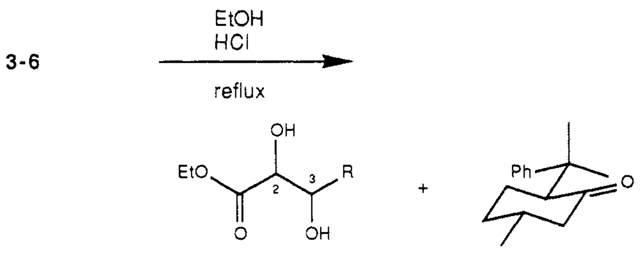
Table II. Ethanolysis of Dioxolanones 3–6

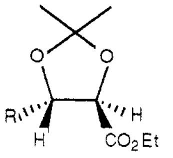


7-10

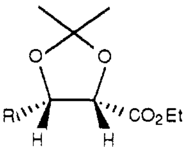
dioxolanone	R	yield (%)[a]	product[b]	stereochemistry
3a	Ph	93	**7a**	2*S*,3*S*
3b	*n*-Pr	92	**7b**	2*S*,3*S*
3c	*i*-Pr	87	**7c**	2*S*,3*S*
4a	Ph	93	**8a**	2*S*,3*R*
4b	*n*-Pr	92	**8b**	2*S*,3*R*
4c	*i*-Pr	81	**8c**	2*S*,3*R*
5a	Ph	95	**9a**	2*R*,3*R*
5b	*n*-Pr	88	**9b**	2*R*,3*R*
5c	*i*-Pr	88	**9c**	2*R*,3*R*
6a	Ph	95	**10a**	2*R*,3*S*
6b	*n*-Pr	84	**10b**	2*R*,3*S*
6c	*i*-Pr	81	**10c**	2*R*,3*S*

[a] Isolated, purified yield. [b] Apparently, none of these dihydroxy esters are known to optically pure form. See ref 16–18 for racemates or related acids.

p-TsOH, room temperature), proved useful for verification of their relative stereochemistry.[15] Cis acetonides **12** derived from the anti dihydroxy esters **7** showed a positive NOE enhancement between the ring protons, whereas the trans dioxolanes **11** showed no enhancement.



11



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In summary, *any of the four possible stereoisomers of simple α,β-dihydroxy esters may be prepared in optically pure form* by selection of an appropriate chiral glycolate enolate and metal counterion. This ability to stereorationally assemble polyoxygenated carbon chains should be of considerable utility. Our investigations into this realm will be reported in due course, as will our studies on the incorporation of other heteroatoms.

Acknowledgment. We thank the Dreyfus Foundation (Award for Newly Appointed Faculty in Chemistry, 1984–9) and the National Institutes of Health for the generous support of this research.

Registry No. 1, 104196-76-1; 2, 104264-82-6; **3a**, 108666-21-3; **3b**, 108666-22-4; **3c**, 108666-23-5; **4a**, 108739-49-7; **4b**, 108739-50-0; **4c**, 108739-51-1; **5a**, 108739-52-2; **5b**, 108739-53-3; **5c**, 108739-54-4; **6a**, 108739-55-5; **6b**, 108739-56-6; **6c**, 108739-57-7; **7a**, 108741-11-3; **7b**, 108666-24-6; **7c**, 108666-25-7; **8a**, 108741-12-4; **8b**, 108666-26-8; **8c**, 108693-47-6; **9a**, 108741-13-5; **9b**, 108666-27-9; **9c**, 108666-28-0; **10a**, 108741-14-6; **10b**, 108666-29-1; **10c**, 108666-30-4; PhCHO, 100-52-7; *n*-PrCHO, 123-72-8; *i*-PrCHO, 78-84-2.

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Received February 27, 1987

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(15) Touzin[4c] has prepared acetonides 11 and 12 where R = Ph for the purpose of determining relative stereochemistry. The cis or trans stereochemistry was related to the chemical shift of the OCH_2CH_3 protons on the ester. Since no basis for this assignment was given, we felt NOE studies were in order. Indeed, Touzin's assignments are correct: in all cases, the NMR correlation was consistent with the NOE data.

(16) For racemic *syn*- and *anti*-ethyl 2,3-dihydroxy-3-phenylpropanoate, see ref 4c. For all four stereoisomers of 2,3-dihydroxy-3-phenylpropanoic acid in optically pure form, see: Collet, A. *Bull. Soc. Chem. Fr.* **1975**, 215–219.

(17) For racemic *syn*- and *anti*-ethyl 2,3-dihydroxyhexanoic acid, see: (a) Mori, N.; Omura, S.; Tsuzuki, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 2199–2201. (b) English, J., Jr.; Heywood, D. L. *J. Am. Chem. Soc.* **1955**, *77*, 4661–4664.

(18) For racemic *anti*-2,3-dihydroxy-4-methylpentanoic acid, see: Dalby, S.; Kenner, G. W.; Sheppard, R. C. *J. Chem. Soc.* **1960**, 968–973.

Photochemistry of the Amide System: Furancarboxanilide[†]

Summary: An investigation of the synthetically useful phototransformation of furan-2-carboxanilide derivatives (**1a**, R = H, and **1b**, R = CH_3) in protic and aprotic solvents is reported. *Unusually large vicinal coupling constants (18–19 Hz) in trans compounds* ***2a*** *and* ***2b*** are shown by an X-ray analysis on **2b** to be mainly due to the presence of unusually short C–C single bonds (1.498 (4) Å).

Sir: During the last 5 years furan and its derivatives have received a resurgence of interest in several areas of organic chemistry.[1-5] Application of an enamide photocyclization for the synthesis of novel heteroaromatic systems, as well as our interest in carbonyl transposition such as lactams to β-keto amines,[6] directed our attention to the photocyclization of the little known furan-2-carboxanilide (**1a**) and *N*-methylfuran-2-carboxanilide (**1b**).[7,8] This paper delineates the phototransformation products of these substances.

[†] This paper is dedicated to Professor Joseph F. Bunnett on the occasion of his 65th birthday.

(1) Furan-terminated cationic cyclizations, see: (a) Tanis, S. P.; Herrinton, P. M. *J. Org. Chem.* **1985**, *50*, 3988. (b) Tanis, S. P.; Chaung, Y. H.; Head, D. B. *Tetrahedron Lett.* **1985**, *26*, 6147. (c) Tanis, S. P.; Herrinton, P. M.; Dixon, L. A. *Ibid.* **1985**, *26*, 5347. (d) Tanis, S. P.; Herrinton, P. M. *J. Org. Chem.* **1983**, *48*, 4572.

(2) Furan in intramolecular Diels–Alder reactions, see: (a) Grootaert, W. M.; De Clercq, P. J. *Tetrahedron Lett.* **1986**, *27*, 2573. (b) Van Royen, L. A.; Mijngheer, R.; De Clercq, P. J. *Bull. Soc Chim. Belg.* **1984**, *93*, 1019 and references cited therein. (c) Sternbach, D. D.; Rossana, D. M. *J. Am. Chem. Soc.* **1982**, *104*, 5833.

(3) Furan carbonyl photoaddition, see: (a) Schreiber, S. L.; Satake, K. *Tetrahedron Lett.* **1986**, *27*, 2575. (b) Schreiber, S. L.; Satake, K. *J. Am. Chem. Soc.* **1983**, *105*, 6723. (c) Schreiber, S. L.; Satake, K. *Ibid.* **1984**, *106*, 4186.

(4) (a) Schreiber, S. L.; Hoveyda, A. H.; Wu, H. J. *J. Am. Chem. Soc.* **1983**, *105*, 660. (b) Zamojski, A.; Kozluk, T. *Tetrahedron* **1983**, *39*, 805.

(5) Furans as intermediates for the synthesis of oxygenated natural products, see: Martin, S. F.; Guinn, D. E. *Tetrahedron Lett.* **1984**, *25*, 5607.

(6) (a) One of us (Y.K.) has also previously shown that this enamide photocyclization provides a facile entry into a novel fused aromatic system, see: Kanaoka, Y.; San-nohe, K. *Tetrahedron Lett.* **1980**, *20*, 3893. (b) Furancarboxanilides derived from dihydrodibenzazepine and diphenylamine on irradiation with a 450-W, medium-pressure mercury lamp (Vycor) in a mixture of benzene and methanol (9:1) for 24 h gave photo-Fries rearrangement products. Unpublished results of the Arizona group. (c) The importance of lactams to β-keto amines can be visualized in the conversion of readily accessible δ-lactams to 3-substituted piperidine derivatives, required in our laboratories in connection with another synthetic project.

(7) Kanaoka, Y.; Itoh, K. *Synthesis* **1971**, 36.

(8) For an excellent review on enamide photocyclization, see: Ninomiya, I.; Naito, T. *Heterocycles* **1981**, *15*, 1433.

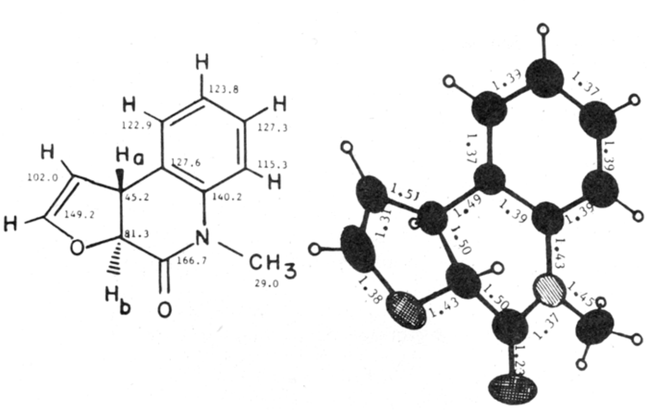
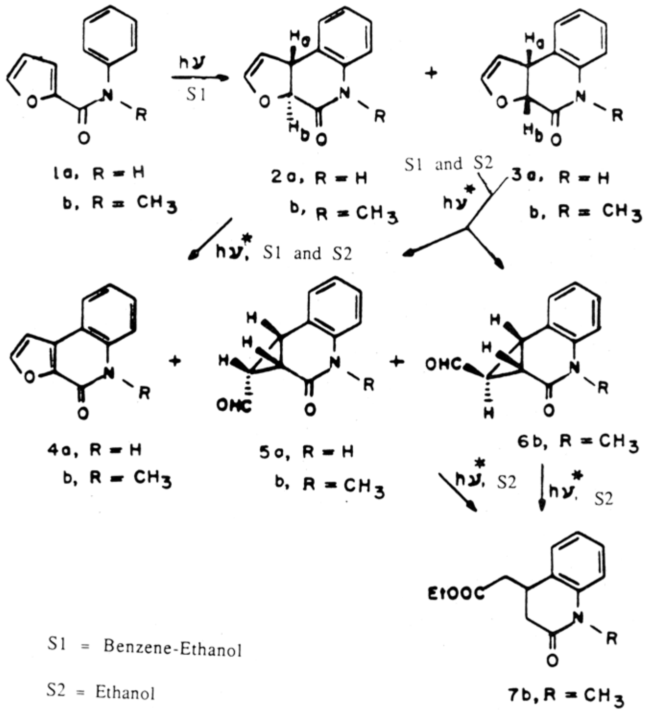
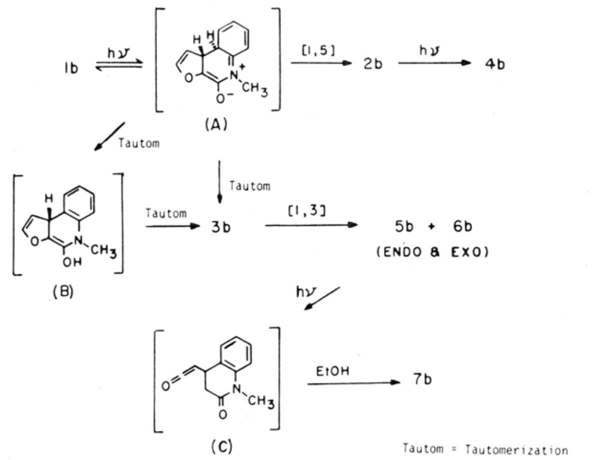


Figure 1. ^{13}C NMR assignments in ppm (δ) and crystal structure of **2b** with bond distances (±0.004) in angstroms.

Scheme I



Scheme II



The readily accessible enamide **1b**[9] on irradiation with a 100-W, high-pressure mercury lamp in a mixture of benzene and ethanol (9:1) for 1 h[10] gave a complex mixture of products (Scheme I), which on separation by silica gel column chromatography using hexane–ethyl acetate gave in order of elution **2b** (8%), **3b** (19%), **5b** (21%), **6b** (11%), and **7b** (7%).[11] Compound **2b** crystallized from benzene as pale yellow needles, mp 105 °C: mass spectrum, *m/e* 201 (M^+); IR 1660 (KBr), 1690 (Nujol) cm^{-1}; UV (EtOH) λ_{max} (ε) 252 (9600), 282 sh (1900) nm; ^1H NMR (600 MHz, $CDCl_3$) includes AB doublets at δ 4.09 (1 H, d, *J* = 18.5 Hz) and 4.18 (1 H, d, *J* = 18.5 Hz). The *unusually large vicinal coupling constant* prompted us to undertake further NMR experiments to prove the correctness of the assigned trans structure **2b**. The ^{13}C NMR assignments given in Figure 1 are in accordance with an APT spectrum. The structure of **2b** was confirmed by X-ray analysis as indicated in Figure 1.[12] The bond in the dihydrofuran ring is significantly short (1.498 (4) Å). The two carbons involved, although sp^3-hybridized, have a considerable amount of sp^2 character associated with them; one is benzylic, and the other carbon center is carrying an oxygen atom and an electron-withdrawing group. The torsional angle associated with the H atoms of the dihydrofuran ring which are so strongly coupled is 160°. We conclude that the short bond distance is largely responsible for this unusually large vicinal coupling constant. Compounds related to **2a** and **2b** have been previously noted to have large coupling constants, but no X-ray study was done on any of them and no explanation of the phenomenon has been offered.[13]

The structures of compounds **3b**, **4b**, **5b**, **6b**, and **7b** were determined by a combination of mass spectrometry, UV absorption, IR, ^1H NMR (250 MHz), and ^{13}C NMR spectroscopy.[11] The assignments for compounds **3b**, **5b**, and **6b** were supported when a comparison of the spectral data was made with identical compounds obtained by Ninomiya and co-workers in their work on the photochemistry of *o*-carboxy enamide.[14] The coupling constant in *cis*-**3b** is 10.5 Hz for the vicinal protons H_a and H_b. This coupling constant is in close agreement with that published for a very similar compound by Jung and Hudspeth.[15]

When the irradiation of **1b** was continued for an additional hour, **5b** (20%), **6b** (13%), and **7b** (20%) were obtained.[10,11] This result clearly indicated that **2b** and **3b** were primary and **4b**, **5b**, **6b**, and **7b** were secondary photoproducts.

In a similar manner, furan-2-carboxanilide **1a** on irradiation with a 450-W, medium-pressure mercury lamp (Vycor) in a mixture of benzene and methanol (9:1) for 24 h gave **2a** (10%), **3a** (13%), and **5a** (20%). In methanol exclusively, irradiation for 24 h gave **2a** (5%), **3a** (15%), **4a** (10%), and **5a** (10%).[11] In the ^1H NMR spectrum of **2a** AB doublets at δ 4.27 (1 H, d, *J* = 18.8 Hz) and 4.37 (1 H, d, *J* = 18.8 Hz) were observed.

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[9] Enamide **2b** was prepared from 2-furoyl chloride and *N*-methylaniline in benzene in the presence of anhydrous potassium carbonate dried at 110 °C for 24 h (yield 95%).

[10] Irradiation with a 450-W, medium-pressure mercury lamp in methanol for 12 h gave **2b** (5%), **3b** (20%), **4b** (10%), **5b** (21%), and **6b** (15%). The same conditions for a period of 24 h gave **4b** (20%), **5b** (10%), and **6b** (10%).

[11] Satisfactory elemental analyses were obtained for all new compounds reported herein.

[12] **2b** was recrystallized from hexane–ethyl acetate for an X-ray study: space group $P2_12_12_1$; $Z = 4$; $a = 7.906$ (2) Å, $b = 8.282$ (3) Å, $c = 15.161$ (6) Å; solved by using MULTAN; final $R = 0.050$; H positions calculated from non-H positions.

[13] (a) Naito, T.; Katsumi, K.; Tada, Y.; Ninomiya, Y. *Heterocycles* **1983**, *5*, 775. (b) Kanaoka, Y.; Nakao, S.; Hatanaka, Y. *Ibid*, **1976**, *5*, 261.

[14] Ninomiya, I.; Kiguchi, T.; Naito, T. *Heterocycles* **1978**, *9*, 1023. We thank Professor Ninomiya and Dr. Naito for NMR data (60 MHz) of compounds **3b**, **5b**, and **6b**.

[15] Jung, M. E.; Hudspeth, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4309. Professor Jung has informed us that compound **9b** in his paper is cis.

In order to elucidate the mechanistic and stereochemical details of this photocyclization further experiments outlined in Scheme I (marked $h\nu$*) were carried out. It was found that **5b** and **6b** arise from irradiation of **3b** and **4b** arises from **2b**. The enamide ester **7b** is a phototransformation product of **5b** and **6b**. From the results shown in Scheme I it is possible to delineate a reaction pathway for this nonoxidative enamide photocyclization (Scheme II). The cyclic trans zwitterionic intermediate A, initially formed by a symmetry-allowed excited-state process, undergoes a thermally allowed suprafacial [1,5]-hydrogen shift to yield trans lactam **2b**. The formation of *cis*-**3b** lactam from **1b** presumably involves solvent-mediated tautomerization of A, perhaps via enol B; such enols give the predominately more stable cis isomer **3b**.[15,16] Photochemical concerted [1,3]-sigmatropic rearrangement of *cis*-**3b** leads to cyclopropane aldehydes **5b** and **6b**. The trans lactam **2b** fails to undergo this rearrangement because the orbitals are not aligned properly.[17] The formation of **7b** involves photochemical transformation of **5b** and **6b** to ketene C, which is quenched by ethanol. Similar mechanisms will operate in the case of furan-2-carboxanilide (**1a**).

Acknowledgment. This investigation was supported by NS 14997, NINCDS to whom we are grateful. Y.K., K.S., and Y.H. thank the Ministry of Education, Science, and Culture (Japan) for a research grant. V.V.K. thanks NMR Facilities for Biomedical Studies, NIH Grant RR00292.

Supplementary Material Available: Selected NMR data and tables of calculated hydrogen atom positions, bond distances, bond angles, and torsional angles for **2b** (6 pages). Ordering information is given on any current masthead page.

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Received February 2, 1987

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(16) Kanaoka, Y.; Itoh, K.; Hatanaka, Y.; Flippen, J. L.; Karle, I. L.; Witkop, B. *J. Org. Chem.* **1975**, *40*, 3003.

(17) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1982; p 212.

(18) Author to whom correspondence should be addressed regarding X-ray data.

(19) Address correspondence to this author at: Department of Chemistry, University of Chicago, Chicago, IL 60637.

Additions and Corrections

Vol. 51, 1986

Alessandro Bongini, Giuliana Cardillo,* Mario Orena, Sergio Sandri, and Claudia Tomasini. Factors Affecting the Regioselection of the Allylic Imidates Iodocyclization.

Page 4906, Table I. The substituents for entries **a**, **b**, **c**, and **e**, should read as follows:

a $R^1 = C_6H_5$; $R^2 = H$; $R^3 = H$
b $R^1 = (E)\text{-}CH{=}CHCH_3$; $R^2 = H$; $R^3 = H$
c $R^1 = (E)\text{-}CH{=}CHC_{13}H_{27}$; $R^2 = H$; $R^3 = H$
e $R^1 = CH_3$; $R^2 = CH_3$; $R^3 = H$

Page 4907, Table III. The substituents for entry **q** should read as follows:

q $R^1 = CH_2OCH_2C_6H_5$; $R^2 = H$

Vol. 52, 1987

Robert O. Hutchins,* Ahmed Abdel-Magid, Yuriy P. Stercho, and Anthony Wambsgans. Asymmetric Reduction of Phosphinyl Imines with Hydride Reagents. Enantioselective Synthesis of Chiral Primary Amines.

Page 703, ref 2, line 9. This sentence should read as follows: Chiral *N*-alkylidenesulfinamides are reduced to the corresponding *N*-alkylsulfinamides by $LiAlH_4$ with good (57–80% ee) asymmetric control but the chiral auxiliary reagent is racemized by the vigorous acidic cleavage procedure used to obtain the free amines (ref 6).

Reference 6 should read as follows: Annunziata, R.; Cinquini, M.; Cozzi, F. *J. Chem. Soc., Perkin Trans 1* **1982**, 339.

Joel C. Barrish,* Hsi Lin Lee, Enrico G. Baggiolini, and Milan R. Uskoković. A New Approach to the Total Synthesis of Pseudomonic Acid C.

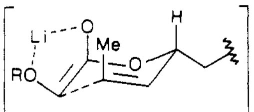
Page 1373, Scheme II. "ref 7" should read "ref 6".

Page 1374, column 1. References 17b and 18 should refer to compounds **13a** and **13b**.

Page 1374, column 2, line 5, should read "of a 4:1 mixture of threo (12*R*,13*R*) and erythro (12*R*,13*S*)".

Page 1374, column 2. Reference 23 should read "**17** was identical with material made by Julia coupling of aldehyde 12..."

Page 1375, column 1, Scheme III. Structure **21** should appear as follows:



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