

## Addition of Iodine Isocyanate to Allenes

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Reactions of iodine isocyanate with allenes have been investigated. Absorption of one mol of the reagent at  $-78^{\circ}$  gave addition preferentially to the substituted double bond of alkyl allenes. Addition at  $0^{\circ}$  gave a 1:1 mixture of isomers from addition to either double bond, except in the case of 1,1-dimethylallene, which gave preferentially addition to the unsubstituted double bond. Phenylallene in both cases furnished a 1:1 mixture of isomers.

Addition of the pseudohalogen iodine isocyanate (INCO) to olefins and acetylenes has been reported.<sup>1-5</sup>

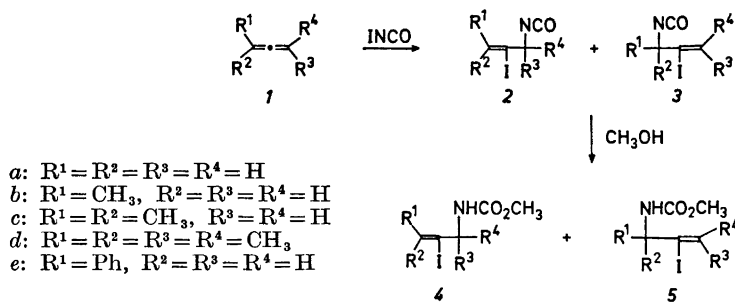
Reactions with cumulated double bonds have not been examined, although Grimwood and Swern<sup>2</sup> observed, without isolating the product that methylallene absorbed one mol of INCO. As a part of our studies on electrophilic reactions with allenes,<sup>6,7</sup> we have investigated the reactions with iodine isocyanate.

Allene (*1a*), methylallene (*1b*), 1,1-dimethylallene (*1c*), tetramethylallene (*1d*), and phenylallene (*1e*) were treated with 2 mol of INCO in ether at  $-78^{\circ}$  to  $0^{\circ}$ . Since INCO is a highly reactive electrophilic agent,<sup>4</sup> addition to both the double bonds of reactive allenes could not be excluded. We were, however, in no case able to observe any diadducts. In order to minimize the amounts of diiodo adducts,<sup>1</sup> further preparations were conducted with equimolar amounts of INCO and allenes. Because of low stability the isocyanates *2*, *3* were transformed to the corresponding carbamates *4*, *5* with methanol.

Allene (*1a*) gave a complex mixture of diiodo compounds, carbamates and polymeric material from which no major component could be separated. The symmetric allene *1d* gave only one product (*4d*), while the allenes *1b* and *1e* gave the isomeric carbamates (*4b*, *5b* and *4e*, *5e*) in a ratio of about 1:1, after reaction at  $0^{\circ}$ . 1,1-Dimethylallene (*1c*) under the same conditions furnished a 1:9 mixture of the isomers *4c* and *5c*. The combined yields in each case were 60–70%. Separation of isomers were effected by chromatography on neutral alumina.

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When the methylallenes *1b* and *1c* were reacted at  $-78^\circ$ , addition to the substituted double bond was preferred in a ratio of 2:1. Phenylallene (*1e*) still gave the 1:1 ratio at  $-78^\circ$ . The NMR spectra showed that without exception iodine had substituted the central carbon atom of the allenic linkage. Together with the mass spectra these spectroscopic data were analogous to those previously observed for iodo carbamates.<sup>5</sup>



Mechanistically the methylallenes are expected to add INCO preferentially at the substituted double bond.<sup>8</sup> This was mainly true when the reaction was performed at low temperature, but not at  $0^\circ$ . In order to examine if the latter was a result of a thermodynamically controlled reaction, as in the addition of bromine to allenes,<sup>9</sup> the isocyanate isomer mixtures *2*, *3c* and *2*, *3e*, synthesized at  $-78^\circ$ , were kept at  $0^\circ$  for 2 h. No change in the isomer ratio was observed. Thus, the product composition must be the result of a kinetically controlled reaction.

### EXPERIMENTAL

The NMR spectra were recorded on a Varian A 60-A spectrometer and the mass spectral data were obtained on a A.E.I. MS 902 mass spectrometer.

**General procedure.** To a preformed solution of INCO<sup>1</sup> (0.03 mol) in dry ether (200 ml) the allene (0.03 mol) in ether (50 ml) was added under nitrogen with stirring at  $-78^\circ$  (or  $0^\circ$ , respectively) during 10 min. After 4 h stirring at the same temperature, the suspension was filtered. To the filtrate methanol (150 ml) and 3 drops of a 0.1 M MeOLi solution (in methanol) was added. After 15 h at  $20^\circ$  in the dark, the solution was concentrated to a small volume, dissolved in ether (100 ml), washed with water containing a trace of sodium bisulfite, then with water, dried ( $\text{MgSO}_4$ ) and evaporated. The carbamate isomers were separated by chromatography on neutral alumina (activity II), whereby the isomers *4*, together with minor amounts of diiodo adducts, were carefully eluted with hexane/cyclohexane. The other isomers (*5*) were then eluted with ether. A second identical chromatography procedure, combined with recrystallization from cyclohexane, was necessary to achieve analytically pure compounds.

**Addition to methylallene (*1b*).** The reaction at  $-78^\circ$  gave 4.8 g of a crude product whose NMR spectrum showed a 2:1 mixture of the isomers *4b* and *5b*, together with some diiodo adducts.

Reaction at  $0^\circ$  gave 6.5 g of carbamates *4b* and *5b* in a ratio of 1:1.

Elution with cyclohexane on neutral alumina gave 2.6 g (34 %) of *4b*, contaminated with small amounts of the other isomer. Further purification on neutral alumina and recrystallisation from cyclohexane gave analytical pure *4b*, m.p.  $81-83^\circ$ . NMR( $\text{CDCl}_3$ )  $\text{CH}_3$   $\delta$  1.25 (d,  $J=7.0$  Hz),  $\text{CH}$   $\delta$  4.0 (q),  $\text{CH}_2$   $\delta$  6.3 (d,  $J=2.0$  Hz) and  $\delta$  5.8 (d)  $\text{NH}$   $\delta$  5.1 (b),  $\text{OCH}_3$   $\delta$  3.7 (s). MS:  $M(m/e$  255)  $-\text{CH}_3\text{OH}$ ,  $M-\text{NHCO}_2\text{CH}_3$ ,  $M-\text{I}$  (base peak).

Elution with ether twice from neutral alumina gave 2.5 g (32 %) of the pure, not crystalline *5b*. NMR(CDCl<sub>3</sub>) CH<sub>3</sub>  $\delta$  1.8 (d,  $J$  = 6.5 Hz), CH  $\delta$  5.8 (q), NCH<sub>2</sub>  $\delta$  4.1 (q), NH  $\delta$  5.3 (b), OCH<sub>3</sub>  $\delta$  3.7 (s). MS: M( $m/e$  255) - CH<sub>3</sub>OH, M - NHCO<sub>2</sub>CH<sub>3</sub>, M - I (base peak).

*Addition to 1,1-dimethylallene (1c)*. The reaction at -78° gave 4.9 g of the crude 2:1 mixture of isomers *4c* and *5c* (together with diiodo adducts).

Reaction at 0° gave 5.5 g of 1:9 mixture of isomers *4c* and *5c*. Elution with ether as above gave 4.4 g (55 %) of pure, not crystalline *5c*. NMR(CDCl<sub>3</sub>) CH<sub>3</sub>  $\delta$  1.95(s), NCH<sub>2</sub>  $\delta$  4.14 (d), NH  $\delta$  5.3 (b), OCH<sub>3</sub>  $\delta$  3.65 (s). MS: M( $m/e$  269) - H, M - CH<sub>3</sub>OH, M - CO<sub>2</sub>CH<sub>3</sub>, M - NHCO<sub>2</sub>CH<sub>3</sub>, M - I (base peak).

From the low temperature reaction crude *4c* was isolated. An analytically pure product was, however, not obtained because of the presence of small amounts of *5c*. NMR(CDCl<sub>3</sub>) CH<sub>3</sub>  $\delta$  1.5 (s), CH<sub>2</sub>  $\delta$  6.25 (d,  $J$  = 2.5 Hz) and  $\delta$  5.85 (d), NH  $\delta$  5.3 (b), OCH<sub>3</sub>  $\delta$  3.6 (s).

*Addition to tetramethylallene (1d)*. Reaction at 0° gave 6.0 g (67 %) of crude *4d*. Recrystallization from petroleum ether (b.p. 40-65°) gave pure *4d*, m.p. 68-69° NMR(CDCl<sub>3</sub>) CH<sub>3</sub>  $\delta$  2.02 (s), CH<sub>3</sub>  $\delta$  2.08 (s), two CH<sub>3</sub>  $\delta$  1.65 (s), NH  $\delta$  5.1 (b), OCH<sub>3</sub>  $\delta$  3.6 (s). MS: M( $m/e$  297) - CH<sub>3</sub>OH, M - CH<sub>3</sub>OH - CH<sub>3</sub>, M - NHCO<sub>2</sub>CH<sub>3</sub>, M - I, M - I - NHCO<sub>2</sub>CH<sub>3</sub> (base peak).

*Addition to phenylallene (1e)*. The reaction at -78° gave 7.2 g of the 1:1 mixture isomers *4e* and *5e*.

Reaction at 0° gave 8.0 g of the same 1:1 mixture. Elution with cyclohexane gave 3.0 g (31 %) of the crude isomer *4e*. A second elution gave pure *4e*, m.p. 88-91°. NMR(CDCl<sub>3</sub>) CH<sub>2</sub>  $\delta$  6.40 (d,  $J$  = 2.0 Hz) and  $\delta$  5.95 (d), CH and NH  $\delta$  5.3 (b), OCH<sub>3</sub>  $\delta$  3.7 (s), Ph  $\delta$  7.3 (s). MS: M( $m/e$  317) - I (base peak), M - I - CH<sub>3</sub>OH, M - I - CO<sub>2</sub>CH<sub>3</sub>, M - I - NHCO<sub>2</sub>CH<sub>3</sub>. Elution with ether gave 2.9 g (30 %) of crude *5e*. Further purification from neutral alumina gave pure *5e*, m.p. 110-115°. NMR(CDCl<sub>3</sub>) CH  $\delta$  6.95 (s), NCH<sub>2</sub>  $\delta$  4.2 (q), NH  $\delta$  5.2 (b), OCH<sub>3</sub>  $\delta$  3.7 (s), Ph  $\delta$  7.3 (m). MS: M( $m/e$  317) - CH<sub>3</sub>OH, M - I (base peak), M - I - CH<sub>3</sub>OH, M - I - CO<sub>2</sub>CH<sub>3</sub>, M - I - NHCO<sub>2</sub>CH<sub>3</sub>.

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