

CARBON-ALKYLATION, ARYLATION AND VINYLATION OF NITRONATE IONS  
WITH ORGANOTHALLIUM(III) COMPOUNDS: ELECTRON-TRANSFER  
ACTIVATION OF THE Tl-C BOND

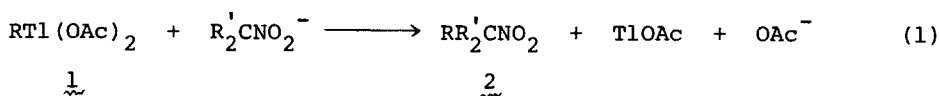
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The reaction of alkyl, aryl and vinylthallium(III) diacetates with nitronate ions gives moderate to good yields of the carbon-carbon bonded products. The reaction of the alkyl and arylthallium(III) analogs proceeds through radical intermediates which are generated by electron-transfer activation of the thallium-carbon bond

There is growing interest in developing those electrophiles which are capable of C-alkylating nitronate ions.<sup>1</sup> Among organometallic electrophiles, alkylmercury(II) compounds have been shown<sup>2</sup> to give the C-alkylated products via the S<sub>RN</sub>1 pathway only under irradiation of light, but aryl and vinylmercurials failed to couple with the nitronate ions. Kozyrod and Pinhey described,<sup>3</sup> without mechanistic details, a successful C-arylation of nitroalkanes with aryllead(IV) compounds, a class of reagents of rather limited accessibility. We report here facile C-C bond formation in the reaction of alkyl, aryl and vinylthallium(III) compounds with the nitronate ions with the reaction path depending on the nature of the organic groups attached to thallium.

Results of the reaction between representative organothallium(III) compounds and the nitronate ions (eq. 1)<sup>4</sup> are shown in the Table. The product yields shown in the Table are, except where noted, those from the reaction carried out under normal room lights.

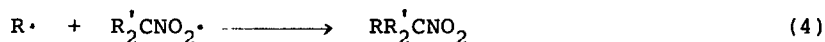
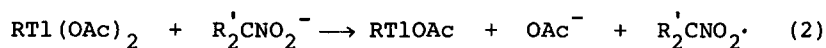


R = alkyl

The reaction of the alkylthallium(III) analogs proceeded cleanly in DMSO and methanol. In THF a higher amount of PhCH(OMe)CH<sub>3</sub> than the coupling product was formed from 1a. Exposure of the reaction mixture in DMSO to oxygen reduced the yield of 2 to some extent. Spin-trapping experiments employing 1a, Me<sub>2</sub>CNO<sub>2</sub><sup>-</sup>Li and perdeuterio-nitrosodurene in MeOH/MeCN (1:1) allowed us to observe the esr signals due to the adduct, C<sub>6</sub>H(CD<sub>3</sub>)<sub>4</sub>N(O·)CH<sub>2</sub>CH(OMe)Ph.<sup>5</sup> Most significantly,

the reaction of  $\text{Me}_2\text{CNO}_2\text{Li}$  with the stereoisomer, threo- $\text{PhCH}(\text{OMe})\text{CHDTl}(\text{OAc})_2$  1a-d<sup>6</sup> afforded  $\text{PhCH}(\text{OMe})\text{CHDCMe}_2(\text{NO}_2)$  of which the threo/erythro ratio was deduced by <sup>1</sup>H nmr spectroscopy<sup>7</sup> as unity, confirming complete epimerization at the  $\alpha$ -carbon. From these results intervention of the alkyl radical intermediate in the reaction of eq. 1 is apparent.

Although the light does have an accelerating effect on the reaction of 1a with  $\text{Me}_2\text{CNO}_2^-$ , high yields of the coupling product could be obtained even from the reaction in DMSO carried out in the complete dark (90 % at 65°C for 3 h, or 68 % at room temperature for 10 days). It is of particular relevance in deducing the pathways involved in this dark reaction that addition of galvinoxyl or *m*-dinitrobenzene (both inhibitors of the  $\text{S}_{\text{RN}}1$  path) in up to 10 mol % amount, or performing the reaction under oxygen scarcely affected the rate of the reaction, and yet stereochemical experiments employing 1a-d both at 65°C and room temperature again revealed complete epimerization at the  $\alpha$ -carbon. Thus, the most probable sequence in the reaction of eq. 1 (R= alkyl) in the dark is eq. 2-4. It may well be that the homolysis of the Tl-C bond through electron-transfer interaction<sup>8</sup> with the nitronate ions takes place with such facility as to allow the alkyl and the nitronate radicals to combine within the solvent cage. A similar non-chain radical coupling mechanism was proposed to operate

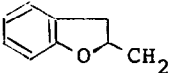


in the C-alkylation of the nitronate ions with N-alkylpyridinium ions,<sup>1</sup> but no direct evidence for the alkyl radical intermediates was provided

R= aryl

In the reaction of the arylthallium(III) analogs with  $\text{Me}_2\text{CNO}_2^-$  in methanol,<sup>9</sup> somewhat higher yields of the coupling products were formed under irradiation of a Xenon lamp as compared to the product yields obtained without irradiation<sup>10</sup> Increase in the concentration of  $\text{Me}_2\text{CNO}_2\text{Li}$  also raised the yield of 2. The balance of the coupling products in the photoreaction is accounted for mostly by aromatic hydrocarbons (RH) which are the principal products in the photolysis of the arylthallium(III) diacetates in the absence of  $\text{Me}_2\text{CNO}_2\text{Li}$ . That aryl radical intermediates participate, more or less, in the reaction of eq. 1 is apparent in view of the observation of the esr signals due to  $\text{C}_6\text{HMe}_4\text{N}(\text{O})\text{C}_6\text{H}_5$ <sup>11</sup> from a reaction mixture containing 1d,  $\text{Me}_2\text{CNO}_2\text{Li}$  and nitrosodurene in MeOH/MeCN (without irradiation). However, since the photoreaction of 1c-1e with  $\text{Me}_2\text{CNO}_2\text{Li}$  under oxygen did not suppress the formation of the coupling products to a very significant extent, the  $\text{S}_{\text{RN}}1$  path similar to that proposed in the alkylmercurials<sup>2</sup>

Table. Reaction of Organothallium(IJI) Compounds,  $\text{RTl}(\text{OAc})_2$  with Nitronate Ions,  $\text{R}_2'\text{CNO}_2^-$ .<sup>a</sup>

<u>R</u>	<u>R</u> ' <sub>2</sub>	Solvent	Time (h)	Yield (%) of $\text{RR}_2'\text{CNO}_2$ <sup>b</sup>	
<u>1a</u>	$\text{PhCH}(\text{OMe})\text{CH}_2$	$\text{Me}_2$	$\text{MeOH}$	6	90 <sup>c,d</sup>
			$\text{DMSO}$	3	91 <sup>e</sup>
			$\text{THF}$	3	22 <sup>f</sup>
		$(\text{CH}_2)_5$	$\text{DMSO}$	3	58
<u>1b</u>		$\text{Me}_2$	$\text{DMSO}$	3	91
		$(\text{CH}_2)_5$	$\text{DMSO}$	3	60
<u>1c</u>	<u>p</u> - $\text{MeC}_6\text{H}_4$	$\text{Me}_2$	$\text{MeOH}$	6	68 <sup>c,g,h,1</sup>
<u>1d</u>	$\text{C}_6\text{H}_5$	$\text{Me}_2$	$\text{MeOH}$	6	60 <sup>c</sup>
<u>1e</u>	<u>p</u> - $\text{ClC}_6\text{H}_4$	$\text{Me}_2$	$\text{MeOH}$	6	70 <sup>c</sup>
<u>1f</u>	$\text{PhCH}=\text{CH}$	$\text{Me}_2$	$\text{DMSO}$	3	99
	(Z/E = 0/100)				(Z/E = 0/100)
	$\text{PhCH}=\text{CH}$	$\text{Me}_2$	$\text{DMSO}$	3	93
	(Z/E = 70/30)				(Z/E = 65/35)

a At room temperature under nitrogen.  $[\text{RTl}(\text{OAc})_2] = 0.1 \text{ mol/l}$ ,  $[\text{R}_2'\text{CNO}_2\text{Li}] = 0.3 \text{ mol/l}$  (1a, 1b, 1f), or  $0.6 \text{ mol/l}$  (1c-1e).

b NMR yields

c Under irradiation of a 500 W Xenon lamp in a pyrex glass tube.

d 32 % at 65°C without irradiation.

e 48 % under oxygen.

f At 65°C.  $\text{PhCH}(\text{OMe})\text{CH}_3$ , 34 %.

g 28 % at  $[\text{Me}_2\text{CNO}_2\text{Li}] = 0.1 \text{ mol/l}$  and 75 % at  $[\text{Me}_2\text{CNO}_2\text{Li}] = 1.0 \text{ mol/l}$ .

h 40 % at 65°C without irradiation

1 52 % under oxygen.

would have made only a minor, if any, contribution to the overall reaction of the arylthallium(III) compounds. Major parts of the reaction would be similar to eq. 2-4.

R= vinyl

In the reaction of eq. 1 (R= styryl), the light had little accelerating effect on the rate, and spin-trapping experiments employing nitrosodurene gave no definite esr signals indicative of the generation of radical intermediates. Nor was observed the reduction of the product yields in the reaction carried out under oxygen. Furthermore, the stereochemistry about the C=C bond was almost retained during the coupling reaction. These results may be consistent with nucleophilic substitution at the vinylic carbon, either in a single- or multi-step fashion.<sup>12</sup> E-But-1-enyl and E-hex-1-enylthallium(III) diacetates were not sufficiently reactive to  $\text{Me}_2\text{CNO}_2\text{Li}$  in the dark to give good yields of the coupling products, and photolyzing these reaction mixtures led to only complex product mixtures.

#### References and Notes

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3. R. P. Kozyrod and J. T. Pinhey, Tetrahedron Lett., 22, 783 (1981).
4. For preparation of the organothallium(III) diacetates, see H. Kurosawa and M. Sato, Organometallics, in press. The coupling products 2 were purified by distillation or preparative glc, and fully characterized by elemental analyses and  $^1\text{H}$  nmr, ir and mass spectra.
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7.  $\delta$  ( $\text{CDCl}_3$ ) of  $\text{PhCH}(\text{OMe})\text{CH}_2\text{CMe}_2(\text{NO}_2)$ : 1.65 (s,  $\text{CMe}_2$ ), 2.05 (dd,  $J_{\text{gem}} = 15.0$ ,  $J_{\text{vic}} = 3.0$  Hz,  $-\text{CHH}-$ ), 2.48 (dd,  $J_{\text{vic}} = 9.8$  Hz,  $-\text{CHH}-$ ), 3.09 (s, OMe), 4.18 (dd,  $\text{CH}-$ ), 7.32 (br s, Ph).
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9. On mixing 1b and  $\text{Me}_2\text{CNO}_2\text{Li}$  in methanol prior to irradiation, we observed precipitation of  $\text{C}_6\text{H}_5\text{Tl}(\text{O}_2\text{NCMe}_2)_2$  (elemental analysis, ir and  $^1\text{H}$  nmr spectra). The reaction in DMSO gave lower yields of the coupling products both under and without irradiation.
10. Some 20 % amounts of diarylthallium(III) compounds were also formed.
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