ASYMMETRIC SYNTHESIS OF (1R, 9S) -13-AZA-13-METHYL-TRICYCLO [7.3.1.$0^{2,7}$] TRIDECA-3,5,7-TRIENE

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An asymmetric total synthesis of an isomer of 6,7-benzomorphan is reported in which the nitrogen at position 3 of the mother compound is interchanged with the carbon at position 11.

Recently, we reported the asymmetric synthesis of (R)-(-)-3-carbomethoxymethyl-3,4-dihydroisocarbostyril [Tet. Lett., 4595 (1977), ibid., 361 (1978)]. Starting from this compound the asymmetric total synthesis of (1R, 9S)-13-aza-13-methyl-tricyclo [7.3.1.$0^{2,7}$]-trideca-3,5,7-triene was accomplished in eight steps. In a key step of this synthesis carbon-carbon bond formation at C-1 position of (R)-3-carbomethoxymethyl-1,2,3,4-tetrahydroisoquinoline-1-thione was performed by applying Eschenmoser's sulfur extrusion reaction.

In Eschweiler-clarke N-methylation of (1R, 3R)-1,3-biscarbomethoxymethyl-1,2,3,4-tetrahydroisoquinoline having two asymmetric centers, we happened to be acquainted with a novel deaminative fragmentation to yield methyl 2-(E)-[2-(E)-methoxycarbonylvinylphenyl]-3-butenoate featured with loss of the chirality and gain of entropy.

This fragmentation contributes not only to the synthetic methodology of such unsaturated compounds but also to the understanding of one aspect of life processes which is featured by the fragmentation of physiological substances (e.g. $PGG_2 \longrightarrow$ HHT + MDA) in terms of extinguishment of chirality and simultaneous gain of entropy.