Methyl ether 3a was prepared in the standard way by reaction of 3 with diazomethane in tetrahydrofuran: mp 170-171° (CH<sub>2</sub>Cl<sub>2</sub>-hexane); nmr (CDCl<sub>3</sub>)  $\delta$  8.09 (m,  $W_{1/2} = 11$  Hz,<sup>12</sup> 2 H), (CH<sub>2</sub>O<sub>2</sub>-nexture); nifr (CDC<sub>13</sub>)  $\delta$  8.09 (m,  $W_{1/2} = 11 \text{ Hz}, 2 \text{ H})$ , 7.74 (m, 2 H), 7.50 (m, 6 H), 4.52 (q, J = 7 Hz, 2 H), 3.31 (s, 3 H), and 1.43 (t, J = 7 Hz, 3 H). Anal. Calcd for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>: C, 68.96; H, 4.63; N, 8.04. Found: C, 68.41; H, 5.10; N, 8.01.

The benzene mother liquor (above) was concentrated and the residue was taken up in 200 ml of boiling ethanol. After standing overnight the solution deposited 4.5 g (23%) of unreacted 1. The solution was concentrated to 75 ml and chilled overnight to yield 4.9 g of a tan powder that was recrystallized from  $C_2H_5OH$ . then from benzene-Skellysolve B to yield pale yellow needles of 2: mp 124-126°; nmr (CDCl<sub>3</sub>)  $\delta$  7.90 (s, 1), 7.2-7.6 (m, 11), 4.1-4.5 (overlapping m, 4), 1.2-1.4 (overlapping m, 6); mass spectrum m/e (rel intensity) 418 (12), 373 (22), 344 (10), 317 (10), 215 (10), 106 (11), 105 (100), 77 (22).

Anal. Calcd for C25H22O6: C, 71.76; H, 5.30. Found: C, 71.33; H, 5.48.

The ethanol mother liquor was evaporated to dryness. The residue was dissolved in 1:1 benzene-Skellysolve B and placed on a silica gel column. Elution with the same solvent mixture yielded an additional 0.18 g of 2, total yield 5.08 g (13%).

Elution with benzene yielded a yellow oil which deposited 0.66 g of yellow crystals from ethanol: mp 189-191°; nmr (CDCl<sub>3</sub>) § 6.9-8.1 (m, 20), 5.13 (s, 1), 4.99 (s, 1), 3.75-4.40 (overlapping m, 7), 1.18 (t, J = 7 Hz, 3), 1.00 (t, J = 7 Hz, 3), 0.89 (t, J = 7 Hz, 3); mass spectrum m/e (rel intensity) 738 (8), 321 (41), 320 (16), 319 (9), 291 (24), 105 (100), 77 (11).

Anal. Calcd for C45H38O10: C, 73.15; H, 5.20. Found: C, 73.03; H, 5.40.

2-Ethoxycarbonyl-5-hydroxy-4,6-diphenylpyrimidine (4).—A mixture of 1.5 g (4.46 mmol) of 3 and 2 ml (10 mmol) of phosphorus trichloride in 20 ml of CHCl<sub>8</sub> was allowed to stand at room temperature overnight. Evaporation of the solvent and recrystallization of the residue from ethanol produced 1 g (76%)of white crystals of 4, mp 227-228°. Traces of this compound were also found in the eluent from the silica gel column separation of the product from the ethyl propiolate reaction.

of the product from the ethyl prophotate reaction. Anal. Calcd for  $C_{19}H_{16}N_2O_3$ : C, 71.23; H, 5.03; N, 8.80. Found: C, 70.05; H, 5.21; N, 8.60. The acctate ester of 4 had mp 113-115° ( $C_2H_5OH$ ).

Anal. Calcd for  $C_{21}H_{18}N_2O_4$ : C, 69.20; H, 5.01; N, 7.73. Found: C, 69.33; H, 5.12; N, 7.50.

Methyl ether 4a had mp 117-119° (C<sub>2</sub>H<sub>5</sub>OH); nmr (CDCl<sub>3</sub>) δ 8.17 (m,  $W_{1/2} = 11 \text{ Hz}$ , <sup>12</sup> 4 H), 7.50 (m, 6 H), 4.51 (q, J = 7 Hz, 2 H), 3.38 (s, 3 H), and 1.45 (t, J = 7 Hz, 3 H); mass spectrum m/e (rel intensity) 334 (32), 213 (14), 262 (100), 261 (29), 129 (10), 89 (16), 77 (12).

Anal. Calcd for  $C_{20}H_{18}N_2O_3$ : C, 71.84; H, 5.43; N, 8.38. Found: C, 71.73; H, 5.55; N, 8.29.

5-Hydroxy-4,6-diphenylpyrimidine (5).---A suspension of 1.0 g (3.2 mmol) of 4 in 25 ml of 20% aqueous KOH was heated on a steam bath for 1 hr. The solution was cooled and acidified to congo red and the solid that separated was collected. It was dried and heated without solvent at 200° for 30 min. Recrystallization of the residue from CH2Cl2-hexane gave a pale yellow solid: mp 181–182°; ir (KBr) 3  $\mu$  (broad), 1570, 1550, 1520 cm<sup>-1</sup>; mass spectrum m/e (rel intensity) 248 (82), 247 (100).

Anal. Calcd for C16H12N2O: C, 77.39; H, 4.87; N, 11.28. Found: C, 77.09; H, 5.08; H, 11.50.

Methyl ether 5a had mp 69-70° from petroleum ether (bp 30-60°); nmr (CDCl<sub>3</sub>)  $\delta$  9.09 (s, 1 H), 8.12 (m,  $W_{1/2} = 11$  Hz, 4 H), 7.50 (m, 6 H), and 3.35 (s, 3 H); mass spectrum m/e(rel intensity) 263 (13), 262 (73), 261 (100), 89 (28).

Anal. Caled for  $C_{17}H_{14}N_{2}O$ : C, 77.84; H, 5.38; N, 10.68. Found: C, 78.35; H, 5.45; N, 10.79.

Dimethyl 4,6-Diphenyl-5-pyrimidyl Phosphate (6).—A mixture of 0.3 g (1.2 mmol) of 4,6-diphenyl-5-hydroxypyrimidine (5) and 5 ml of POCl<sub>3</sub> were heated under reflux for 1 hr. After evapo ration of excess POCl<sub>3</sub> the residue was dissolved in 5 ml of CH<sub>3</sub>OH and this solution was diluted with water. The white solid that separated was recrystallized from  $CH_3OH-H_2O$ , mp 123-125°.

Anal. Calcd for  $C_{18}H_{17}N_2O_4P$ : C, 60.67; H, 4.82; N, 7.86. Found: C, 60.87; H, 4.86; N, 7.87.

4,6-Diphenylpyrimidine (7).—Small pieces of sodium (45 mg) were added to a refluxing solution of 356 mg of phosphate 6 in liquid NH<sub>3</sub>-tetrahydrofuran. After the usual work-up, 132 mg

(12) Band width at half height.

(57%) of 7, mp 99.5-101° (n-C<sub>6</sub>H<sub>14</sub>), was obtained. It was identical with an authentic sample<sup>8</sup> (mixture melting point, ir spectra)

Ethyl 2-Hydroxy-4.6-diphenyl-1.6-dihydropyrimidine-5-carboxylate.—A mixture of 10.6 g (0.1 mol) of benzaldehyde and 12.0 g (0.2 mol) of urea in 100 ml of C<sub>2</sub>H<sub>5</sub>OH was treated with 8 ml of concentrated HCl and warmed on a steam bath for 15 min. Ethyl benzoylacetate,  $19.2~{\rm g}~(0.1~{\rm mol})$ , was added and the solution was heated under reflux overnight. The solvent was evaporated and the residual oil was crystallized from ethanolhexane to yield 17.0 g (53%) of pale yellow crystals. Upon recrystallization from ethanol, two forms were observed, mp 158-159° and mp 172-173°. The low-melting modification partially resolidified on heating above its melting point and finally melted at  $172-173^{\circ}$ : nmr (CDCl<sub>3</sub>)  $\delta$  7.90 (br s, 1), 7.17– 7.50 (m, 10), 6.68 (br s, 1), 5.40 (br d, J = 3 Hz, 1 H), 3.81 (q, J = 7 Hz, 2 H), 0.80 (t, J = 7 Hz, 3 H).

Anal. Calcd for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.56; H, 5.45; N, 8.57.

Ethyl 2-Hydroxy-4,6-diphenylpyrimidine-5-carboxylate.--A solution of 3.22 g (0.01 mol) of the dihydro compound and 1.8 g (0.011 mol) of Br<sub>2</sub> in 30 ml of acetic acid was heated under reflux overnight. The solvent was evaporated in vacuo to yield a mixture of the pyrimidine and its dibromo intermediate. The dehydrobromination was completed by dissolving the mixture in ethanol and stirring overnight in the presence of excess solid K<sub>2</sub>CO<sub>3</sub> at room temperature. The mixture was filtered, and the filtrate was evaporated to yield 2.68 g (84%) of white solid. A sample was recrystallized from ethanol-water and sublimed at sample was recrystallized from ethaloi-water and solutiled at 180° (0.5 mm): mp 215-216°; nmr (CDCl<sub>3</sub>)  $\delta$  7.25-7.80 (m, 10 H), 3.90 (q, J = 7 Hz, 2 H), 0.83 (t, J = 7 Hz, 3 H) Anal. Calcd for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: C, 71.24; H, 5.03; N, 8.75. Found: C, 71.04; H, 5.12; N, 8.83.

**Registry No.**-1, 34982-07-5; 2, 34906-18-8; 3, 34906-19-9; 3a, 34906-20-2; 4, 34906-21-3; 4 acetate ester, 34906-22-4; 4a, 34906-23-5; 5, 34906-24-6; 5a, 34906-25-7; 6, 34906-26-8; 7, 3977-48-8; ethyl 2hydroxy-4,6-diphenyl-1,6-dihydropyrimidine-5-carboxvlate, 34906-28-0; ethyl 2-hydroxy-4,6-diphenylpyrimidine-5-carboxylate, 34906-29-1.

## New Synthetic Methods from Dithianes. A Convenient Oxidation of Aldehydes to **Acids and Esters**

ROBERT A. ELLISON,\* WARREN D. WOESSNER, AND CRAIG C. WILLIAMS

School of Pharmacy, University of Wisconsin, Madison, Wisconsin 53706

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The considerable literature on the chemistry of 2-lithio-1,3-dithianes which has been accumulating recently<sup>1</sup> attests to their great utility in organic synthesis. This contrasts with the present utility of metalated orthothioformates which suffer from being simultaneously less reactive and somewhat unstable.<sup>2</sup> Furthermore, neither their hydrolysis<sup>2</sup> nor alcoholysis<sup>3</sup> has produced outstanding yields. We wish to report a combination of reactions which leads from 2-substituted 1,3-dithianes to carboxylic acids and esters in good overall yields via 2-substituted 2-methylthio-1,3dithianes.

Treatment of 2-lithio 2-substituted 1,3-dithianes

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		Orthothio- formates <b>3</b>	Yield,° %	Ethyl esters <b>5</b> <sup>b</sup> reflux time, hr	Yield, <sup>d</sup> %	Acids <b>4</b> reflux time, hr	$\stackrel{\mathrm{Yield},d}{\%}$
R	Reaction time, hr	reaction temp, °C					
Phenyl	2	-78	94.5	4.5	92.4	24	65
n-Butyl	3	-20	89.8	4.0	99.0	25	40
trans-Cinnamyl®	$^{2}$	-78	90.0	7.5	92.1	21	46

<sup>a</sup> All new compounds were characterized by nmr and infrared spectra as well as satisfactory elemental analyses. <sup>b</sup> Methyl benzoate was prepared in 95% yield by refluxing for 4.5 hr in 30% aqueous methanol. <sup>c</sup> Crude yield from 1. <sup>d</sup> Crude yield from 3. <sup>e</sup> All trans by nmr analysis.

(2) in tetrahydrofuran with 1 equiv of methyl disulfide gave high yields of the corresponding orthothioformates (3).<sup>4</sup> These were converted in similar yields



to the corresponding esters by refluxing in aqueous alcohols in the presence of mercury(II) salts for periods of 4.0-7.5 hr. Representative examples are shown in Table I. In keeping with the lower acidity of the butyl derivative (1, R = n-butyl), reaction times to form the anion were substantially longer than with the benzylic analogs. The orthothioformates were readily recognizable due to a three-proton singlet in their nmr spectra at about  $\delta$  2.00 corresponding to the S-methyl protons. Interestingly, although the styryl derivative 2 (R =  $C_6H_5CH=CH$ -) could in principle be expected to give two methylthic adducts (6 or 7), nmr analysis of the product obtained under our conditions showed it to be entirely 6. Furthermore, treatment of this anion with deuterium oxide resulted in recovery of only monodeuterated starting material  $(1, R = C_{\theta}H_{\delta}CH=CH_{-}, R' = D)$ . As may have been expected, there was no evidence for cis product. However, it was subsequently found that 7 may be



obtained by pyrolysis of 6. Distillation of 6 at  $190^{\circ}$ and  $50_{-\mu}$  pressure yielded a 2.6:7.4 mixture of 6 and 7 by nmr integration. In accord with expectation, alcoholysis of this mixture yielded typical yields of ethyl cinnamate. It should also be noted that at least in the cinnamyl case alkoxymercuration of the double bond either does not occur or is reversible under the reaction conditions. As the beginning of an exploration of the scope of the alcoholysis, the phenyl orthothioformate was treated with *tert*-butyl alcohol under typical conditions. The reaction time to completion was much longer (*ca.* 70 hr) and gave the unexpected result of producing benzoic acid in 60% yield. Since we have demonstrated that *tert*-butyl benzoate is stable to the reaction conditions, it may be that in this case steric factors permit water to successfully compete with *tert*-butyl alcohol for reaction at the benzylic carbon.

The corresponding carboxylic acids were obtained in lower yield (Table I) by reaction of **3** in refluxing 35%aqueous acetone for 24 hr with mercury(II) salt catalysis. Considerable experimental variation in conditions did not improve these yields. The neutral material recovered from these reactions showed no starting material upon the analysis. We are exploring this reaction more thoroughly and will report more details in due course.

We expect the oxidative procedure we have described to be of value in systems which are sensitive to conventional oxidizing reagents and are continuing to explore further ramifications of this work.

#### **Experimental Section**

Nmr spectra were recorded on a Varian A-60A spectrometer and chemical shifts are reported in parts per million ( $\delta$ ) from internal tetramethylsilane. Infrared spectra were recorded on a Beckman IR-5A spectrometer. Melting points were taken with a Thomas-Hoover apparatus and are uncorrected. Deuterium oxide (99.7%) was purchased from Merck Sharp and Dohme, Canada. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. The 1,3-dithianes were prepared by the method of Seebach, *et al.*<sup>5</sup>

Ethyl Benzoate.—A solution of 2.0 g (10.68 mmol) of 2-phenyl-1,3-dithiane<sup>4</sup> in 20 ml of tetrahydrofuran in a 50-ml, two-neck, round-bottomed flask equipped with magnetic stirring, nitrogen inlet, and septum cap was cooled to  $-78^{\circ}$ , and 5.70 ml of 2.24 M n-butyllithium in hexane was injected over 25 min. The clear yellow solution was stirred for 2 hr at  $-78^\circ$ , and then 1.73 ml (19.35 mmol) of methyl disulfide was injected over 10 min. The reaction mixture was allowed to warm to  $25^{\circ}$  and then poured into 100 ml of 0.05 N hydrochloric acid. Tetrahydrofuran was removed by rotary evaporation and the remaining aqueous solution was extracted with two 100-ml portions of 1:1 pentanemethylene chloride. The extracts were combined, washed with 10% aqueous sodium bicarbonate, water, and saturated brine, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and evaporated in vacuo to afford 2.44 g (94.5%) of 2-thiomethoxy-2-phenyl-1,3-dithiane as white plates:  $mp 67-71^{\circ}$  (from methanol, 76-78°); nmr (CCl<sub>4</sub>)  $\delta$  1.90 (s, 3 H, SCH<sub>3</sub>). Anal. Calcd: C, 54.50; H, 5.82. Found: C, 54.70, H, 5.86. Crude product (238 mg, 0.98 mmol) was placed in a 50-ml round-bottom flask with 27 ml of 95% ethanol, 1.14 g (4.20 mmol) of mercuric chloride, and 353 mg (1.62 mmol) of mercuric oxide and refluxed for 4.5 hr under nitrogen. The mixture was filtered and the solid residue was washed with two 20-ml portions of methylene chloride. The filtrate was diluted with 75 ml of water and extracted with two 75-ml portions of methylene chloride. These extracts were combined, washed with 4 Maqueous ammonium chloride and saturated brine, dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and evaporated in vacuo to yield 133 mg of ethyl benzoate (92.4%) as a clear oil. Characterization by nmr and infrared spectroscopy indicated no significant impurities: ir

<sup>(4)</sup> Although it is not an oxidative procedure, we have found that orthothioformates may also be obtained in high yields by treating 2-lithio-2-thiomethoxy-1,3-dithiane with alkyl halides under carefully controlled conditions. See Experimental Section for details.

<sup>(5)</sup> D. Seebach, B. W. Erickson, and G. Singh, J. Org. Chem., **31**, 4303 (1966).

Notes

(CHCl<sub>3</sub>) 5.82  $\mu$ ; nmr (CCl<sub>4</sub>)  $\delta$  1.40 (t, 3 H, J = 7.0 Hz), 4.37 (q, 2 H, J = 7.0 Hz).

Methyl Benzoate.---Treatment of 144 mg of phenyl orthothioformate with 665 mg of mercuric chloride and 213 mg of mercuric oxide in 14 ml of 7.7% aqueous methanol under conditions identical with those above yielded 66 mg (95.5%) of methyl benzoate: ir (CCl<sub>4</sub>) 5.78  $\mu$ , nmr (CDCl<sub>3</sub>)  $\delta$  3.89 (s, 3 H).

Ethyl Pentanoate.-Treatment of 1.88 g (8.46 mmol) of 2-butyl-1,3-dithiane in 20 ml of tetrahydrofuran with 5.70 ml (12.8 mmol) of n-butyllithium followed by 1.72 ml (19.35 mmol) of methyl disulfide in a manner identical with the above procedure yielded 2.13 g (89.8%) of crude orthothioformate derivative as an orange oil: nmr (CCl<sub>4</sub>)  $\delta$  2.00 (s, 3 H). Anal. Calcd: C, 48.60; H, 8.16. Found: C, 49.12; H, 8.15. Crude product (222 mg, 1 mmol) was refluxed for 4 hr in 27 ml of 95% ethanol with 1.14 g of mercuric chloride and 353 mg of mercuric oxide. Work-up as above yielded 132 mg (quantitative) of the ester as a clear, light brown oil: ir  $(CHCl_3)$  5.80  $\mu$ .

Ethyl Cinnamate.—A solution of 2.38 g (10.68 mmol) of 2-(βstyryl)-1,3-dithiane in 20 ml of tetrahydrofuran was treated with 5.70 ml (12.8 mmol) of n-butyllithium and subsequently with  $1.73~\mathrm{ml}$  (19.35 mmol) of methyl disulfide as above to give  $2.56~\mathrm{g}$ (90%) of the orthothioformate derivative as a clear yellow oil: mmr (CDCl<sub>3</sub>)  $\delta$  2.04 (s, 3 H), 6.30 (d, 1 H, J = 10.0 Hz), 6.90 (d, 1 H, J = 10.0 Hz). Anal. Calcd: C, 58.16; H, 6.01. Found: 57.80; H, 5.83. Crude product (268 mg, 1 mmol) was refluxed for 7.5 hr in 95% ethanol with 1.14 g of mercuric chloride and 353 mg of mercuric oxide. The standard work-up yielded and 355 mg of mercuric oxide. The standard work-up yielded 162 mg (92.1%) of oily ethyl cinnamate: nmr (CCl<sub>4</sub>) 1.24 (t, 3 H, J = 7.0 Hz), 4.15 (q, 2 H, J = 7.0 Hz), 6.37 (d, 1 H, J =16.5 Hz), 7.63 (d, 1 H, J = 16.5 Hz); ir (CCl<sub>4</sub>) 5.82, 6.10  $\mu$ . Isomerization of 6 to 7.—The cinnamyl orthothioformate was

bulb to bulb distilled in a Kugelrohr apparatus at 192° and 50  $\mu$ to give an oil. The nmr spectrum (CDCl<sub>3</sub>) of this material showed peaks corresponding to a small amount of 9 and new resonances at  $\delta$  1.98 (s, 3 H), 5.08 (d, 1, H, J = 10.0 Hz), and 6.05 (d, 1 H, J = 10.0 Hz) which were attributed to isomer 10. Integration of the spectrum showed 9 and 10 to be present in a ratio of 2.6:7.4.

Benzoic Acid.-Phenyl orthothioformate 3 (238 mg, 1 mmol) was refluxed in 27 ml of 35% aqueous acetone with 1.14 g of The mercuric chloride and 353 mg of mercuric oxide for 24 hr. reaction was cooled and worked up in a manner identical with the esterification reaction. The methylene chloride extract was washed with 10% aqueous sodium carbonate. Acidification of the aqueous layer followed by extraction with methylene chloride yielded 80 mg (69%) of benzoic acid which was homogeneous in the nmr spectrum, mp 122°.

Cinnamic Acid.-The cinnamyl orthothioformate (508 mg, 2 mmol) was similarly refluxed in 50 ml of 35% aqueous acetone with 1.63 g of mercuric chloride and 1.30 g of mercuric oxide for 21 hr. Typical work-up yielded 131 mg (46%) of cinnamic acid: mp 133-144°; nmr (CDCl<sub>2</sub>)  $\delta$  6.55 (d, 1 H, J = 16.5 Hz), 7.88 (d, 1 H, J = 16.5 Hz), 10.7 (s, 1 H); ir (CDCl<sub>3</sub>) 5.93, 6.13  $\mu$ .

Pentanoic Acid .-- Butyl orthothioformate (224 mg, 1 mmol) was similarly refluxed in 25 ml of 35% aqueous acetone with 823 mg of mercuric chloride and 658 mg of mercuric oxide for 25 hr. Typical work-up yielded 42 mg (40%) of oily pentanoic acid: nmr (CDCl<sub>8</sub>)  $\delta$  9.58 (s, 1 H); ir (CDCl<sub>8</sub>) 3.05-4.35, 5.85  $\mu$ .

Reaction of Phenyl Orthothioformate (3, R = Phenyl) with tert-Butyl Alcohol.-A mixture of 142 mg (0.6 mmol) of phenyl orthothioformate, 665 mg of mercuric chloride, and 213 mg of mercuric oxide was refluxed with 12 ml of tert-butyl alcohol and 1 ml of water for 67.5 hr. The reaction was cooled and filtered and the residue was washed with methylene chloride. The filtrate was washed with 20% aqueous ammonium chloride and saturated aqueous sodium chloride, dried, and evaporated to yield 62 mg of amorphous solid. This material was dissolved in methylene chloride and extracted with 10% aqueous sodium bicarbonate. Acidification of the aqueous layer followed by methylene chloride extraction yielded 43 mg (60.3%) of benzoic acid, mp 119-120°

Stability of tert-Butyl Benzoate .--- tert-Butyl benzoate was prepared according to procedure 1 of Raha.<sup>6</sup> *tert*-Butyl benzoate (173 mg, 1 mmol) was dissolved in 24 ml of *tert*-butyl alcohol and 2 ml of distilled water with 1.4 g of mercuric chloride and 430 mg of mercuric oxide. The mixture was refluxed for 72 hr and then worked up as above to give 172 mg of recovered tert-butyl benzoate. No additional products were evident in the nmr spectrum.

Orthothioformates via 2-Thiomethoxy-1.3-dithiane. Ethyl Pentanoate .--- 2-Thiomethoxy-1,3-dithiane was prepared from 1,3-dithiane (1.0g, 8.32 mmol) by treatment with n-butyllithium (4.0 ml, 8.8 mmol) followed by methyl disulfide (0.752 ml, 8.5 mmol) in a manner identical with that above. The crude product was isolated as an oil (1.72 g, 92%). To 168 mg (1.01mmol) of crude thiomethoxy derivative in 5 ml of tetrahydrofuran at  $-20^{\circ}$  was injected 0.5 ml (1.02 mmol) of *n*-butyllithium over a period of 1 min. After 3 min of stirring, 0.114 ml (1.0 mmol) of methyl iodide was added and stirring was continued for 2.5 hr. The reaction was brought to 0° and stored for 17 hr followed by 3 hr at 25°. The reaction was subjected to the usual work-up to yield 175 mg of yellow oil with properties identical with those of the butyl orthothioformate previously described. Treatment of 166 mg of this oil with 95% ethanol under typical alcoholysis conditions yielded crude ethyl pentanoate (94 mg, 97%).

Registry No.—Ethyl benzoate, 93-89-0; 2-thiomethoxy-2-phenyl-1,3-dithiane, 34858-82-7; methyl benzoate, 93-58-3; ethyl pentanoate, 539-82-2; ethyl cinnamate, 4192-77-2; benzoic acid, 65-85-0; cinnamic acid. 621-82-9: pentanoic acid. 109-52-4.

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# A Nuclear Magnetic Resonance Technique for **Distinguishing Isomers of 3,5-Disubstituted** Nortricyclenes<sup>1a</sup>

Boris Franzus,\* Stephen Wu,<sup>16</sup> W. C. Baird, Jr.,<sup>10</sup> and MONTE L. SCHEINBAUM

Department of Chemistry, East Tennessee State University, Johnson City, Tennessee 36701

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Known techniques for assigning relative stereochemistry to the 3,5 positions of nortricyclene derivatives are generally limited to compounds with a "trans" arrangement of substituent groups as in 1a.2-6 Nmr techniques for distinguishing between the "cis" isomers **1b** and **1c** (X = Y) have not been reported.

The symmetry of the parent nortricyclene system includes a threefold axis of rotation through the bridgehead carbon  $(C_4)$  and the center of the cyclopropyl ring ( $C_{3v}$  symmetry). The same sets of rules employed in the interpretation of spectra of norbornene and norbornadiene systems do not apply to the nortricyclyl system. The terms endo and exo do not have the same significance in considering the nortricyclene system, for which of the three carbons chosen as the

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<sup>(1) (</sup>a) Presented in part at the Southeast Regional Meeting of the American Chemical Society, Nashville, Tenn., Nov 4-6, 1971; (b) Abstracted in part from the M.S. Thesis of Stephen Wu, East Tennessee State University, Aug 1970; (c) Corporate Research Laboratories, Esso Research and Engineering Company, Linden, N. J.

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