## (UDC) 542.91)

T. I. Naryshkina and I. F. Bel'skii

N. S. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 570-571, March, 1965 Original article submitted July 9, 1964

Up to now the synthesis of cyclopentadiene homologs has been a difficult problem. To a large degree this problem has been solved as the result of using catalytic methods for the dehydrocyclization of 1,3-alkadienes [1] and the dehydrogenation of cyclopentanes and cyclopentenes [2]. Recently methods have been developed for the synthesis of  $\gamma$ -diketones using furan compounds for this purpose. Two simple reactions—the hydrolysis of 2,5-dialkylfurans [3] and the isomerization of  $\gamma$ -tetrahydrofurylalkanols [4]—lead to the formation of  $\gamma$ -diketones in high yields. As is known,  $\gamma$ -diketones under the influence of alkaline agents are cyclized to cyclopentenones [3]. The latter may be converted to cyclopentadiene homologs. This synthesis route was used in the present paper, starting with 2,5-heptanedione. The latter was obtained by the hydrolysis of 2-methyl-5-ethylfuran (I) [3]. Then a number of consecutive transformations were made: the cyclization of 2,5-heptanedione (II) to 1,2-dimethyl-1-cyclopenten-3-one (III); the formation of 1,2-dimethyl-3-ethyl-1-cyclopenten-3-ol (IV) from (III) and ethyl bromide via the Grignard reaction; and the dehydration of (IV) to yield 1,2-dimethyl-3-ethyl-1,3-cyclopentadiene (V) and 1,2-dimethyl-3-ethylidene-1-cyclopentene (VI)



The dehydration of cyclopentenol (IV) to cyclopentadiene (V) and (VI) was run in the vapor phase over magnesium sulfate at 310°. The yield of the cyclopentadienes in this last step was 92%. The Raman and infrared spectra obtained for the dehydration product exhibited bands at 1582 and 1655 cm<sup>-1</sup>. The first band testifies to the presence of the 1,3-cyclopentadiene (V), while the second can be attributed to the structure of a cyclopentene with an exocyclic double bond (VI). The absorption bands in the ultraviolet spectrum include a long-wave band with  $\lambda_{\text{max}}$  241;  $\varepsilon$  4700, and a short-wave band with  $\lambda_{\text{max}}$  199;  $\varepsilon$  3350, characteristic for a mixture of cisoid and transoid five-membered dienes. As a result, the described synthesis leads to the formation of two structures, (V) and (VI). This ambiguity in the synthesis arises in the last step—the dehydration of the 3-alkylcyclopenten-3-ol (IV).

It was established recently [5] that for trisubstituted cyclopentadiene homologs the dominant structure is the one with one alkyl substituent in the  $\alpha$ -position and two substituents in the  $\beta$ ,  $\beta$ '-positions. The amount of such isomers in a mixture reaches 90%. The use of 2,5-diketones for the synthesis makes it possible to go in succession to the pure cyclopentenones (III) and cyclopentenols (IV), and then to the trialkyl-substituted homologs of cyclopentadiene and cyclopentene (VI).

## EXPERIMENTAL

2-Methyl-5-ethylfuran (I) was obtained by the vapor-phase reduction of 2-methyl-5-acetylfuran overskeletal Cu-Al catalyst [6]; b.p. 117-118° (750 mm);  $n_D^{20}$  1.4455,  $d_4^{20}$  0.8930.

2-Methyl-5-ethylfuran was hydrolyzed by refluxing it with a mixture of glacial acetic acid and water for 3 h [3]. From 110 g of 2-methyl-5-ethylfuran, to which were added 165 g of acetic acid, 55 g of distilled water and 2 drops of sulfuric acid, we obtained 86.1 g (63% of theory) of 2,5-heptanedione, b.p. 84-87° (18 mm),  $n_D^{20}$  1.4300;  $d_A^{20}$  0.9563.

For the cyclization reaction we took 80 g of 2,5-heptanedione, 8 g of NaOH, 40 ml of water and 80 g of methyl alcohol. The mixture was heated under reflux for 10 h, after which the reaction product was extracted with ether and dried over sodium sulfate. The residue from distilling off the ether was vacuum-distilled. The yield of 1,2-dimethyl-1-cyclopenten-3-one was 61.6 g (91% of theory); b.p. 90-94° (30 mm);  $n_D^{20}$  1.4900;  $d_4^{20}$  0.9685.

1,2-Dimethyl-3-ethyl-1-cyclopenten-3-ol was obtained by the Grignard reaction. To an ether solution of ethylmagnesium bromide (from 75 g of  $C_2H_5Br$  and 19 g of Mg), cooled to  $-15^\circ$ , was added 56 g of 1,2-dimethyl-1-cyclopenten-3-one. We obtained 17.2 g (24% of theory) of 1,2-dimethyl-3-ethyl-1-cyclopenten-3-ol with b.p. 60-62° (15 mm);  $n_D^{20}$  1.4845;  $d_4^{20}$  0.8481.

The dehydration of 15 g of 1,2-dimethyl-3-ethyl-1-cyclopenten-3-ol by passage over magnesium sulfate at 310° and a feed rate of 0.2 h<sup>-1</sup> gave 12.1 g (92% of theory) of the hydrocarbon with b.p. 40-42° (5 mm);  $n_D^{20}$  1.4900;  $d_A^{20}$  0.8497. Found: C 88.51; 88.70; H 11.68, 11.66%. Calculated: C 88.53; H 11.47%.

The spectra were taken by E. V. Sobolev, for which the authors wish to express their sincere thanks.

## SUMMARY

1. A method was developed for the synthesis of  $\alpha$ ,  $\beta$ ,  $\beta$ '- trialkyl-substituted cyclopentadienes from  $\gamma$ -diketones, which were obtained from furan compounds.

2. It was shown that it is possible to go from compounds of the furan series to trialkylcyclopentadienes.

## LITERATURE CITED

- 1. N. I. Shuikin and T. I. Naryshkina, Izv. AN SSSR, Otd. Khim. Nauk, <u>1958</u>, 316; <u>1958</u>, 508; Neftekhimiya, No. 1, 44 (1962).
- 2. N. I. Shuikin and T. I. Naryshkina, Neftekhimiya, No. 4, 473 (1962); No. 6, 859 (1963).
- 3. H. Hunsdiecker, Ber., 75, 447 (1942).
- 4. I. F. Bel'skii and R. A. Karakhanov, Izv. AN SSSR, Otd. Khim. Nauk, 1962, 907.
- 5. V. A. Mironov, S. N. Kostina, E. V. Sobolev, and A. N. Elizarova, Izv. AN SSSR, Ser. Khim., 1964, 864.
- 6. N. I. Shuikin and I. F. Bel'skii, Dokl. AN SSSR, 131, 109 (1960).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-tocover English translations appears at the back of this issue.