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Bridging of macrodithionolactones to bicyclic systems. Synthesis and modeling of oxapolycyclic frameworks.[*]

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A new reaction involving bridging of macrodithionolactones to bicyclic systems is described. A series of macrodiolides was prepared and converted to the requisite macrodithionolactones. The latter substrates were induced to undergo bridging across the macrocyclic ring by exposure to sodium naphthalenide, leading to stable bicyclic systems upon addition of methyl iodide. The mixed thioketals so obtained were converted to a number of saturated or unsaturated bicyclic or polycyclic systems by removal of the sulfurs. The stereochemistry of bridging follows the relative energy of the cis and trans products rather than the conformational preferences of the macrocycles. This is confirmed by MM2 calculations and X-ray crystal structure determinations. The unusual stereochemical course of some of the reported reactions, elucidated by X-ray, has been given a mechanistic basis by conformation searching coupled by energy evaluation by MM2 and PRDO. Several new sets of MM2 parameters were evolved during this work.

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