FORMATION OF HETEROSPIRANS, CONTAINING A γ-LACTONE RING, UPON TREATMENT OF DIALKYLACETYLCARBINOLS WITH MALONIC ESTER

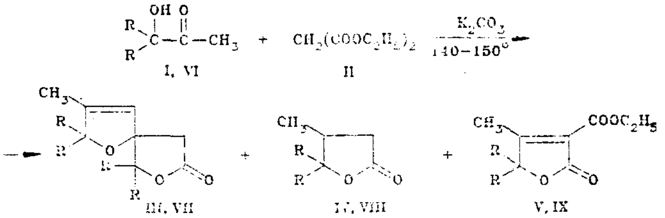
A. A. Avetisyan, V. V. Ovsepyan, and G. G. Tokmadzhyan

UDC 547.361'642'725.07

One of the most general methods for the synthesis of functionally substituted 2-buten-4-olides is the condensation of α-hydroxyketones with esters containing an active methylene group, in the presence of basic reagents [1].

During the course of a study of the reaction conditions for the preparation of 2-carboethoxy-3,4,4-trimethyl-2-buten-4-olide (V) [2] via treatment of dimethylacetylcarbinol (I) with malonic ester (II) at a 2:1 mole ratio, in the presence of potassium carbonate, we observed that, when the starting materials were heated at 140-150°C, a mixture of three reaction products was obtained; one of these was the desired lactone V (yield 15%), a second product was 3,4,4-trimethyl-2-buten-4-olide (IV) (yield 20%), but the major product was a white crystalline substance. IR spectroscopic analysis of these crystals revealed the presence of a lactonic carbonyl group (1770 cm^{-1}) in the substance, as well as a C=C double bond (1660 cm^{-1}). The following signals were observed in the PMR spectrum: singlet at 1.1 ppm (12H), doublet at 1.6 ppm (3H, J = 2 Hz), AB quartet at 2.2 and 2.8 ppm (2H, J = 18 Hz), quartet at 5.15 ppm (1H, J = 2 Hz). Based on these data, as well as its mass spectrum (M$^+$ 210), we have assigned the structure 2,2,3,6,6-pentamethyl-1,7-dioxaspiro[4.4]non-3-ene-8-one (III) to this material.

An analogous result was obtained in an attempt to prepare 2-carboethoxy-3-methyl-4,4-pentamethylene-2-buten-4-olide (VII) from pentamethyleneacetylcarbinol (VI) and ester (II) in the presence of potassium carbonate: once again, the predominant product, in a mixture with the previously known compounds 3-methyl-4,4-pentamethylene-2-buten-4-olide (VIII) (24% yield) and 2-carboethoxy-3-methyl-4,4-pentamethylene-2-buten-4-olide (IX) (12% yield), was 19-methyl-7,15-dioxatrispiro[5.1.0.5.3.2]nonadec-18-ene-16-one (VII).



I, III—V R=CH$_3$; VI—IX R—R=(CH$_2$)$_5$

2,2,3,6,6-Pentamethyl-1,7-dioxaspiro[4.4]non-3-ene-8-one (III). Yield 45%, bp 160-165°C (2.66 hPa), mp 113°C (from hexane).

19-Methyl-7,15-dioxatrispiro[5.1.0.5.3.2]nonadec-18-ene-16-one (VII). Yield 35%, bp 220-225°C (2.66 hPa, with extensive decomposition), mp 97-98°C (from hexane). IR spectrum: 1660 (C=C), 1770 (C=O lactone). Mass spectrum: M$^+$ 290. PMR spectrum (DMSO-D$_6$): 1.20-1.90 (20H, m), 2.00 (3H, J = 2 Hz), 2.65 and 3.05 (2H, AB quartet, J = 18 Hz), and 5.40 ppm (1H, q, J = 2 Hz). Elemental analysis agreed with calculations.

LITERATURE CITED

1. A. A. Avetisyan and M. T. Dangyan, Usp. Khim., 46, 1250 (1977).
2. A. A. Avetisyan, G. E. Tatevosyan, G. E. Mangasaryan, S. G. Matsoyan, and M. G. Dangyan, Zh. Org. Khim., 6, 962 (1970).

Erevan State University, Erevan 375049. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, p. 1426, October, 1986. Original article submitted February 17, 1986.