crystals which had formed were separated by filtration and washed with a little cold cyanomethane. Chromatography on a 1 in. × 18 in. CC-7 silica gel column (CH_2Cl_2) gave yellow needles from the yellow-orange band. Recrystallization from cyanomethane–water afforded 420 mg (68%) of **10**: mp 173–174 °C; NMR ($CDCl_3$) δ 7.67 (m, 5, C_6H_5), 8.72 (d, 1, H-1), 8.80 (d, 1, H-4); UV max (ether) 268 nm (ε 38 600), 295 (43 400), 322 (sh, 9650), 422 (3380); mass spectrum, *m/z* 383.8676 (M^+ calcd for $C_{13}H_7N_2{}^{79}Br_2{}^{35}Cl$: 383.8666), with the natural abundances of ^{79}Br, ^{81}Br, ^{35}Cl, and ^{37}Cl.

7-Bromo- and 5,7-Dibromo-2*H*-cyclopenta[*d*]pyridazine (11). To a stirred solution of 230 mg (1.95 mmol) of 2*H*-cyclopenta[*d*]pyridazine[8] in 60 mL of cyanomethane cooled by a dry ice bath was added a solution of 357 mg (2.01 mmol) of NBS[7] in ca. 15 mL of cyanomethane over a period of 1 h. TLC (9:1 CH_2Cl_2–ether) showed three components, one corresponding to starting material. NMR indicated a 2:5:3 ratio for starting material and the two products, respectively. Additional NBS solution was added slowly with periodic TLC monitoring until no starting material was present [ca. 200 mg (1.12 mmol) of NBS]. A mixture of the products was isolated by solvent removal (rotary evaporator) and chromatography on a 1 in. × 2 in. CC-7 silica gel column (CH_2Cl_2). The separation of the products was accomplished with difficulty on an analytical TLC plate with 90:10 CH_2Cl_2–acetone. The 7-bromo compound was removed with ether and amounted to 29.1 mg (8%) of yellow plates: mp 120 °C dec; NMR ($CDCl_3$) δ 6.96 (d, 1, J = 2 Hz, H-5), 7.43 (d, 1, J = 2 Hz, H-6), 8.66 (d, 2, J = 1 Hz, H-1 and H-4); UV max (ether) 243 nm (ε 35 600), 248 (sh, 34 000), 262 (sh, 21 000), 312 (2610), 325 (2600), 401 (887); mass spectrum, *m/z* 195.9634 (M^+ calcd for $C_7H_5N_2{}^{79}Br$: 195.9632), with the natural abundances of ^{79}Br and ^{81}Br.

The 5,7-dibromo derivative (**11**) was removed with ether and amounted to 141 mg (24%) of yellow plates: mp 125 °C dec; NMR (acetone) δ 7.26 (s, 1, H-6), 8.83 (s, 2, H-1 and H-4); UV max (ether) 248 nm (ε 22 100), 265 (19 400), 321 (1550), 330 (1530), 412 (1240); mass spectrum, *m/z* 273.8756 (M^+ calcd for $C_4H_7N_2{}^{79}Br_2$: 273.8742), with the natural abundances of ^{79}Br and ^{81}Br.

Registry No. 1, 55268-18-3; 2, 73038-13-8; 3, 73038-14-9; 4, 73038-15-0; 5, 73038-16-1; 6, 73038-17-2; 7, 73038-18-3; 8, 73038-19-4; 9, 73038-20-7; 10, 73038-21-8; 11, 73038-22-9; NCS, 128-09-6; 5,7-dibromo-2-methyl-2*H*-cyclopenta[*d*]pyridazine, 55268-20-7; 5,7-dichloro-2-phenyl-2*H*-cyclopenta[*d*]pyridazine, 55268-27-4; 2-phenyl-2*H*-cyclopenta[*d*]pyridazine, 22291-84-5; 2*H*-cyclopenta[*d*]-pyridazine, 270-64-4; 7-bromo-2*H*-cyclopenta[*d*]pyridazine, 73038-23-0.

A Method for Transfer of Labeled Methyl Groups

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Since their inception a decade ago,[1,2] the use of chiral methyl groups has become an established tool of bioorganic investigation. Generation of chiral methyl groups on biotransformation of an appropriately labeled substrate to product followed by excision, typically by Kuhn–Roth oxidation, of the labeled groups as acetic acid and determination of their absolute configuration by established methodology[1,2] has allowed the stereochemical course of a variety of enzymatic reactions to be defined. Conversely, examples where a substrate has borne a chiral methyl group which, in the course of a biochemical reaction, undergoes conversion to a methylene group or transfer or migration of the methyl group have generally been limited to cases in primary metabolism wherein acetate or pyruvate has been the reactant. Instances where substrates more complex than acetic acid have been employed have been fewer in number. These investigations[3] exemplify two general approaches to the synthesis of substances having chiral methyl groups. The first involves elaboration of chiral acetic acid itself by (a) reaction of the corresponding ester,[4] (b) reduction to ethanol and reaction of the derived sulfonate ester,[9] or (c) Schmidt degradation to methylamine (retention) and transfer of the chiral methyl group by displacement of ditosylimide **2a** (R = CHDT) (inversion).[5,6] The second relies upon the fact that aldehydes of considerable structural diversity can be reduced stereospecifically with horse liver alcohol dehydrogenase.[11] In principle, the resulting primary alcohol may be converted to the tosylate and the latter displaced by labeled lithium aluminum hydride. In practice, three potential experimental difficulties must be faced with this second approach: (a) although the stereochemical course of the enzymic reduction may be presumed by analogy with known examples, in principle, it should be proved for each new case;[12] (b) the dehydrogenase is not completely indiscriminate with respect to substrate and, in general, those which are largely nonpolar fare best;[11,13] and (c) the displacement of sulfonate esters by hydride is sensitive to steric effects,[14] and, owing to isotope effects, the efficiency of tritium transfer from radiolabeled lithium aluminum hydride is low.

The introduction of chiral methyl groups, therefore, by the alcohol dehydrogenase route may be fraught with serious experimental restrictions. Similarly, the use of chiral acetate or ethyl tosylate, while suited to the particular applications noted above, is synthetically limiting. In this paper we describe a partial solution to this problem which exploits the availability of chiral acetic acid of high optical purity and high specific radioactivity[1,2,15] to develop the

(1) J. W. Cornforth, J. W. Redmond, H. Eggerer, W. Buckel, and C. Gutschow, *Nature (London)*, **221**, 1212 (1969); *Eur. J. Biochem.*, **14**, 1 (1970).

(2) J. Lüthy, J. Rétey, and D. Arigoni, *Nature (London)*, **221**, 1213 (1969).

(3) These notable exceptions include the following: investigation of methyl migration in lanosterol biosynthesis[4] wherein mevalolactone having a chiral C-6 methyl was required; studies of *S*-adenosylmethionine as a biological methylating agent which necessitated the synthesis of methionine having CHDT groups of known absolute configurations;[5,6] independent investigations by two groups[7,8] of cyclopropane formation in the last step of cycloartenol biosynthesis which required the synthesis of 2,3-oxidosqualene having a chiral C-6 methyl group; and recently the stereochemical studies of ω-hydroxylation of hydrocarbons.[9,10]

(4) K. H. Clifford and G. T. Phillips, *J. Chem. Soc., Chem. Commun.*, 419 (1975); G. T. Phillips and K. H. Clifford, *Eur. J. Biochem.*, **61**, 271 (1976).

(5) D. Arigoni, *Ciba Found. Symp.*, **60**, 243 (1978).

(6) L. Mascaro, Jr., R. Hörhammer, S. Eisenstein, L. K. Sellars, K. Mascaro, and H. Floss, *J. Am. Chem. Soc.*, **99**, 273 (1977).

(7) L. J. Altman, C. T. Han, A. Bertolino, G. Handy, D. Laungani, W. Muller, S. Schwartz, D. Shanker, W. H. deWolf, and F. Yang, *J. Am. Chem. Soc.*, **100**, 3235 (1978).

(8) D. Arigoni, W. Blättler, and A. A. Ponaras, unpublished results.

(9) D. Arigoni, A. Gautier, and J. M. Greenfield, unpublished results.

(10) B. T. Golding, P. V. Ioanou, and I. F. Eckhard, *J. Chem. Soc., Perkin Trans. 1*, 774 (1978).

(11) For a review see J. B. Jones and J. F. Beck in "Applications of Biochemical Systems in Organic Chemistry", Part 1, J. B. Jones, C. J. Sih, and D. Perlman, Eds., Wiley-Interscience, New York, 1976, pp 107–401.

(12) However, see R. Bentley, "Molecular Asymmetry in Biology", Vol. 2, Academic Press, New York, 1970, pp 1–86; and G. Popják in "The Enzymes", Vol. 2, P. D. Boyer, Ed., Academic Press, New York, 1970, pp 115–215.

(13) A dismutation reaction is also possible. A recent example is R. J. Parry and D. A. Trainor, *J. Am. Chem. Soc.*, **100**, 5244 (1978), and references cited therein. Also relevant is A. R. Battersby, J. R. Staunton, and H. R. Wiltshire, *J. Chem. Soc., Perkin Trans. 1*, 1156 (1975).

(14) S. Krishnamurthy and H. C. Brown, *J. Org. Chem.*, **41**, 3064 (1976).

(15) C. A. Townsend, T. Scholl, and D. Arigoni, *J. Chem. Soc., Chem. Commun.*, 921 (1975); M. Kajiwara, S.-F. Lee, A. I. Scott, M. Akhtar, C. R. Jones, and P. M. Jordan, *ibid.*, 967 (1978).

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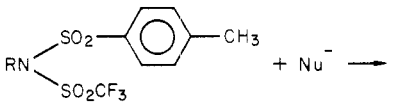
Table I. Reactions of Sulfonimides 1a and 1b with Nucleophiles in HMPT

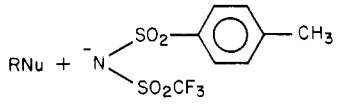
nucleophile (K^+ salt)	sulfonimide	product (% yield)[a]
$CH_2(COOEt)_2$[b]	1a	$CH_3CH(COOEt)_2$ (60) $(CH_3)_2C(COOEt)_2$ (0)
$CH_2(COOEt)_2$	1b	$PhCH_2CH(COOEt)_2$ (23)
$CH_2(CN)COOEt$	1b	$PhCH_2CH(CN)COOEt$ (19) $(PhCH_2)_2C(CN)COOEt$ (44)
$PhCH_2CH(COOEt)_2$	1a	$PhCH_2(CH_3)C(COOEt)_2$ (56)
PhSH	1b	$PhCH_2SPh$ (54)

[a] Yields are based on sulfonimide used and represent isolated product after preparative layer chromatography except as noted. [b] Yields are based on GC comparison with authentic samples and internal standard (column temperature 115 °C).

use of mixed sulfonimides such as 1 for the alkylation of simple carbon anions.



1a, R = CH_3
b, R = CH_2Ph

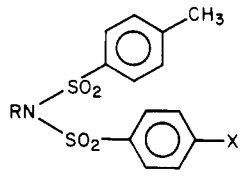


The use of arylsulfonimides, e.g., 2a–c, to allow displacement of nitrogen by iodide, bromide, and aniline was pioneered by Baumgarten.[16] This approach has been extended to include the nucleophiles 3,5-dinitrobenzoate and tosylate,[17] hydride,[18] and homocysteinethiolate.[5,6] Yet, apart from the reaction in variable yields of benzylic and allylic *N,N*-disulfonimides with lithium dimethylcuprate,[19] Glass has reported[20] the only known case where sulfonimide displacement has been carried out with a carbon nucleophile: reaction of (trifluoromethane)sulfonimides 3a and 3b in HMPT with sodium cyanide and diethyl sodiomalonate. Subsequent work,[21] however, has clearly shown that these and other related reactions proceed largely if not entirely by the intermediate formation of the HMPT salt 4, which in turn reacts in well-precedented

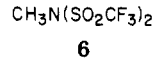
$$RN(SO_2CF_3)_2 + O{=}P[N(CH_3)_2]_3 \rightarrow \underset{4}{ROP^+[N(CH_3)_2]_3}\,^-N(SO_2CF_3)_2$$

fashion[22] with the added nucleophile to give the observed products. If R in 3 were chiral methyl, solvent participation of this kind would lead to racemization.

Our efforts to transfer labeled methyl groups to carbon nucleophiles began with the reaction of ditosylimide 2a (R = CH_3) and dimethyl malonate under a variety of conditions of solvent, temperature, and method of anion formation. In all cases either no reaction took place or S–N bond cleavage of the sulfonimide predominated rather than the desired C–N bond cleavage. The absence of alkyl-group transfer was also observed with the mixed sulfonimides 5a (R = CH_3) and 5b (R = CH_3). The oily,



5a, X = NO_2
b, X = OCH_3



6

moisture-sensitive methyltriflylimide 6 was then synthesized and found to react with dibenzyl potassiomalonate in HMPT at room temperature to give monoalkylated diester in 50% yield. HMPT was necessary to obtain synthetically useful amounts of alkylated product, but, as was anticipated from Glass' earlier work[21] with 3a and 3b, reaction of 6 was found to be rapid with HMPT ($t_{1/2}$ ~0.5 h at 32 °C) to form the salt 4 (R = CH_3). The formation of 4 (R = CH_3) was easily monitored by the disappearance in the NMR spectrum of the methyl singlet in 6 at δ 3.8, the formation of the characteristic doublet in 4 (R = CH_3) at δ 4.0 ($^3J_{P\text{-}H}$ = 11 Hz[23]) and concomitant shift of the HMPT methyl doublets downfield. Addition of an aqueous solution of sodium tetraphenylboron to the HMPT solution of 4 (R = CH_3) gave the corresponding known[23] tetraphenylboron salt, mp 202–204 dec (lit.[23] mp 198–201 °C).

The problem of solvent participation was circumvented and alkyl-group transfer was successfully accomplished by the use of the crystalline mixed sulfonimides 1a and 1b which were prepared by reaction of the corresponding tosylamides with trifluoromethanesulfonic anhydride. General reaction conditions were developed with *N*-methylsulfonimide 1a and diethyl malonate. It was found that addition of the mixed sulfonamide to 2.0 equiv of nucleophile preformed by reaction of substrate with 2.4 equiv of potassium hydride in dry HMPT was procedurally simple and gave reproducible results. The reaction was best carried out at room temperature, and it was found, as expected, that addition of crown ether did nothing to improve the yield. The results of reaction 1a and 1b for 72 h with several simple carbon and sulfur nucleophiles are shown in Table I.[24] One illustrative case is the reaction of diethyl benzylmalonate with *N*-methylsulfonimide 1a to give diethyl benzylmethylmalonate in 56% isolated yield after preparative layer chromatography.

It is known that methyl transfer from tosylimide 2a (R = CHDT) to homocysteinethiolate in HMPT proceeds with clean inversion.[5] The absence of intermediate displacement by solvent may be implied from this stereochemical result, but we have demonstrated the fact by observation of 2a (R = CH_3) by NMR spectroscopy in HMPT. In contrast to the rapid reaction of *N*-methyltriflylimide 6 with HMPT described above, the ditosyl-

(16) P. J. DeChristopher, G. D. Lyon, J. P. Adamek, R. J. Swedo, S. A. Klein, and R. J. Baumgarten, Abstrasts, 161st National Meeting of the American Chemical Society, Los Angeles, CA, March-April, 1971, ORGN-14. P. J. DeChristopher, J. P. Adamek, G. D. Lyon, J. J. Galante, H. E. Haffner, R. J. Boggio, and R. J. Baumgarten, *J. Am. Chem. Soc.*, 91, 2384 (1969). See also J. B. Hendrickson, S. Okano, and R. K. Bloom, *J. Org. Chem.*, 34, 3434 (1969).
(17) V. A. Curtis, H. S. Schwartz, A. F. Hartman, R. M. Pick, L. W. Kolar, and R. J. Baumgarten, *Tetrahedron Lett.*, 1969 (1977).
(18) R. O. Hutchins, F. Cistone, B. Goldsmith, and P. Heuman, *J. Org. Chem.*, 40, 2018 (1975); R. O. Hutchins, D. Kandasamy, F. Dux III, C. A. Maryanoff, D. Rotstein, B. Goldsmith, W. Burgoyne, F. Cistone, J. Dallessandro, and J. Puglis, *ibid.*, 43, 2259 (1978).
(19) P. Müller and N. T. M. Phuong, *Tetrahedron Lett.*, 4727 (1978).
(20) R. S. Glass, *J. Chem. Soc., Chem. Commun.*, 1546 (1971).
(21) R. S. Glass and R. J. Swedo, *J. Org. Chem.*, 43, 2291 (1978).
(22) See ref 21 footnotes 9e, 10, and 11.
(23) A. Anselmi, B. Macchia, F. Macchia, and L. Monti, *J. Chem. Soc., Chem. Commun.*, 1152 (1971).
(24) Highly stabilized carbanions are necessary for successful alkylation. It was found that for the anions of [(carboethoxy)methylene]triphenylphosphonium bromide, a stabilized ylide, dimethyl succinate, and even ethyl acetoacetate that self-condensation of the nucleophile competed with synthetically useful amounts of alkylation.

imide **2a** (R = CH_3) was completely unaffected by the solvent. Similarly, the mixed sulfonimide **1a** failed to give any detectable reaction with HMPT after 2 weeks at room temperature (five times the duration of reactions in Table I).

Syntheses of chiral acetic acid of high optical purity and high specific radioactivity are currently available.[1,2,15] Schmidt degradation to methylamine and synthesis of the corresponding crystalline *p*-toluenesulfonamide may be carried out in about 80% overall yield. In conclusion, therefore, the ease of generation of the mixed sulfonimide **1a**, an air-stable, highly crystalline compound, combined with its facile reaction with simple carbanions opens the way to use of this reagent for the synthesis of complex substances bearing labeled methyl groups.[25]

Experimental Section

^1H NMR spectra were recorded with a Jeol MH-100 spectrometer and resonances are reported in parts per million downfield from tetramethylsilane as internal standard. Infrared spectra were obtained with a Perkin-Elmer Model 457A spectrometer and are reported in reciprocal centimeters. Ultraviolet spectra were determined with a Beckman Model DB-G instrument. Mass spectra were measured on a Hitachi Perkin-Elmer RMU-6 mass spectrometer. Gas chromatograms were obtained with a Varian-Aerograph Series 1200 gas chromatograph fitted with a 10-ft column of 5% SE-30 on 100–140 Chromosorb G. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were determined in open glass capillaries with a Thomas-Hoover apparatus and are uncorrected. Preparative layer chromatography was carried out with 20 × 20 cm plates, 0.5-mm or 2.0-mm thickness, of Merck silica gel F-254. Column chromatography was conducted with silica gel-60, Merck. Dry HMPT was prepared by distillation at reduced pressure from calcium hydride.

***N*-Methyl(*p*-toluenesulfonyl)trifluoromethanesulfonimide (1a).** A suspension of *p*-toluenesulfonyl chloride (21.2 g, 111 mmol) in 300 mL of water and methylamine hydrochloride (5.0 g, 74 mmol) was rapidly stirred and cooled to 0–5 °C. Aqueous potassium hydroxide (1 N, 148 mL) was then added slowly. After 15 min the ice bath was removed and the solution was stirred at room temperature for 1 h and finally at 60 °C for 2 h. The cooled aqueous solution was acidified (pH <2) and extracted with ether (3 × 500 mL). The combined organic extracts were dried, and the solvent was removed in vacuo to yield 13.7 g of white crystalline solid. The sulfonamide was recrystallized once from hot 2-propanol and used in the next step. *N*-Methyl-*p*-toluenesulfonamide (5.96 g, 32.2 mmol) was added in one portion to a stirred suspension of sodium hydride (50% dispersion, 2.0 g, 41.7 mmol) and 20 mL of dry methylene chloride cooled to −78 °C under an argon atmosphere. When hydrogen evolution was complete (~20 min), trifluoromethanesulfonic anhydride (7.0 mL, 10.9 g, 40 mmol) was added slowly over 15 min. The resulting solution was stirred at −78 °C for 1 h and at room temperature for 2.5 h. Ice water was added and the solution was adjusted to pH 3 with 6 N hydrochloric acid. The aqueous layer was extracted with methylene chloride (3 × 100 mL). The combined organic extracts were dried over anhydrous magnesium sulfate and the solvent was evaporated to give 9.52 g of brown oil. Chromatography of the oily product on 180 g of silica gel and elution with methylene chloride afforded 6.82 g (67%) of **1a** as white needles which were recrystallized from hot 2-propanol: mp 81–82 °C, NMR ($CDCl_3$) δ 2.50 (s, 3 H), 3.49 (s, 3 H, NCH_3), 7.52 (d, J = 8 Hz, 2 H), 8.06 (d, J = 8 Hz, 2 H); IR (CCl_4) 1405, 1380, 1220, 1125 cm^{-1}. Anal. Calcd for $C_9H_{10}F_3NO_4S_2$: C, 34.07; H, 3.18; N, 4.41; S, 20.21; F, 17.96. Found: C, 34.12; H, 3.28; N, 4.37; S, 20.29; F, 17.86.

***N*-Benzyl(*p*-toluenesulfonyl)trifluoromethanesulfonimide (1b).** This mixed sulfonimide was prepared (82%, mp 52.5–53.5 °C) in a fashion analogous to that carried out for **1a** but by using benzylamine: NMR ($CDCl_3$) δ 2.42 (s, 3 H), 5.12 (s, 2 H), 7.2–7.6 (m, 9 H); IR (CCl_4) 1405, 1380, 1220, 1130 cm^{-1}. Anal. Calcd for $C_{15}H_{14}F_3NO_4S_2$: C, 45.80; H, 3.59; S, 16.30. Found: C, 45.78; H, 3.60; S, 16.42.

Reaction of Sulfonimides 1a and 1b with Nucleophiles. A general procedure was developed and adhered to for the reactions shown in Table I. This procedure is illustrated for the alkylation of diethyl benzylmalonate with **1a**: A 10-mL three-neck flask was flamed dry in a stream of argon and charged with potassium hydride (23.6% dispersion, 254 mg, 1.50 mmol). Under an argon atmosphere the hydride was washed several times with cyclohexane and 3 mL of dry HMPT was added. Freshly distilled diethyl benzylmalonate (300 μL, 322 mg, 1.29 mmol) was added cautiously. When hydrogen evolution was complete (~10 min), sulfonimide **1a** (200 mg, 0.63 mmol) was added in one portion. The resulting solution was stirred at room temperature under a positive argon pressure for 72 h. Water (3 mL) was added followed by 8 mL of methylene chloride. The aqueous layer was adjusted to pH 3 with 6 N hydrochloric acid and extracted with methylene chloride (4 × 10 mL). The combined organic extracts were washed with water (2 × 10 mL) and dried over anhydrous magnesium sulfate, and the solvent was removed to yield 473 mg of oil. The products were separated by preparative layer chromatography and the results are shown in Table I. Spectral data and GC and TLC retention times for the products shown in Table I were compared with those obtained from authentic samples.

Registry No. 1a, 73062-44-9; **1b**, 73062-45-0; $CH_2(COOEt)_2K$, 37892-24-3; $CH_2(CN)COOEtK$, 37892-17-4; $PhCH_2CH(COOEt)_2K$, 73062-46-1; PhSHK, 3111-52-2; $CH_3CH(COOEt)_2$, 609-08-5; $(CH_3)_2C(COOEt)_2$, 1619-62-1; $PhCH_2CH(COOEt)_2$, 607-81-8; $PhCH_2CH(CN)COOEt$, 6731-58-4; $(PhCH_2)_2C(CN)COOEt$, 73062-47-2; $PhCH_2(CH_3)C(COOEt)_2$, 55114-30-2; $PhCH_2SPh$, 831-91-4; *p*-toluenesulfonyl chloride, 98-59-9; methylamine hydrochloride, 593-51-1; *N*-methyl-*p*-toluenesulfonamide, 640-61-9; trifluoromethanesulfonic anhydride, 358-23-6; benzylamine, 100-46-9.

(25) Partial support of this work by the National Institutes of Health (5 S07-RR 07041 and 1 R01-Al 14937) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

On the Reported Preparation of Diethyl Diacetylmaleate

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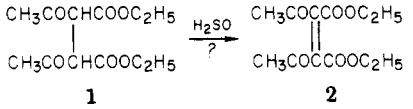
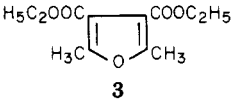
Recently the conversion of diethyl diacetylsuccinate (**1**) to diethyl diacetylmaleate (**2**) by treatment with



1 **2**

H_2SO_4-CCl_4 (but not H_2SO_4–ether or HCl–CCl_4) has been reported.[1] This "unusual acid-catalyzed oxidation" seems most unlikely, especially in view of the authors' own observation that dehydrogenation of **1** with platinum or palladium was unsuccessful.

Evidence for the structure of **2** included IR, Raman, mass, and ^1H NMR spectra and elemental analysis. We have repeated the reaction, obtaining an oil with the same IR and ^1H NMR spectra as described by the authors. However, it is clear from the ^{13}C NMR and mass spectra that the product is the furan **3**[2] rather than the maleate



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(1) S. C. Airy, C. Martin, and J. M. Sullivan, *J. Org. Chem.*, **44**, 1891 (1979).