulting precipitates from 95% ethanol afforded 2.27 g (87% yield) of pure 4-acetyl-3-phenylsydnone oxime *O*-acetate as colorless needles: mp 127–128 °C; IR (KBr) $\nu_{C=O}$ 1770 and 1746 cm^{-1}; MS, *m/e* 261 (M^+); ^1H NMR (chloroform-d_1, Me_4Si) δ 1.83 (s, 3 H), 2.34 (s, 3 H), 7.55 (s, 5 H). Anal. Calcd for $C_{12}H_{11}N_3O_4$: C, 55.17; H, 4.22; N, 16.04. Found: C, 55.06; H, 3.99; N, 16.02. In the reaction at 30 °C for 2 days, the yield was 93%.

To 5 mL of cooled sulfuric acid was added 1.30 g (0.005 mol) of the oxime *O*-acetate stepwise with stirring. After heating (below 70 °C) for 3 h, the reaction mixture was poured into crushed ice. Recrystallization of the resulting precipitates from 95% ethanol afforded 0.70 g (66% yield) of pure 4-acetyl-3-phenylsydnone oxime, which was identified with the original sample.

The reaction of **1a** in concentrated sulfuric acid did not give any solid product. To cooled concentrated sulfuric acid (7 mL)

(1) Kato, H.; Ohta, M. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 282.
(2) Hashimoto, M., Dr. Eng. Dissertation, Tokyo Institute of Technology, Tokyo, Japan, 1969.
(3) Tien, H.-J. *Ch'eng-kung Ta Hsueh Hsueh Pao* **1979**, *14*, 19; *Chem. Abstr.* **1980**, *92*, 181090x.
(4) Tien, H.-J.; Ohta M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2944.
(5) Tien, H.-J. *Hua Hsueh* **1977**, *1*, 8; *Chem. Abstr.* **1980**, *92*, 110930k.
(6) Stewart, F. H. C. *Chem. Rev.* **1964**, *64*, 129.
(7) Greco, C. V.; Tobias, J.; Kier, L. B. *J. Heterocycl. Chem.* **1967**, *4*, 160.

Table II. Properties of 3-Arylsydnones-4-*N*-methylcarboxamides (2)[a]

compd	yield,[b] %	mp, °C	mass spectrum (M^+, *m/e*)	IR (KBr), cm^{-1} ν_{N-H}	IR (KBr), cm^{-1} $\nu_{C=O}$	NMR ($CDCl_3$), δ
2a	50	185-186	219	3350	1740	2.86 (d, 3 H)
					1655	7.62 (s, 6 H)
2b	77	228-229	233	3340	1742	2.52 (s, 3 H)
					1660	2.94 (d, 3 H)
						7.42 (m, 5 H)
2c	74	220-222	297	3344	1740	2.78 (d, 3 H)
			299		1660	7.58 (q, 5 H)
2d	58	158-160	249	3344	1746	2.96 (d, 3 H)
					1670	3.94 (s, 3 H)
						7.26 (q, 5 H)
2e	63	163-164	263	3352	1743	1.49 (t, 3 H)
						2.95 (d, 3 H)
					1670	4.16 (q, 2 H)
						7.28 (q, 5 H)

[a] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds listed in the table. [b] After purification.

was slowly added 0.22 g (0.001 mol) of **1a** with stirring. The reaction mixture was heated at 80 °C for 3 h, and after cooling it was poured into crushed ice. Unreacted **1a** (0.11 g) was collected by filtration, and the filtrate, after neutralized with sodium bicarbonate, was extracted with dichloromethane (3 × 30 mL). Additional **1a** (0.03 g) was recovered by evaporating the extract. The overall recovery of **1a** was 0.14 g (64%). In the reaction at temperatures below 70 °C, the starting **1a** was almost quantitatively recovered.

Preparation of 4-Acetyl-3-arylsydnones (4a-e). The 4-acetylsydnones were prepared by a modified method of the literature.[4,5] A typical procedure was as follows: To a well-cooled suspension of 3-phenylsydnone (6.84 g, 0.04 mol) in acetic anhydride (20 mL) in a strongly cooled bath (−15 °C) was added well-cooled solution of 60% perchloric acid (1 mL) in acetic anhydride (20 mL) gradually with stirring. After cooling and stirring the solution for 1 h, the temperature of the reaction mixture was elevated to 12 °C to dissolve completely the starting 3-phenylsydnone, and then the mixture was allowed to stand at room temperature for 2 h. The resulting light-brown solution was poured into ice–water to decompose excess acetic anhydride. Recrystallization of the resulting precipitates from 95% ethanol afforded 5.10 g (63% yield) of pure **4a** as colorless plates.

Schmidt Reaction of 4-Acetyl-3-arylsydnones (4a-e). A typical procedure for the Schmidt reaction of **4** is given below. To an ice-cooled solution of **4a** (1.00 g, 0.0049 mol) in concentrated sulfuric acid (15 mL) and water (5 mL) was added sodium azide (0.40 g, 0.062 mol) in small potions with stirring. After cooling and stirring the solution for 1 h, the cooling bath was removed and stirring was continued at room temperature for 5 h. The reaction mixture was poured into crushed ice, and the crude product (0.5 g) was collected by filtration. By extracting filtrate with benzene (3 × 100 mL) and evaporating the benzene under reduced pressure, more crude product (0.2 g) was obtained. Recrystallization of the combined crude product from 95% ethanol afforded pure **2a** (0.54 g, 50% yield) as colorless needles.

Synthesis of 3-Arylsydnone-4-*N*-methylcarboxamides (2a,b) from 3-Aryl-4-sydnonecarboxylic Acid Chlorides and Methylamine. 3-Phenyl- and 3-*p*-tolyl-4-sydnonecarboxylic acid chlorides were prepared from the corresponding 4-sydnonecarboxylic acids by the method of the literature.[8] To ice-cooled *N,N*-dimethylformamide (15 mL) containing 1 mL (0.013 mol) of 40% methylamine was added 0.22 g (0.001 mol) of 3-phenyl-4-sydnonecarboxylic acid chloride slowly. After cooling for 1 h, the reaction mixture was allowed to stand at room temperature for 3 h and then poured into ice–water. Recrystallization of the resulting precipitates from 95% ethanol afforded 0.16 g (72% yield) of pure **2a** which was identified with the sample obtained in the Schmidt reaction. Similarly, **2b** was synthesized in 83% yield from 3-*p*-tolyl-4-sydnonecarboxylic acid chloride and methylamine.

Acknowledgment. We are grateful for valuable discussions with Dr. T. Fuchigami and thank Mr. C.-S. Chen for doing part of the experiments.

Registry No. **1a**, 13973-41-6; **2a**, 84877-58-7; **2b**, 84877-59-8; **2c**, 84877-60-1; **2d**, 84877-61-2; **2e**, 84877-62-3; **4a**, 13973-33-6; **4b**, 72913-08-7; **4c**, 84877-63-4; **4d**, 34356-36-0; **4e**, 63935-02-4; 4-acetyl-3-phenylsydnone oxime *O*-acetate, 84877-64-5; 3-phenylsydnone, 120-06-9; acetic anhydride, 108-24-7; 3-phenyl-4-sydnonecarboxylic acid chloride, 21074-30-6; 3-*p*-tolyl-4-sydnonecarboxylic acid chloride, 21074-35-1; methylamine, 74-89-5; 3-(4-bromophenyl)sydnone, 26537-61-1; 3-(4-methoxyphenyl)sydnone, 3815-80-3; 3-(4-ethoxyphenyl)sydnone, 3815-82-5.

(8) Kishimato, K.; Ohta, M. *Nippon Kagaku Zasshi* **1962**, *83*, 833.

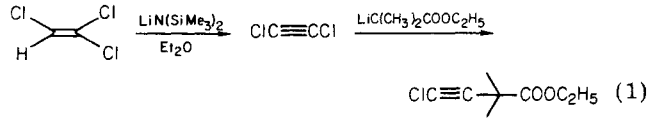
Direct Difluorovinylation of Tertiary Enolates

Andrew S. Kende* and Pawel Fludzinski

Department of Chemistry, University of Rochester, Rochester, New York 14627

Received October 5, 1982

We have recently described a method for the efficient dichlorovinylation of tertiary ester and ketone enolates employing dichloroacetylene as a Michael acceptor.[1] In such reactions it has proven advantageous to generate preformed dichloroacetylene[2] and then react it with the enolate nucleophile (eq 1).



(1)

Since the literature suggests that difluoroacetylene is extremely unstable and probably not readily isolable,[3] we have attempted to achieve the difluorovinylation of eno-

(1) (a) Kende, A. S.; Benechie, M.; Curran, D. P.; Fludzinski, P.; Swenson, W.; Clardy, J. *Tetrahedron Lett.* **1979**, 4513. (b) Kende, A. S.; Fludzinski, P. *Ibid.* **1982**, *23*, 2369. (c) Kende, A. S.; Fludzinski, P. *Ibid.* **1982**, *23*, 2373.

(2) Kende, A. S.; Fludzinski, P. *Synthesis* **1982**, 455.

(3) Syntheses have been limited to subjecting difluoromaleic anhydride to pyrolysis (600 °C) or to passing fluorocarbons through electrical discharge tubes; in both cases, difluoroacetylene was not isolated but only detected by mass spectrometry or gas chromatography. Bruce, M. I.; Cullen, W. R. In "Fluorine Chemistry Reviews"; Tarrant, P.; Ed., Marcel Dekker: New York, 1969; Vol. 4. The preparation and chemistry of fluoroacetylene and arylfluoroacetylenes have recently been reported: Sauvetre, R.; Normant, J. F. *Tetrahedron Lett.* **1982**, *23*, 4325. Martin, S.; Sauvetre, R.; Normant, J. F. *Ibid.* **1982**, *23*, 4329.

0022-3263/83/1948-1384$01.50/0