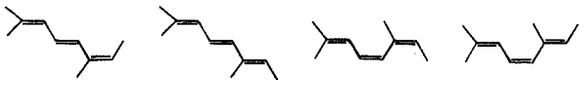
mers of 7-cis vitamin A and carotenoids. Such possibilities are being examined in our laboratory.

For less hindered compounds the method of selective sensitization for quantitative conversion to the cis isomer apparently does not apply. For example, in the case of alloocimene,[13] a model for the C_9–C_{13} fragment of carotenoids containing the less hindered C_{11}–C_{12} double bond, sensitization by a variety of sensitizers fails to give mixtures containing entirely the central cis isomers even though some enrichment is noted (Table II).[14]

TABLE II
PHOTOSTATIONARY STATE MIXTURES OF ALLOOCIMENE



Sensitizer (E_T)	Alloocimene i	ii	iv	v
Benzophenone (68.5)	25	39	19	15
Benzanthrone (47)	25	34	25	15
Dimethylbenzanthracene (44)	19	38	26	18

Acknowledgment.—The work was partially supported by grants from the Sloan Foundation, The Public Health Service (RO1 EY-AM 00918-01), and the U. H. Biomedical Research Program.

(13) R. S. H. Liu and Y. Butt, *J. Amer. Chem. Soc.*, **93**, 1532 (1971).

(14) In this case there is a dependence of stationary composition on triene and sensitizer concentrations; therefore values extrapolated to zero sensitizer and triene concentration are reported.

(15) (a) NSF Undergraduate Summer Research Fellow. (b) Alfred P. Sloan Research Fellow, 1970–1972.

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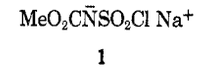
DECEMBER 15, 1972

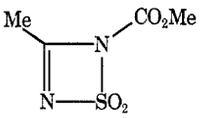
The Fragmentation of Substituted 1,4,3,5-Oxathiadiazine Dioxides to *N*-Sulfonylamines

Summary: Certain nitriles react with the sodium salt of carbomethoxysulfamoyl chloride to afford 6-substituted 2-methoxy-1,4,3,5-oxathiadiazine dioxides, **2**, whose thermal cycloreversion gives methyl-*N*-sulfonylurethane, **4**, which participates in subsequent cycloadditions with alkenes.

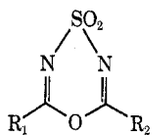
Sir: In connection with synthetic studies[1,2] on the generation of *N*-sulfonylamines *via* dehydrohalogenation of sulfamoyl chlorides we investigated the chemistry of adducts derived from nitriles and this heterocumulene. The salt (**1**) derived[2] from reaction of carbomethoxysulfamoyl chloride with sodium hydride at −78° reacts with acetonitrile at 0–30° to afford (75%) an adduct,[3] mp 102–102.5° dec, which displayed nmr[4] singlets at δ 4.08 and 2.37 and intense ir ($CHCl_3$) absorption at 1705 and 1615 cm^{-1}, and underwent facile hydrolysis (H_2O/THF, 30°) to *N*-acetyl-*N'*-carbomethoxysulfamide, mp 149–150° dec. Although such spectral[5,6] and chemical evidence is consistent with either structure **2a** or **3** for this adduct, the former was shown to be correct based on the following results. The reaction of *N*-chlorosulfonyl-*N'*-methyl-*N'*-phenylurea[7] with an excess of phenylmethylcyanamide in THF at 30° gave (80%) of the symmetrically disubstituted oxathiadiazine **2b**, mp 175–176°, which exhibited the same C=N ir double absorption at 1685 and 1605 cm^{-1} but had symmetry consistent with the observed unsplit 6 H methyl group signal at δ 3.26 in the nmr. As final support for this argument, **1** reacts



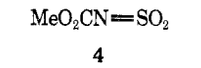
1



3



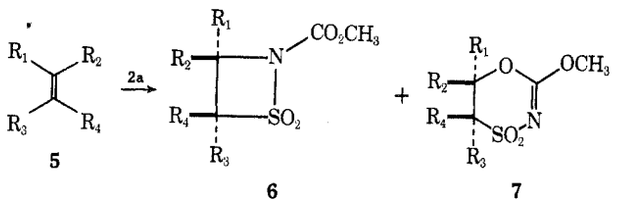
2a, R_1 = Me; R_2 = OMe
b, R_1 = R_2 = $C_6H_5(CH_3)N$
c, R_1 = *p*-$MeOC_6H_5$; R_2 = OMe
d, R_1 = Me_2N; R_2 = OMe



4

with dimethylcyanamide to give **2d**, mp 162–163°, whose ir (in $CHCl_3$, 1700 and 1620 cm^{-1}) and nmr [δ 4.08 (s, 3 H), 3.13 (s, 6 H)] are similar to those of **2a**.

These substituted 1,4,3,5-oxathiadiazine dioxides apparently undergo a thermal [2 + 4] cycloreversion at moderate temperatures in a variety of solvents to provide, along with the corresponding nitrile, *N*-sulfonylurethane **4** as evidenced by the isolation of cycloadducts by reaction with appropriate alkenes. Reaction of **2a** with **5a**, **5b**, and **5c** in THF or acetonitrile at



5 **6** **7**

Compd	R_1	R_2	R_3	R_4
a	Ph	Ph	H	H
b	Ph	H	H	H
c	Me	Me	Me	H
d	Ph	H	Ph	H

30–60° gave the 2-carbomethoxy-1,2-thiazetidines[2] **6a**, **6b**, and **6c** and the 2,3-dihydro-6-methoxy-1,4,5-oxathiazines[2] **7b** and **7c** whose distribution was both

(1) E. M. Burgess and G. M. Atkins, Jr., *J. Amer. Chem. Soc.*, **94**, 6135 (1972).

(2) E. M. Burgess and W. M. Williams, *ibid.*, **94**, 4386 (1972).

(3) Satisfactory elemental analyses and exact mass spectra were obtained on the new compounds reported herein.

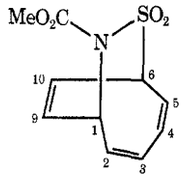
(4) All nmr spectra were recorded in $CDCl_3$ at 60 MHz.

(5) The possibility that the oxathiadiazine **2a** has a coupled C=N vibration leading to resonance splitting to give the 1705 cm^{-1} ir signal could not be discounted at this point.

(6) The nitrogen core binding energy signal observed in the ESCA spectrum was so broad that no definitive structural assignment could be made. We thank Dr. David Hercules at the University of Georgia for this measurement.

(7) This precursor is available from the reaction of chlorosulfonylisocyanate and *N*-methylaniline: R. Graf, *Angew. Chem. Int. Ed. Engl.*, **7**, 172(1968).

temperature and solvent dependent.[8] Employing the advantage of higher reaction temperature accessible by this method of *N*-sulfonylamine generation, cycloadducts were obtained from otherwise unreactive alkenes. For example, a mixture of *cis*-stilbene (**5d**) and **2a** when melted (105°) affords the adduct **7d**, mp 157–159°, whose cis stereochemistry is evident from the benzylic hydrogen doublet nmr signals at δ 6.42 and 4.60 with a J = 3.0 Hz.[9] Cyclooctatetraene and **2a** in acetonitrile at 80° led in low yield to the bicyclic sulfonamide **8**, mp 172–173° dec, whose structural fea-



8

tures were revealed by nmr signals at δ 6.09 (m, $H_{2-5,9,10}$), 5.07 (d of d, J = 6.5 Hz, H_6), 4.45 (d of d, J = 8.0 Hz, H_2), 3.85 (s, 3 H); uv λ_{max}^{EtOH} 261 nm (ϵ 2050); and ir absorption ($CHCl_3$) at 1735 cm^{-1} (C=O); and whose genesis probably involves closure of an appropriately substituted dipolar homotropylium cation intermediate.[10] Finally, new oxathiadiazines result from a cycloreversion–addition interchange of the incipient nitrile function in **2a**. A melt (60°) of *p*-methoxybenzonitrile and **2a** results in the formation of **2c**, mp 138–139°, whose thermal decomposition at 160° likewise provides **4**.

Acknowledgments.—We sincerely wish to thank the National Institutes of Health (GM-12672) and the National Science Foundation (GP-27956) for support.

(8) The mechanistic explanation for these effects on the cycloaddition mode has been advanced in ref 2.

(9) *Some trans-stilbene is formed in the reaction but no cycloadducts with this stereochemistry were present.*

(10) L. A. Paquette, J. R. Malpass, and T. J. Barton, *J. Amer. Chem. Soc.*, **91**, 4714 (1969).

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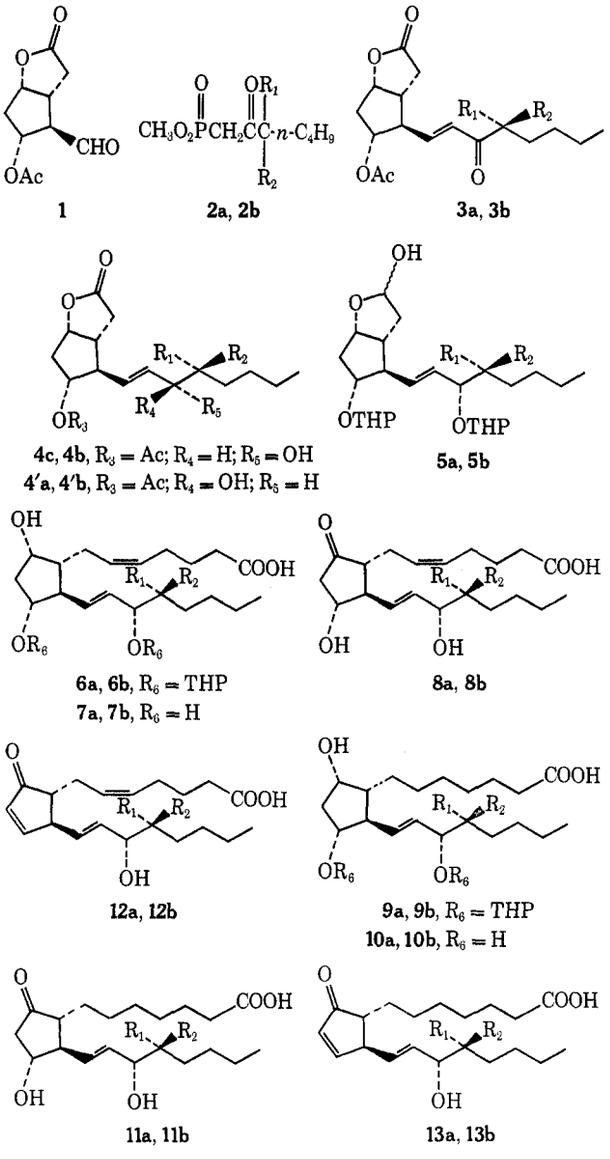
RECEIVED JANUARY 10, 1973

The Synthesis of 16(*R*)- or 16(*S*)-Methylprostaglandins

Summary: The synthesis of 16(*R*)- or 16(*S*)-methylprostaglandins and their C-15 epimers has been accomplished starting from the lactone **1**, the intermediate for the synthesis of natural prostaglandins.

Sir: We have recently investigated the synthesis of compounds having a prostanoic acid skeleton. The present paper describes the synthesis of 16(*R*)- or 16(*S*)-methylprostaglandins. Recently, synthesis and biological activities of 16,16-dimethylprostaglandins have been reported by Robert, *et al.*[1]

(1) A. Robert and B. J. Magerlein, International Conference on Prostaglandins, Vienna, Sept 25, 1972.



1 **2a, 2b** **3a, 3b**

4c, 4b, R_3 = Ac; R_4 = H; R_5 = OH
4′a, 4′b, R_3 = Ac; R_4 = OH; R_5 = H

5a, 5b

6a, 6b, R_6 = THP
7a, 7b, R_6 = H

8a, 8b

12a, 12b

9a, 9b, R_6 = THP
10a, 10b, R_6 = H

11a, 11b **13a, 13b**

2a–13a, $R_1 = CH_3$; R_2 = H [16(*R*)-methyl series]

2b–13b, R_1 = H; $R_2 = CH_3$ [16(*R*)-methyl series]

For the synthesis of 16(*R*)- or 16(*S*)-methyl-PGs, we used as starting material β-acetoxyaldehyde (**1**), which was prepared by Corey, *et al.*,[2] for the synthesis of natural PGs. Synthesis of 16(*R*)-methyl-PGs was initiated by the reaction of **1** with the sodium derivative of the 2-oxophosphonate **2a** {$[\alpha]^{25}D$ −11.6° (*c* 8.6, Et_2O)} in THF at room temperature for 1 hr to form trans enone lactone **3a** [ir (liquid film) ν 1775, 1740, 1690, 1640, 1625 cm^{-1}] in 62% yield. Similarly, **3b** [ir (liquid film) ν 1780, 1740, 1690, 1660, 1630 cm^{-1}] was obtained from **1** with the sodium derivative of the 2-oxophosphonate **2b** {$[\alpha]^{25}D$ +15.1° (*c* 6.11, Et_2O)} in 55% yield. **2a** and **2b** were prepared from the α-lithio derivative of dimethyl methylphosphonate and ethyl 2(*R*)-methylhexanoate[3] and 2(*S*)-methylhexanoate,[3] respectively.

3a and **3b** were reduced with excess $NaBH_4$ and separated from the 15β-hydroxy compounds by column chromatography on silica gel. This gave **4a** [ir (liquid

(2) E. J. Corey, T. K. Schaaf, W. Huber, U. Koelliker, and N. M. Weinshenker, *J. Amer. Chem. Soc.*, **92**, 397 (1970).