THE FACILE SYNTHESIS OF DIIODOALKENES BY THE ADDITION OF I₂ TO ALKYNES ON ALUMINA. Steven Larson, Teresa Luidhardt, George W. Kabalka*, and Richard M. Pagni*

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<u>Abstract</u> Iodine adds to a variety of alkynes on alumina at or slightly above room temperature to form diiodoalkenes.

Previously we have shown that aromatic substrates react with I_2 on dehydrated γ alumina to form iodinated aromatic products,¹ while alkenes react with the same inorganic reagents to form monoiodoalkanes.² It is clear that I_2 reacts with the surface of alumina to form an electrophilic iodine species, which reacts with aromatic substrates, and HI, which adds to alkenes. We now report that I_2 readily adds to alkynes stereospecifically at or near room temperature on γ -alumina (eq. 1).

$$RC=CR' + I_2/AI_2O_3 \longrightarrow R C=C R'$$
(1)

When a mixture of 1-hexyne (37.0 mmol), iodine (44.8 mmol), dehydrated alumina (35.0 g)³ and low boiling (bp 35-36°) petroleum ether (75 ml) was refluxed for four hours, (E)-1,2-diiodo-1-hexene was produced in 86% yield; no (Z)-1,2-diiodo-1-hexene or any other iodinated product was formed.⁴ As seen in Table 1, this result is typical for a variety of alkynes.

These iodinations, which do not occur in the absence of Al_2O_3 , occur stereospecifically via the anti addition of the two iodine atoms. Some of the reactions appear to be very rapid: in the iodination of 1-hexyne, for example, the color of the I_2 disappears within ten minutes. On the other hand, alkynes with electron withdrawing substituents react much more slowly with I_2/Al_2O_3 . Unlike the iodination of alkynes in solution,^{5,6} where the addition is believed to occur by a free radical mechanism, the iodination of

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alkynes on alumina surfaces appears to proceed via an ionic mechanism, a postulation which is supported by the fact that no reaction occurs in the absence of alumina and that the reaction is retarded by electron withdrawing groups.

The rapid rate of reaction and the ready availability of chromatographic alumina make this a convenient procedure for the stereospecific anti addition of I_2 to alkynes.

| <u>Table 1</u> . Addition of 1_2 | to Alkynes on Alumina. | | |
|---|-----------------------------------|---|----------------|
| Alkyne | <u>Reaction Conditions</u> | Product | <u>Yield</u> a |
| 1-Hexyne (<u>1</u>) | Reflux, 4 hr | (E)-1,2-Diiodo-1-hexene (<u>2</u>) | 86 |
| <u>1</u> | RT, 4 hr | <u>2</u> | 92 |
| <u>1</u> | RT, 12 hr., No Al ₂ 03 | 2 | trace |
| Phenylacetylene (<u>3</u>) | Reflux, 2 hr. | (E)- α , β -Diiodostyrene (<u>4</u>) | 96 |
| Propiolic Acid (<u>5</u>) | Reflux, 24 hr. | (E)-2,3-Diiodoacrylic acid (<u>6</u>) | 23(18) |
| 3-Hydroxypropyne (7) | Reflux, 5 hr. | (E)- α , β -Diiodoallyl alcohol (<u>8</u>) | 84(55) |
| Dimethyl acetylene- dicarboxylate (<u>9</u>) | Reflux, 2 hr. | Dimethyl diiodofumarate (<u>10</u>) | 50 |
| 5-Chloro-1-pentyne (<u>11</u>) | Reflux, 2 hr. (E) | -5-Chloro-1,2-diiodo-1-pentene (<u>12</u>) | 82 |
| 3-Hexyne (<u>13</u>) | Reflux, 2 hr. | (E)-3,4-diiodo-3-hexene (<u>14</u>) | 97 |
| | | | |

^aA number in parentheses refers to yield of recrystallized product.

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References and Notes

- (1) Boothe, R.; Dial, C.; Pagni, R. M.; Kabalka, G. W. Tetrahedron Lett. 1986, 2207.
- (2) Stewart, L. J.; Gray, D.; Pagni, R. M.; Kabalka, G. W. Tetrahedron Lett. in press.
- (3) Gaetano, K.; Pagni, R. M.; Kabalka, G. W.; Bridwell, P.; Walsh, E.; True, J.; Underwood, M. J. Org. Chem. 1985, 50, 499.
- (4) We previously misassigned this product as 2-iodo-1-hexene.²
- (5) Hollins, R. A.; Campos, M. P. A. J. Org. Chem. 1979, 22, 3931.
- (6) Heasley, V. L.; Shellhamer, D. F.; Heasley, L. E.; Yaeger, D. B.; Heasley, G. E. J. Org. Chem. 1980, 45, 4649.

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