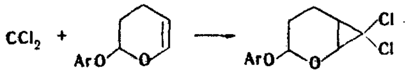
LETTERS TO THE EDITOR

HIGH-TEMPERATURE SYNTHESIS OF 3-ARYLOXY-7,7-DICHLORO-2-OXANORCARANES

M. G. Voronkov, V. G. Kozyrev,
and O. B. Bannikova

UDC 547.811:542.915

Our previously developed method for the preparation of 3-aryloxy-7,7-dichloro-2-oxanorcaranes (I) [1] was based on the reaction of 2-aryloxy-3,4-dihydropyran (II) with the dichlorocarbene generated from chloroform in an aqueous alkaline medium in the presence of triethylbenzylammonium chloride as the catalyst. We have found that I is formed when an equimolar mixture of dihydropyran II and $CHCl_3$ is passed in a stream of nitrogen through a hollow quartz tube heated to 500°C. In addition to this process, partial decomposition of dihydropyran II to a vinyl ether and acrolein and reaction of the latter with dichlorocarbene and hydrogen chloride are also observed.



II I

The condensate obtained was dissolved in ether, and the ether solution was washed with water. Workup gave 3-phenoxy-7,7-dichloro-2-oxanorcarane [mp 78°C (from alcohol), 36% yield based on the converted pyran II, 43% conversion; PMR spectrum (CCl_4): 7.00 (5H, s, 3-C_6H_5), 5.25 (1H, m, 3-CH), 1.83 (4H, m, 4-CH_2, 5-CH_2), 1.92 (1H, m, 6-CH), and 3.60 ppm (1H, d, 1-CH)].

We similarly obtained 3-(4-methoxyphenoxy)-7,7-dichloro-2-oxanorcarane[mp 91.5°C, 27% yield based on the converted pyran II, 52% conversion; PMR spectrum (CCl_4): 6.75 (4H, m, 3-C_6H_4), 3.37 (3H, s, 3-CH_3), 5.25 (1H, m, 3-CH), 1.83 (4H, m, 4-CH_2, 5-CH_2), 1.92 (1H, m, 6-CH), and 3.50 ppm (1H, d, 1-CH)].

The results of elementary analysis of the compounds obtained for their C, H, and Cl content were in agreement with the calculated values, and their individuality was estimated from the data from gas—liquid and thin-layer chromatography. The stereochemistry of the compounds was not investigated.

LITERATURE CITED

1. M. G. Voronkov, S. M. Shostakovskii, V. G. Kozyrev, Ya. V. Artst, L. N. Balabanova, and O. B. Bannikova, Inventor's Certificate No. 488814 (1974); Byull. Isobr., No. 39, 65 (1975).

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, p. 562, April, 1979. Original article submitted November 3, 1978.

0009-3122/79/1504-0462$07.50