1, HC═C). Anal. Calcd for $C_{11}H_{16}N_2O$: C, 68.72; H, 8.39. Found: C, 68.80; H, 8.46.

8: mp 122–123 °C; IR (Nujol) 3050, 1695 (C═O), 1605 cm^{-1} (C═C); ^1H NMR ($CDCl_3$) δ 1.29 (d, J = 6.5 Hz, 6, CH_3), 3.32 (d, J = 2 Hz, 2, CH_2N), 3.76 (s, 3, OCH_3), 4.37 (m, 1, CH–N), 7.53 (t, J = 2 Hz, 1, CH═C). Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15. Found: C, 58.90; H, 7.22.

12: bp 86–88 °C (1 mm); IR (neat) 3080, 1720 (ester C═O), 1682, 1618, 1588 cm^{-1} (C═C); ^1H NMR ($CDCl_3$) δ 1.34 (t, J = 7 Hz, 3, CH_3), 1.38 (d, J = 7 Hz, 6, CH_3), 2.21 (s, 3, $COCH_3$), 4.22 (m, 1, CH–N), 4.25 (q, J = 7 Hz, 2, CH_2O), 5.78 (d, J = 14 Hz, 1, CH═C), 7.93 (d, J = 14 Hz, 1, HC═C). Anal. Calcd for $C_{10}H_{17}NO_3$: C, 60.28; H, 8.60. Found: C, 60.34; H, 8.56.

Registry No. **1a** (R^1 = H), 96-33-3; **1a** (R^1 = CH_2CO_2Me), 617-52-7; **1b** (R^1 = Me), 80-62-6; **1b** (R^1 = H), 107-13-1; **2a** (R^1 = H, R^2 = *i*-Pr), 98013-99-1; **2a** (R^1 = Me, R^2 = c-C_6H_{11}), 98014-00-7; **2a** (R^1 = CH_2CO_2Me, R^2 = *i*-Pr), 98014-01-8; **2b** (R^1 = H, R^2 = c-C_6H_{11}), 17526-82-8; **3a** (R^1 = H, R^2 = *i*-Pr), 98014-02-9; **3a** (R^1 = Me, R^2 = c-C_6H_{11}), 98014-03-0; **3a** (R^1 = CH_2CO_2Me, R^2 = *i*-Pr), 98014-04-1; **3b** (R^1 = H, R^2 = c-C_6H_{11}), 98014-05-2; **4a** (R^1 = H), 7424-91-1; **4a** (R^1 = Me), 76526-43-7; **4a** (R^1 = CH_2CO_2Me), 98014-06-3; **4b** (R^1 = H), 57597-62-3; **5a** (R^1 = H, R^2 = *i*-Pr), 98014-07-4; **5a** (R^2 = Me, R^2 = c-C_6H_{11}), 98049-90-2; **5b** (R^1 = H, R^2 = c-C_6H_{11}), 98014-08-5; **6**, 98014-09-6; **7**, 43135-01-9; **8**, 98014-10-9; **9**, 78-94-4; **10**, 98014-11-0; 11, 98014-12-1; **12**, 98014-13-2; cyclohexylamine, 108-91-8; *N*-isopropylacetamide, 1118-69-0; isopropylamine, 75-31-0; *N*-cyclohexylacetamide, 1124-53-4.

1,4-Addition of Certain 2-Lithio-1,3-dithianes to α,β-Unsaturated Nitriles

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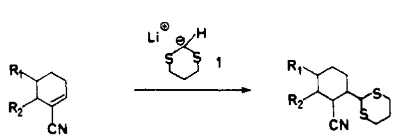
Received December 20, 1984

The metallated 1,3-dithiane derivatives are among the most widely used Umpolung reagents.[1] The 1,4-addition of these acyl anion equivalents to α,β-unsaturated aldehydes,[2] ketones,[3] and amides[4] resulting in the formation of a new C–C bond has received considerable attention. However, the use of the 1,3-dithiane anion in the 1,4-addition to unsaturated nitriles is virtually unexplored. We now report the first examples of the 1,4-addition of 1,3-dithianes to a series of α,β-unsaturated nitriles as shown in eq 1.



(1)

Formation of 2-lithio-1,3-dithiane (**1**) was accomplished by the dropwise addition of *n*-butyllithium to a solution of 1,3-dithiane in THF at −20 °C under nitrogen. The reaction mixture was allowed to stir at this temperature for 30 min and then cooled to −78 °C. The solution of the unsaturated nitrile in THF was added dropwise to the anion **1**, resulting in immediate discharge of a dark color. This afforded, after workup, the desired 1,4 Michael products **2** and **3** in a ratio of 2.2:1 (cis/trans) in 90% overall yield.

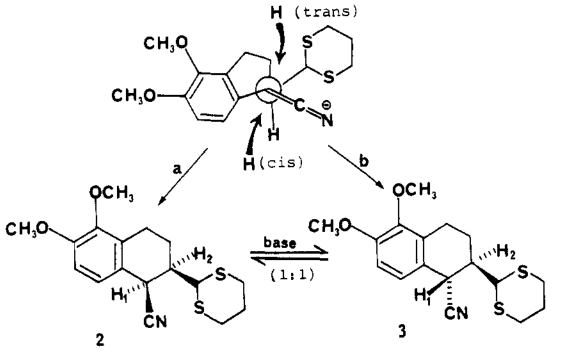
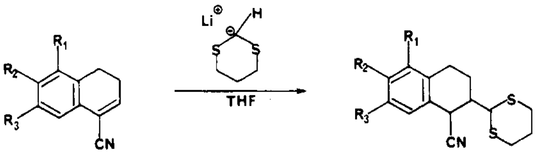


Figure 1. Equilibration of **2** with DBU/CH_2Cl_2 or 2 N NaOH/CH_2Cl_2/THF gave a 1:1 equilibrium mixture consisting of the trans-**3** and cis-**2** isomers, respectively.

Table I. NOE Difference Data for Compound 9

proton	case 1	case 2	case 3
2	IRR (−100)	3.1	8.0
I-CH_3	2.9	IRR (−100)	6.0
8		3.7	
9	5.5		IRR (−100)
10 axial			4.8
12 axial			6.1

Table II. Addition of 1,3-Dithiane Anion to α,β-Unsaturated Nitriles[8a,b]



R_1	R_2	R_3	product	c/t[a]	yield,[b] %
CH_3O	CH_3O	H	**2**	2.2/1	90
H	H	H	**4**	2/1	90
CH_3O	H	H	**5**	3/1	90
H	CH_3O	H	**6**	2.2/1	85
H	CH_3O	CH_3O	**7**	2/1	70

[a] Cis/trans ratio based on high field NMR. [b] No attempts were made to optimize yield.

The stereochemistry of **2** was assigned to be cis on the basis of a coupling constant of H_1 and H_2 ($^3J_{H_1-H_2}$ = 4.6 Hz) and a W coupling constant of H_1 and H_3 eq ($^4J_{H_1-H_3}$ eq = 1.8 Hz), consistent with an equatorial arrangement for H_3 relative to an axial H_1. The stereochemistry of **3** was assigned trans on the basis of a $^3J_{H_1-H_2}$ coupling constant of 9.0 Hz and the lack of a W coupling.[5]

The formation of **2** as the major product is in agreement with the results of the alkylation of α-cyano carbanions,[6] which undergo equatorial protonation/alkylation as shown in path a (Figure 1). The alternative path b would lead to the trans product **3**.

The intermediate carbanion from compound **2** has been trapped with D_2O, affording product **8** with a cis/trans ratio of 2.1/1 (95% yield). Trapping the carbanion with CH_3I gave only the cis product **9** in 70% yield, with no detectable trans isomer by high field nuclear magnetic resonance (NMR). The stereochemistry of **9** was determined from coupling constant and NOE difference data. The proton H-2 shows three coupling constants of $^3J_{2,9}$ =

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[1] For excellent review on this subject, see: (a) Groebel, B.-t., Seebach, D. *Synthesis* **1977**, 357. (b) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 639.

[2] Wartski, L.; et al. *Tetrahedron* **1982**, *38*, 3285.

[3] (a) Brown, C. A.; Tamaichi, A. *J. Chem. Soc., Chem. Commun.* **1979**, 100. (b) Ostrowski, P. C.; Kane, V. V. *Tetrahedron Lett.* **1977**, 3549. (c) Luchetti, J.; et al. *Tetrahedron Lett.* **1979**, 2695.

[4] Mango, G. B., Mahalanabis, K. K.; Mahdavi-Damghani, Z.; Snieckus, V. *Tetrahedron Lett.* **1980**, *21*, 4823 and references cited therein.

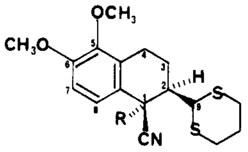
[5] Bovey, F. A. "Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1969; pp 133–143.

[6] Bare, T. M.; Hershey, N. D.; House, H. O.; Swain, C. G. *J. Org. Chem.* **1972**, *37*, 997.

Table III. Pertinent ^1H Chemical Shifts and Coupling Constants of the 1,4-Addition Products

	chemical shift, ppm				coupling constant, Hz				
	cis H-1–H-9		trans H-1–H-9		cis H-1–H-9			trans H-1–H-9	
compd	*dd*	*d*	*d*	*d*	$^3J_{1,2}$	$^4J_{1,3}$	$^3J_{2,9}$	$^3J_{1,2}$	$^3J_{2,9}$
2	4.36	4.12	4.34	4.41	4.6	1.8	10.8	9.0	5.1
4	4.25	4.01	4.23	4.3	4.5	2.0	12.0	11.0	6.0
5	4.4	4.13	4.37	4.4	5.0	1.5	12.0	8.6	5.0
6	4.37	4.16	4.33	4.43	6.0	1.5	11.0	9.0	5.0
7	4.32	4.15	4.35	4.42	6.0	1.5	11.0	10.0	5.0

3.6, $^3J_{2,3}$ = 11 and 9 Hz. The coupling constants between H-2 and the H-3 protons are consistent with the H-2 proton being axial and the dithiane ring being equatorial. As seen in Table I, irradiation of the methyl group gives a positive NOE of 3.1% to H-2 (case 3) and irradiation of H-2 gives a positive NOE of 2.9% to the CH_3 group (case 1). These results indicate that the methyl group and the C-2 proton are spatially close and consistent with the cis relationship in **9**.



8, R = O
9, R = ''''CH_3

The results[7] of the addition of **1** to a series of other unsaturated dihydronaphthalene nitriles are summarized in Table II. As seen in Table II, the reaction of **1** with α,β-unsaturated nitriles provides an efficient route to 2-substituted nitriles in good yields. In all cases the cis isomer is favored over the trans isomer. The cis/trans ratios were determined by high field NMR, and the results are shown in Table III.

Under our standard reaction conditions 1-cyclohexanecarbonitrile (cf. eq 1, $R_1 = R_2 = H$) afforded only traces of Michael addition products with recovered starting material. The Michael adduct was obtained in 50% yield only when the reaction was run at ambient temperatures and allowed to proceed for 14 h. We attribute the fact that the other unsaturated nitriles illustrated in Table II undergo a more facile Michael addition to stabilization of the intermediate carbanion by the adjacent aromatic ring.

The Michael addition product **3** was hydrolyzed[9] with $HgCl_2$ and $CaCO_3$ in CH_3CN/H_2O, affording the corresponding aldehyde in 90% yield. The hydrolyzed product of the 1,4-addition of dithiane to α,β-unsaturated nitriles provides an easy entry to an homologous aldehyde which is otherwise difficult to obtain.

In summary, we have demonstrated the first example of the addition of 1,3-dithiane to α,β-unsaturated nitriles and furthermore illustrated useful conversions of the products.

Experimental Section

NMR spectra were recorded on either a GE QE-300 or a Nicolet HT-360 wide bore instrument. The infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer. Mass spectra were obtained with either a Kratos MS50 high resolution (10000 resolution) with a DS/55 Rev. 4.0 software and Nova/312 computer or a Varian CH7 spectrometer. Melting points were determined on a Thomas-Hoover "Uni-Melt" melting point apparatus and are uncorrected.

General Procedure for the 1,4-Addition of 1,3-Dithiane to α,β-Unsaturated Nitrile. To a solution of 1,3-dithiane (Fluka) (360 mg, 3 mmol) in 20 mL of THF was added a solution of *n*-butyllithium (3.2 mmol, 1.6 M in hexane) at −20 °C under nitrogen. The reaction mixture was allowed to stir at this temperature for 30 min and then cooled to −78 °C. The solution of the unsaturated nitrile (538 mg, 2.5 mmol) in 20 mL of THF was added dropwise to 2-lithio-1,3 dithiane (**1**), resulting in immediate discharge of a dark color. The reaction was warmed to −20 °C, stirred at this temperature for 1 h, cooled to −78 °C, and then quenched with a saturated NH_4Cl solution. The reaction mixture was diluted with CH_2Cl_2, and the combined organic layers were washed with brine and then dried over magnesium sulfate. The organic solvent was removed in vacuo and the resulting solid was triturated with ether to give *cis*-**2**: yield 498 mg (60%) recrystallized from ether/hexane; mp 177–178 °C; IR ($CHCl_3$) 2240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–1.77 (1 H, m), 1.85–2.05 (1 H, m), 2.08–2.22 (2 H, m), 2.5–2.72 (2 H, m), 2.85–3 (4 H, m), 3.05–3.17 (1 H, m), 3.78 (3 H, s), 3.84 (3 H, s), 4.12 (1 H, d, J = 10.8 Hz), 4.36 (1 H, dd, J = 4.6, 1.5 Hz), 6.79, (1 H, d, J = 8.0 Hz), 6.97 (1 H, d, J = 8.0 Hz); mass spectrum, m/z 335 (M^+), 229 (M^+ − 106); high resolution mass spectrum, obsd m/z 335.1016 ($C_{17}H_{21}NO_2S_2$ (M^+) requires 335.1014). Anal. Calcd for $C_{17}H_{21}NO_2S_2$: C, 60.89; H, 6.26; N, 4.17. Found: C, 60.82; H, 6.35; N, 4.09. *trans*-**3**: mp 115–119 °C; ^1H NMR ($CDCl_3$) δ 1.75–1.98 (2 H, m), 2.1–2.22 (1 H, m), 2.22–2.32 (1 H, m), 2.39–2.5 (1 H, m), 2.62–2.78 (1 H, m), 2.85–3.05 (5 H, m), 3.78 (3 H, s), 3.85 (3 H, s), 4.33 (1 H, d, J = 9.0 Hz), 4.41 (1 H, d, J = 5.1 Hz), 6.83 (1 H, d, J = 8.0 Hz), 7.14 (1 H, d, J = 8.0 Hz).

Compound 4: cis, mp 150–152 °C; IR ($CHCl_3$) 2240 cm^{-1}; ^1H NMR δ 1.6–1.7 (1 H, m), 1.8–2.2 (1 H, m), 2.1–2.22 (2 H, m), 2.4–2.66 (2 H, m), 2.8–3.0 (5 H, m), 4.16 (1 H, d, J = 12.0 Hz), 4.4 (1 H, dd, J = 4.5, 2.0 Hz), 3.82 (3 H, s), 6.78 (1 H, d, J = 8.0 Hz), 6.87 (1 H, d, J = 8.0 Hz), 7.2 (1 H, dd, J = 8.0, 8.0 Hz); mass spectrum, m/z 305 (M^+); high resolution mass spectrum, obsd m/z 275.0786 ($C_{15}H_{17}NS_2$ (M^+) requires 275.0772). Anal. Calcd for $C_{15}H_{17}NS_2$: C, 65.45; H, 6.18; N, 5.09. Found: C, 65.85; H, 6.24; N, 4.89.

Compound 5: cis, mp 130–133 °C; IR ($CHCl_3$) 2240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–1.7 (1 H m), 1.8–22 (1 H, m), 2.1–2.22 (2 H, m), 2.4–2.66 (2 H, m), 2.8–3.0 (5 H, m), 4.13 (1 H, d, J = 12.0 Hz), 4.41 (1 H, dd, J = 4.5, 1.5 Hz), 3.82 (3 H, s), 6.78 (1 H, d, J = 8.0 Hz), 6.87 (1 H, d, J = 8.0 Hz), 7.2 (1 H, dd, J = 8.0; mass spectrum, m/z 305 (M^+); high resolution mass spectrum, obsd m/z 305.0885 ($C_{16}H_{19}NOS_2$ (M^+) requires 305.0908). Anal. Calcd for $C_{16}H_{19}NOS_2$: C, 62.95; H, 6.22; N, 4.59. Found: C, 63.35; H, 6.30; N, 4.15.

Compound 6: cis, mp 134–136 °C; IR ($CHCl_3$) 2240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65–1.85 (1 H, m), 1.85–2.05 (1 H, m), 2.1–2.25 (2 H, m), 2.5–2.6 (1 H, m), 2.7–3.0 (1 H, m), 3.79 (3 H, s), 4.16 (1 H, d, J = 11.0 Hz), 4.37 (1 H, dd, J = 6.0, 1.5 Hz), 6.66 (1 H, d, J = 3.0 Hz), 6.77 (1 H, dd, J = 9.0, 3.0), 7.16 (1 H, d, J = 9.0 Hz); mass spectrum, m/z 305 (M^+); high resolution mass spectrum, obsd m/z 305.0907 ($C_{16}H_{19}NOS_2$ (M^+) requires 305.0908). Anal. Calcd for $C_{16}H_{19}NOS_2$: C, 62.95; H, 6.22; N, 4.59. Found: C, 63.10; H, 6.27; N, 4.08.

Compound 7: cis, mp 183–185 °C; IR ($CHCl_3$) 2240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.7–2.0 (2 H, m), 2.1–2.25 (2 H, m), 2.5–2.6 (1 H, m), 2.8–3.0 (6 H, m), 3.85 (3 H, s), 3.9 (3 H, s), 4.15 (1 H, d,

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(7) As would be expected, the diphenyl thioacetal anion[a] as well as the 2-phenyl-1,3-dithiane anion[b] reacts in a similar fashion affording only 1,4-addition products in 68% and 83% yields on addition to **3**. (a) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1966**, *31*, 4097. (b) Corey, E. J.; Erickson, B. W. *J. Org. Chem.* **1971**, *36*, 3553.

(8) The unsaturated nitriles were prepared in two steps from the corresponding tetralones by the addition of trimethylsilyl-protected cyanohydrin (8a) by using MeOH/HCl or $POCl_3$/pyridine (8b). (a) Evans, A.; Carrol, G. *J. Chem. Soc. Chem. Commun.* **1973**, 55. (b) Oda, M.; Yamamuro, A.; Watabe, T. *Chem. Lett.* **1979**, 1327.

(9) Corey, E. J.; Hua, Dug H.; Bai-Chuan, P.; Seitz, S. P. *J. Am. Chem. Soc.* **1982**, *104*, 6819.

J = 11.0 Hz), 4.32 (1 H, dd, *J* = 6.0, 1.5 Hz), 6.61 (1 H, s), 6.7 (1 H, s); mass spectrum, *m/z* 335 (M^+); high resolution mass spectrum obsd *m/z* 335.1024 ($C_{17}H_{21}NO_2S_2$ (M^+) requires 335.1014). Anal. Calcd for $C_{17}H_{21}NO_2S_2$: C, 60.89; H, 6.26; N, 4.17. Found: C, 60.69; H, 6.36; N, 4.04.

1,4-Addition product of 1-cyclohexenecarbonitrile (cf. eq 1, $R_1 = R_2$ = H): cis, mp 133–134 °C; IR ($CHCl_3$) 2240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17–1.4 (3 H, m), 1.55–1.68 (1 H, m), 1.72–1.92 (3 H, m), 1.94–2.05 (2 H, m), 2.1–2.2 (2 H, m), 2.7–2.85 (1 H, m), 2.85–3.0 (4 H, m), 3.42 (1 H, ddd, *J* = 3.5, 2.9, 1.4,2.9 Hz), 4.0 (1 H, d, *J* = 10.8 Hz); mass spectrum, *m/z* 227 (M^+); high resolution mass spectrum, obsd *m/z* 227.0791 ($C_{11}H_{17}NS_2$ (M^+) requires 227.0801); trans, mp 120–131 °C; IR ($CHCl_3$) 2240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17–1.3 (3 H, m), 1.55–1.68 (1 H, m), 1.71–1.92 (3 H, m), 1.93–2.05 (2 H, m) 2.1–2.2 (2 H, m), 2.7–2.85 (1 H, m), 2 .85–2.95 (3 H, m), 3.04 (1 H, ddd, *J* = 12.1, 11.1, 4.0 Hz), 4.56 (1 H, d, *J* = 3.6 Hz).

Hydrolysis of the Product 3. A mixture of the dithiane (335 mg, 10 mmol), mercuric chloride (1.62 g, 6 mmol), and calcium carbonate (800 mg, 8 mmol) in aqueous 80% acetonitrile (20 mL) was allowed to stir at ambient temperature for 10 h. The dithiane–mercuric chloride complex separated as a flocculent white precipitate. The mixture was stirred and heated at 80 °C under nitrogen for 12 h, cooled, diluted with 150 mL of methylene chloride, and passed through a 1 in. silica bed, and the solvent was evaporated. The residue was extracted with ether/hexane, and the organic layer was washed with saturated NH_4Cl and brine, dried ($MgSO_4$), and evaporated to afford a colorless oil 90%: IR ($CHCl_3$) 2245, 1720 cm^{-1}; ^1H NMR δ 1.8–1.95 (1 H, m), 2.3–2.45 (1 H, m), 2.85 (2 H, t, *J* = 7.0 Hz), 3.05–3.1 (1 H, m), 4.3 (1 H, d, *J* = 7.0 Hz), 6.9 (1 H, d, *J* = 8.0 Hz), 7.2 (1 H, d, *J* = 8.0 Hz), 9.8 (1 H, s); mass spectrum, *m/z* 245 (M^+), 216 (M^+ – CHO).

Acknowledgment. We thank Dr. Steven Crowley for chemical literature searches and Ms. Joan Doerrer for typing this manuscript.

Registry No. 1, 36049-90-8; *cis*-**2**, 98218-24-7; *trans*-**3**, 98218-25-8; *cis*-**4**, 98218-26-9; *trans*-**4**, 98218-27-0; *cis*-**5**, 98218-28-1; *trans*-**5**, 98218-29-2; *cis*-**6**, 98218-30-5; *trans*-**6**, 98218-31-6; *cis*-**7**, 98218-32-7; *trans*-**7**, 98218-33-8; *cis*-**8**, 98218-34-9; *trans*-**8**, 98218-35-0; **9**, 98218-36-1; 1,3-dithiane, 505-23-7; 3,4-dihydro-5,6-dimethoxy-1-naphthalenecarbonitrile, 89047-59-6; 3,4-dihydro-1-naphthalenecarbonitrile, 73599-59-4; 3,4-dihydro-5-methoxy-1-naphthalenecarbonitrile, 98218-37-2; 3,4-dihydro-6-methoxy-1-naphthalenecarbonitrile, 6398-50-1; 3,4-dihydro-6,7-dimethoxy-1-naphthalenecarbonitrile, 85221-58-5; 1-cyclohexenecarbonitrile, 1855-63-6; *cis*-2-(1,3-dithian-2-yl)cyclohexanecarbonitrile, 98218-38-3; *trans*-2-(1,3-dithian-2-yl)cyclohexanecarbonitrile, 98218-39-4; *trans*-1-cyano-1,2,3,4-tetrahydro-5,6-dimethoxy-2-naphthalenecarboxaldehyde, 98218-40-7.

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^{60}Co γ-Irradiation:[1] Homolytic Alkylation of Methyl Nicotinate

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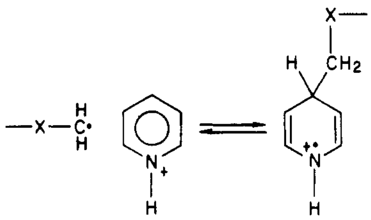
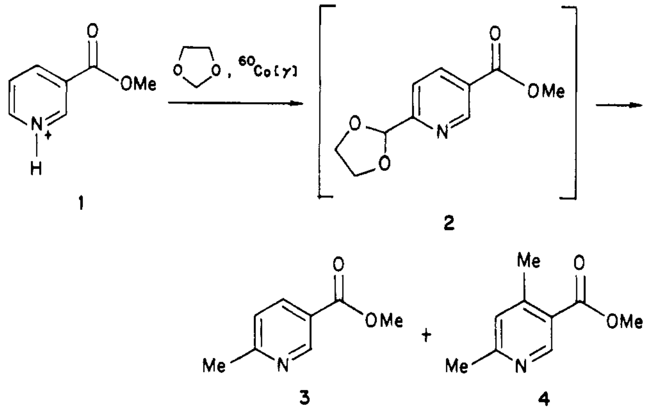
Received February 11, 1985

Recent developments in homolytic substitution reactions induced by chemical[2–4] and photochemical[5,6] methods have generated new, simple avenues for rapid direct functionalization of heterocycles. In contrast, γ-irradiation-induced alkylation and hydroxyalkylation procedures have been less frequently employed[7,8] due to limited availability of radiation sources. As with many radical processes, the indiscriminate nature of the reactive intermediate can lead to a product distribution with limited synthetic value. However, the nucleophilic character[9] of radicals, generated via γ-irradiation and specifically those with α-heteroatoms,[10–12] can be utilized for the homolytic alkylation of protonated electron-deficient heteroaromatics.[7,8,13]



During our evaluation of new methodologies to functionalize alkyl 6-methylnicotinates, the direct transformation of **1** to acetal **2** by a γ-ray-induced alkylation was attempted. We herein report the facile methylation of protonated methyl nicotinate via ^{60}Co γ-ray-induced homolytic substitution by 1,3-dioxolane.



Treatment of a deaerated solution of methyl nicotinate (**1**), sulfuric acid, and dioxolane with ^{60}Co γ-irradiation (overall dose; 1.0 × 10^7 rad) gave a clean mixture of methyl 6-methyl- (**3**, 21%)[13] and methyl 4,6-dimethyl-(**4**, 5%)[7,8] nicotinates. The only other ingredient was unchanged starting ester (71%). In contrast, analogous chemically induced reactions[2–4] gave exclusively the acetal products. On the basis of the work of Sugimori[7,8] in which **1** was γ-irradiated in the presence of diverse alcohols, mixtures of alkyl and α-hydroxyalkyl derivatives were realized; in unexpected contrast, no trace of acetal products was herein observed.

Apparently under the harsh "mega dose" γ-irradiation[7,8] conditions and a readily available hydrogen atom source, the acetal **2** can undergo a facile double homolytic cleav-

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[1] Chemistry of Heterocyclic Compounds Series, 110. For previous related part in the series, see: Newkome, G. R.; Kiefer, G. E.; Majestic, V. K. *J. Org. Chem.* **1983**, *48*, 5112.

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