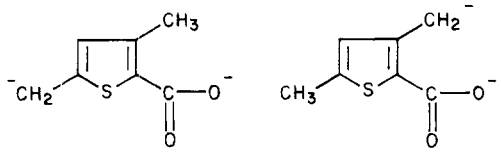


17 18

In conclusion, we have shown that methylated thiophene-2-carboxylic acids can be easily dilithiated with LDA (2 equiv). Treatment of the resulting dianions with carbon-containing electrophiles provides a variety of homologues of the starting acids. It should be noted that acids 1–4, used in this study, are either commercially available or are readily accessible.[2] Therefore, direct homologation of the appropriate methylated carboxylic acid offers a convenient and efficient method for the synthesis of various substituted thiophene-2-carboxylic acids which, in turn, can be transformed into a variety of substituted thiophenes by virtue of the inherent versatility of the carboxy group. It is therefore anticipated that our procedure will lead to an even broader use of the thiophene nucleus as a template in organic synthesis.

Acknowledgment. We are indebted to Drs. R. F. Hirschmann and E. J. Cragoe for their encouragement and to Drs. J. B. Bicking, M. G. Bock, and R. L. Smith for many helpful discussions throughout the course of this investigation. We also thank Dr. W. C. Randall and his staff for elemental analyses and Mr. A. Augenblick for GC analyses.

Registry No. 1, 1918-79-2; 2, 14282-78-1; 3, 23806-24-8; 4, 65613-27-6; 5, 74965-72-3; 9, 74965-73-4; 10, 74965-74-5; 11, 74965-75-6; 12, 74965-76-7; 13, 74965-77-8; 14, 74965-78-9; methyl 5-hexylthiophene-2-carboxylate, 74965-79-0; 5-(2-hydroxy-2-methylpropyl)thiophene-2-carboxylic acid, 74965-80-3; methyl 4-methyl-5-pentylthiophene-2-carboxylate, 74965-81-4; 3-methyl-5-deuteriothiophene-2-carboxylic acid, 74965-82-5; 3-deuteriomethylthiophene-2-carboxylic acid, 74965-83-6; 3-ethylthiophene-2-carboxylic acid, 74965-84-7; 3-methyl-5-(2-hydroxy-2-methylpropyl)thiophene-2-carboxylic acid, 74965-85-8; pentyl bromide, 110-53-2; 2-(2-bromoethyl)-1,3-dioxolane, 18742-02-4; acetone, 67-64-1; water-d_2, 7789-20-0; methyl iodide, 74-88-4; butyl bromide, 109-65-9.

Supplementary Material Available: Experimental details for the preparation of 5 and NMR data of the products (3 pages). Ordering information is given on any current masthead page.

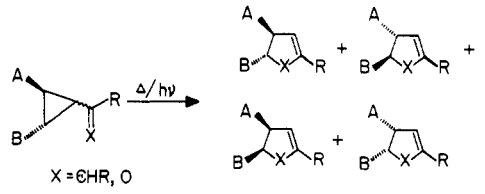
Norman P. Gould, Ta-Jyh Lee*
Department of Medicinal Chemistry
Merck Sharp & Dohme Research Laboratories
West Point, Pennsylvania 19486
Received July 8, 1980

Aluminum Oxide Assisted Stereoselective Rearrangement of a Cyclopropyl Ketone to 4,5-Dihydrofuran

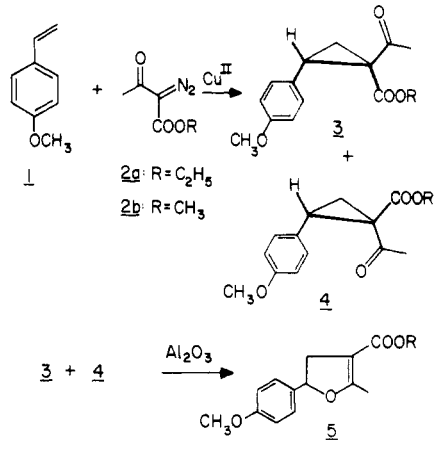
Summary: Contrary to the general observation that thermally and photochemically induced cyclopropyl ketone to dihydrofuran arrangements take place with partial loss of the stereochemical identity of the starting cyclopropane, a characteristic shared by the closely related vinylcyclopropanes and vinyloxiranes, a case of totally stereospecific, alumina-assisted cyclopropyl ketone to dihydrofuran rearrangement at room temperature was observed.

Sir: The thermal and photochemical isomerization of cyclopropyl ketones and imines to dihydrofurans and dihydropyrroles has been known since Cloke[1] first described the irreversible rearrangement of phenylcyclopropanimine to 2-phenyl-4,5-dihydropyrrole at 170 °C. Ever since the extension of this discovery to cyclopropyl aldehydes and ketones was reported by Wilson,[2] only a limited number of reports have appeared in the literature,[3-6] in contrast to the extensive kinetic, stereochemical, and theoretical studies of the closely related vinylcyclopropane to cyclopentene[7] and vinyloxirane to dihydrofuran[8] rearrangements. These three processes share in common the fact that the stereochemical identity of the starting cyclopropane derivative is not reflected in the five-membered-ring product (see Scheme I),[6,9] presumably due either to the intervention of diradical species[10] free to rotate, to what has been termed by Doering as continuous diradical transition states,[11] or to the combination of four concerted [1,3] sigmatropic shifts,[7] although the issue remains at present under intense debate.

Scheme I



Scheme II



In addition, the stereomutation of cyclopropanes[12] and cyclopropyl ketones[6] that would tend to randomize even further the stereochemistry of rearranged products has been shown to take place under the same thermal and photochemical conditions. In the present communication

(1) Cloke, J. B. *J. Am. Chem. Soc.* **1929**, *51*, 1174.
(2) Wilson, C. L. *J. Am. Chem. Soc.* **1947**, *69*, 3002. Armitage, D. M. A.; Wilson, C. L. *Ibid.* **1959**, *81*, 2437.
(3) Dauben, W. G.; Shaffer, G. W. *J. Org. Chem.* **1969**, *34*, 2301.
(4) Zimmerman, H. E.; Boettcher, R. J.; Braig, W. *J. Am. Chem. Soc.* **1973**, *95*, 2155.
(5) Doering, W. v. E.; Birladenau, L. *Tetrahedron* **1973**, *29*, 499.
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(7) Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6705, 6706.
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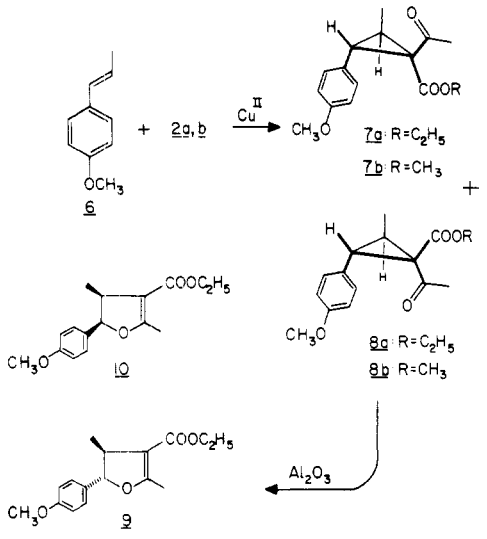
(9) Wilcott, M. R., III; Cargle, V. H. *J. Am. Chem. Soc.* **1967**, *89*, 723.
(10) Mazzocchi, P. H.; Tamburin, H. J. *J. Am. Chem. Soc.* **1975**, *97*, 554.
(11) Doering, W. v. E.; Sachdev, K. *J. Am. Chem. Soc.* **1975**, *97*, 5512.
(12) Berson, J. A.; Pedersen, L. D.; Carpenter, B. K. *J. Am. Chem. Soc.* **1976**, *98*, 122. Baldwin, J. E.; Carter, C. G. *Ibid.* **1979**, *101*, 1325 and references cited therein.

0022-3263/80/1945-4530$01.00/0

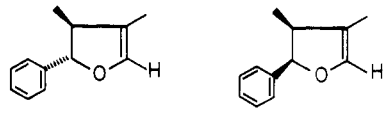
Scheme III



we would like to report what is to our knowledge not only the first example of Lewis acid assisted cyclopropyl ketone to dihydrofuran rearrangement at room temperature but also, more importantly, the first such transformation to occur with *complete retention of cyclopropane stereochemistry*.

When purification of a syn–anti mixture of cyclopropyl β-keto esters **3** and **4**[13,14] (Scheme II) in a 1.9:1 ratio, prepared in 30% yield from the bis(copper(II) hexafluoroacetoacetonate)-catalyzed thermolysis of ethyl 2-diazo-3-oxobutyrate (**2a**) and *p*-methoxystyrene, was attempted by means of column chromatography through neutral alumina activity III in chloroform, the collected fractions contained a variable proportion of a third component not present in the initial mixture. When the contact time with neutral alumina activity I was increased to 24 h, cyclopropanes **3** and **4** disappeared completely whereas the third component was recovered in nearly quantitative yield. This fraction proved to be homogeneous by high-performance liquid chromatography (LC) and displayed signals in the proton NMR spectrum at δ 1.23 (t, 3 H, J = 7.0 Hz), 2.20 (t, 3 H, J = 1.8 Hz),[15,16] 2.62–3.40 (m, 2 H), 3.78 (s, 3 H), 4.10 (q, 2 H, J = 7.0 Hz), 5.45 (dd, 1 H, J_1 = 10.0 Hz, J_2 = 8.0 Hz), and 6.98 (2 d, 4 H) attributable only to dihydrofuran **5**.[17] The transformation of **3** and **4** into **5**, formally a [1,3] sigmatropic shift not previously recorded at room temperature under Lewis acid catalysis, generally requires more demanding conditions.[6]

For evaluation of the stereochemical outcome of this rearrangement, the stereochemically defined cyclopropanes **7a,b** and **8a,b** were subjected to scrutiny. These were prepared in 17% yield from diazo ketones **2a,b** and *trans*-anethole (**6**)[14] (Scheme III). When a mixture of **7a** and **8a** in a 1.25:1 ratio (0.932 g) was brought into contact with neutral alumina activity I in a column, with chloroform as solvent, elution after 72 h furnished 0.910 g of homogeneous (high-performance LC) material whose infrared, UV, and proton NMR spectra resembled closely, not unexpectedly, those of compound **5**. Particular attention was paid to the C_4 methyl and C_5 oxymethyne signals. The former at δ 1.28 (d, J = 7.1 Hz) compared more favorably with δ 1.15 (d, J = 7.1 Hz) of trans compound **11**[16] than with the value of δ 0.51 (d, J = 7.1 Hz)



11 **12**

of cis compound **12**,[16] in which the *cis*-methyl group is appreciably shielded by the vicinal phenyl substituent. The additional 0.13-ppm deshielding observed for the C_5 methyl group of **9** is probably the consequence of the deshielding effect of the vicinal carboxylic ester at C_3. On the other hand, the signal of δ 4.88 (d, J = 7.0 Hz) of the oxymethyne at C_5 is closer to the value of δ 4.86 (d, J = 8.1 Hz) assigned to the C_5 proton of trans compound **11** than to δ 5.47 (d, J = 9.4 Hz) of the same proton of cis compound **12**, which does not experience the shielding effect of the *trans*-phenyl ring. These data suggest the *trans*-C_4-methyl-C_5-*p*-methoxyphenyl structure for compound **9**.[18] Not a trace of cis epimer **10** could be detected by high-performance LC or NMR methods, indicating that the cyclopropyl ketone to dihydrofuran rearrangement had taken place in a hitherto unrecorded stereospecific fashion.

Quenching of the **7** and **8** to **9** process by elution after 24 h yielded a mixture of these three products in a 1.0:1.40:2.08 ratio, which became 1.0:3.17:9.92 after 48 h of contact time. This result shows that transformation of **7** into **9** occurs appreciably faster than that of **8** into **9**. Although detailed kinetic studies, presently in progress in our laboratory, will be required to assess the mechanistic contribution of aluminum oxide to this rearrangement, the occurrence of the well-known stereomutation of cyclopropanes[12] would suggest that, alternatively, compounds **5** and **9** are formed only from syn isomers **3** and **7**, respectively, whereas anti compounds **4** and **8** undergo solely stereomutation to **3** and **7** at a slower rate, presumably via selective bond disconnection of the C_1–C_2 cyclopropane bond, in analogy with Baldwin's conclusions.[7] Yet the formation of diradical species[6] to account for this stereomutation would not be possible in the present situation since the stereochemical identity of cyclopropanes **7** and **8** would be, at least partially, lost. On the other hand, the intervention of aluminum oxide assisted continuous diradical intermediates,[11] symmetry-allowed processes,[19] or symmetry-forbidden migration allowed under the control of subadjacent orbitals[20] cannot be ruled out at the present stage. A discussion in greater detail of the mechanistic implications based on formal kinetic data of further model compounds will be forthcoming.

Acknowledgment. This investigation has been generously supported by Grant No. S1-0726 of the Consejo Nacional de Investigaciones Cientificas y Tecnológicas CONICIT, of Venezuela.

Registry No. 1, 637-69-4; **2a**, 2009-97-4; **2b**, 24762-04-7; **3a**, 74947-69-6; **3b**, 74947-70-9; **4a**, 74964-94-6; **4b**, 74947-71-0; **5a**,

(13) Elemental analyses were performed by Drs. H. Malissa and G. Reuter in Elbach, Germany.

(14) Cyclopropanes **3**, **4**, **7**, and **8** were characterized spectroscopically as the corresponding methyl esters **3b**, **4b**, **7b**, and **8b** and by comparison with closely related cyclopropanes reported earlier.[6] Their isolation as pure diasteroisomers was rendered impossible in view of their unavoidable tendency to rearrange to the dihydrofuran system.

(15) This signal contains a characteristic transannular coupling between the C_2 methyl protons and the C_4 methylene, typical of dihydrofurans such as **5**.[16]

(16) Scribe, M. P.; Delêphine, M. M. *C. R. Hebd. Seances Acad. Sci.* **1965**, *261*, 160.

(17) Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.67; H, 6.92; O, 24.41. Found:[13] C, 68.72; H, 6.95; O, 24.36.

(18) Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.53; H, 7.30; O, 23.17. Found:[13] C, 69.58; H, 7.22; O, 23.02.

(19) Woodward, R. B.; Hoffmann, R. *Angew. Chem.* **1969**, *81*, 797.

(20) Berson, J. A.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 8917.

74947-72-1; **6**, 104-46-1; **7a**, 74947-73-2; **7b**, 74947-74-3; **8a**, 74984-76-2; **8b**, 74984-77-3; **9**, 74947-75-4; Al_2O_3, 74947-76-5; **5b**, 1344-28-1.

Miguel E. Alonso,* Angelina Morales
Centro de Quimica
Instituto Venezolano de Investigaciones Cientificas
IVIC, Apartado 1827, Caracas 1010 A, Venezuela
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Photochemistry of Dimethylthioketene Dimers

Summary: Thioketones and dithioesters, using 1,3-cyclobutanedithione and 3-mercapto-2,2,4-trimethyldithio-3-pentenoic acid β-thiolactone as models are found to undergo α-cleavage to give the diradical and carbene as reactive intermediates.

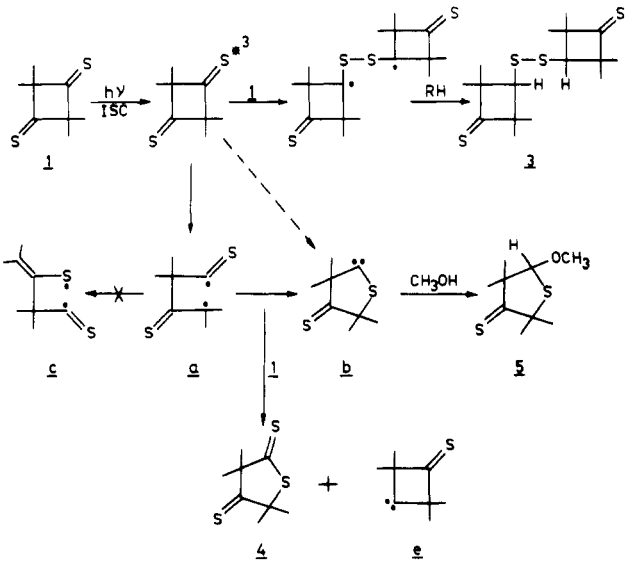
Sir: During the past several years, considerable research has been directed toward an understanding of the chemistry of electronically excited thioketones.[1] Analyses of the data from this research have revealed that thioketones are capable of undergoing three general types of reactions from both lower and higher excited states: (a) photoreduction, (b) cycloaddition to multiple bonds, and (c) intramolecular cyclization. These reactions are also primary photoreactions of ketones. But, thioketones have not yet been reported to undergo one of the primary photoreactions of ketones, namely, Norrish type I α-cleavage. In an attempt to explore the possibility of type I reactions in thioketones, we have studied the photochemistry of tetramethyl-1,3-cyclobutanedithione (**1**) and 3-mercapto-2,2,4-trimethyldithio-3-pentenoic acid β-thiolactone (**2**). The preliminary results are presented in this communication.

The electronic absorption spectrum of **1** shows three bands due to the thiocarbonyl group around 500 nm (n,π^*, ϵ 22), 298 (π,π^*, 409), and 227 (n,σ^*, 21 600). That of **2** shows three bands around 460 nm (n,π^*, ϵ 12), 344 ($\pi,\pi^*_{C=S}$, 4500), and 244 ($\pi,\pi^*_{C=C}$, 3800).

Irradiation of **1** (450-W medium-pressure mercury lamp with Pyrex filter; $\sim 5 \times 10^{-2}$ M) in nonhydroxylic solvents (cyclohexane, benzene, diethyl ether) gives two major products. These were identified as **3** and **4**.[2,3] Irradiation in methanol under similar conditions yields an additional product **5** (a 1:1 adduct) along with **3** and **4**.[3] All of these products are believed to originate from the lowest n,π^* triplet state of **1** since selective excitation of the S_1 band ($\lambda > 450$ nm; isolated by the Corning glass filter CS-3.71) and triplet sensitization (fluorenone, 2-acetylnaphthalene, benzil, and biacetyl) gave all these products. Also, consistent with this, the triplet quenchers alloocimene (47 kcal/mol) and cyclooctatetraene (<40 kcal/mol) quenched the formation of photoproducts **3**–**5** upon direct excitation.

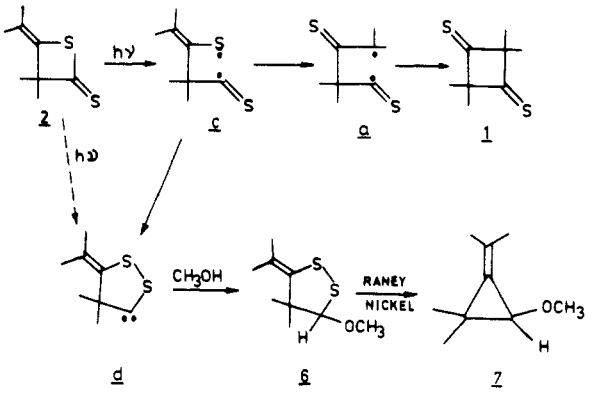
Irradiation of **2** (450-W medium-pressure mercury lamp with Pyrex filter; $\sim 2 \times 10^{-2}$ M) in nonhydroxylic solvents such as cyclohexane, ether, and benzene gave 1,3-dithione **1** in 60% yield. On the other hand, irradiation of **2** in methanol gave a 1:1 adduct as the major product (80%) identified to be **6**.[4] In accordance with the proposed structure, Raney nickel desulfurization of **6** gave **7**. The appearance of photoproducts **1** and **6** only when the S_1

Scheme I



SOLVENT	PRODUCTS
Cyclohexane	3 (15%); 4 (45%)
Methanol	3 (20%); 4 (30%); 5 (<10%)

Scheme II



SOLVENT	PRODUCT
Cyclohexane	1 (>60%)
Methanol	6 (80%)

(1) de Mayo, P. *Acc. Chem. Res.* **1976**, *9*, 52.

(2) In addition to **3** and **4**, we have isolated two products believed to be some type of dimers of the intermediate carbenes **b** and **e**. Characterization of these two products is hampered by the inability to obtain pure samples of these compounds for spectral identification.

(3) All three compounds **3**–**5** gave satisfactory elemental analyses. Their spectral data are shown below. **3**: IR (neat) 2960, 2920, 2860, 1440, 1350, 1290, 1250, 1120, 990, 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (s, 12 H), 1.382 (s, 12 H), 3.720 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.054 (q), 28.569 (q), 63.251 (s), 65.649 (d), 281.536 (s); mass spectrum (70 eV), *m/e* 346 (M^+). Anal. Calcd for $C_{16}H_{26}S_4$: C, 55.48; H, 7.57. Found: C, 56.08; H, 7.87. **4**: IR (neat) 2970, 2920, 2860, 1440, 1360, 1220, 1170, 1060, 960, 900, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.578 (s, 6 H), 1.802 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 33.563 (q), 33.723 (q), 70.963 (s), 77.891 (s), 245.175 (s), 267.671 (s); mass spectrum (70 eV), *m/e* 204 (100%), 172 (17.9), 141 (42.9), 128 (59.5), 113 (40.5), 96 (38.1), 86 (83.3), 85 (48.8), 81 (53.6), 71 (57.1), 59 (33.3), 41 (35.7). Anal. Calcd for $C_8H_{12}S_3$: C, 47.06; H, 5.92. Found: C, 46.71; H, 6.401. **5**: ^1H NMR ($CDCl_3$) δ 1.352 (s, 3 H), 1.393 (s, 3 H), 1.593 (s, 6 H), 3.349 (s, 3 H), 4.809 (s, 1 H). A careful search for **2** during the irradiation of **1** failed to show the presence of any **2**.

(4) Compound **6** gave satisfactory elemental analysis and had the following spectral properties: IR (neat) 2970, 2930, 2860, 1450, 1360, 1190, 1090, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.341 (s, 3 H), 1.431 (s, 3 H), 1.847 (s, 3 H), 1.891 (s, 3 H), 3.495 (s, 3 H), 4.609 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.546 (q), 23.131 (q), 26.478 (q), 26.830 (q), 51.489 (s), 58.299 (q), 105.796 (d), 123.526 (s), 137.087 (s); mass spectrum (70 eV), *m/e* 204 (100%), 172 (47.0), 141 (45.5), 139 (37.9), 128 (36.4), 108 (50.0), 96 (56.1), 86 (51.5), 85 (50.0); 81 (86.4), 71 (39.4), 59 (62.1), 41 (77.3). Anal. Calcd for $C_9H_{16}OS_2$: C, 52.93; H, 7.90. Found: C, 52.77; H, 7.702.

0022-3263/80/1945-4532$01.00/0