Hexacarbonyltungsten and Carbon Tetrachloride as a Photochemical System for Olefin Metathesis

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Summary The irradiation of hexacarbonyltungsten and carbon tetrachloride affords a catalyst for the metatheses of hept-3-ene, pent-2-ene, and *E,E*-deca-2,8-diene.

WE report that photochemical activation of $[W(CO)_6]$ in CCl_4 produces a species which is catalytic for olefin metathesis. No cocatalyst is required. Previously, the irradiation product of $[W(CO)_6]$ was shown to be catalytic in the presence of $EtAlCl_2$ but not so alone in octane or benzene.

When $[W(CO)_6]$ (0·04 mmol) in degassed CCl_4 (3 ml) containing *trans*-hept-3-ene (1·3 mmol) was irradiated under nitrogen overnight in a Rayonet reactor (2537 Å), metathesis to hex-3-ene and oct-4-ene took place with 73% selectivity at 57% conversion. We define selectivity as (mol. metathesis products)/(mol. starting olefin consumed). Other olefins which underwent metathesis under these conditions were *cis*-pent-2-ene, non-4-ene, and 4-methylpent-2-ene. The *cis*-pent-2-ene reaction time could be as short as 30 min, wherein the conversion was 61% and the selectivity 56% for an olefin to tungsten ratio of 40:1. The photochemical system also catalyses the metathesis of *E,E*-deca-2,8-diene to cyclohexene and but-2-ene.

Replacement of $[W(CO)_6]$ with $[Mo(CO)_6]$ or $[Re_2(CO)_{10}]$ afforded no metathesis but (mesitylene)tricarbonyltungsten and $[W(CO)_5MeCN]$ could be used to give lower metathesis yields in the hept-3-ene reaction. The CCl_4 could not be replaced by any of the following solvents: chlorobenzene, benzene, $CHCl_3$, octane, or MeCN. It appears that CCl_4 is more than just a specialized solvent because the addition of it in quantities as small as 0·5 mol to 1 mol of $[W(CO)_6]$ in cyclohexane afforded a combination upon irradiation which catalysed the metathesis of *cis*-pent-2-ene. Although irradiation of the catalytic components in the presence of olefin gives the best yields, irradiation followed by olefin addition does give some metathesis of *cis*-pent-2-ene (5—15%).

There is no evidence yet on the active species in these reactions. The initially clear $[W(CO)_6]$ solution darkens with irradiation and a precipitate forms. Association of activity with this substance is being examined.

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[1] G. M. Graff, Thesis, New York University, 1973, *Diss. Abstr. B*, 1974, **34**, 5900.