$\alpha,\beta-\text{UNSATURATED}$ ALIPHATIC-AROMATIC KETONES IN SUBSTITUTIVE

ADDITION REACTIONS WITH 2-ALKYLFURANS

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Substitutive addition in the furan series was extended to α,β -unsaturated aliphatic-aromatic ketones.

Substitutive addition in the furan series has been quite widely studied [1-4] and is used for the synthesis of diverse carbonyl derivatives of the furan series. The latter are used as intermediates in numerous syntheses (for example, the synthesis of jasmone and its analogs [1], syntheses based on menthofuran [1, 2], etc.). α,β -Unsaturated aldehydes and ketones containing diverse aliphatic substituents and α,β -nitrocompounds [2], α,β -unsaturated acid chlorides [4], etc. have been introduced as the carbonyl component in this reaction.

In the present research we have investigated the reaction of furans with α , β -carbonyl compounds containing aromatic substituents.

We have found that α , β -unsaturated aliphatic-aromatic ketones react with 2-alkylfurans via a substitutive addition scheme:

$$R = CH = CH COR^{"} = R = CH COR^{"}$$

Although the reaction does proceed to give products in only moderate yields, it is a general reaction. Considering the simplicity of the synthesis, it can be recommended for the preparation of β -furyl- β -arylethyl ketones (Table 1), which are difficult to obtain by other methods.

The data from the IR spectra confirm the structure of the synthesized compounds. Thus the spectrum of 1-phenyl-1-(5-methyl-2-furyl)-3-butanone (I) contains absorption bands at 1718 (C=O), 1540 (furan ring), 1458 (-CH₂-) 1360 (CO-CH₃), and 700 cm⁻¹ (benzene ring). The PMR spectral data also unambiguously prove the structure of the ketones. The principal signals are the signal of the methylidyne proton at 4.3-4.5 ppm (lH, triplet, J = 7.4 Hz) and a signal at 2.7-3.2 ppm (2H), which is the superimposition of two quartets with J = 7.4 and 16.4 Hz. Thus the PMR spectrum of the protons of the aliphatic chain is of the ABX type. It is obvious that J = 7.4 Hz is a vicinal constant and J = 16.4 Hz is a geminal constant. All of this indicates that the protons of the CH₂ group are diastereotopic and that the anisochronicity is quite large and amounts to 0.25 ppm, on the average.

EXPERIMENTAL METHOD

General Method for Substitutive Addition with 2-Alkylfurans. A 0.25-ml sample of 96% H_2SO_4 was added with stirring to an α,β -unsaturated ketone (0.2 mole) in the presence of 0.2 g of hydroquinone at such a rate that the temperature of the reaction mixture did not exceed 7-10°. A 0.2-mole sample of 2-aklylfuran was then added in the course of 3 h at 60°,

S. M. Kirov Azerbaidzhan State University, Baku. M. V. Lomonosov Moscow State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 736-737, June, 1975. Original article submitted April 15, 1974.

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| Jbstituted Ketones I-XIV | $\frac{\eta_0}{1}$ Yield. | | .0 31 | ,8 14 | 7,8 27 | 3,5 26 | 3,8 26 | 7,5 24 | 3,2 19 | 3,2 20 | 7,0 19 | 7,4 17 | 11 11 | 7,7 20 | 8,0 13 | 8,0 18 | |
|--------------------------|---------------------------|-----------------|-------------------|-----------------|---------------------------------|----------------------------------|-------------------------|-------------------------------|-------------------------------|---------------------------------|------------|---|----------------------------------|---------------------|-------------------------------|---------------------------------|---|
| | alculated, 6 | c 1 | 78,9 7 | 79,6 7 | 79,6 7 | 80,0 8 | 80,5 8 | 79,3 7 | 80,0 | 89,0 8 | 74,4 7 | 75,0 7 | 75,5 7 | 75,5 7 | 76,0 8 | 76,0 8 | |
| | Found, 7/0 C | н | 7,0 | 7,6 | 7,6 | 8,2 | 8,6 | 7.2 | 7,8 | 7,5 | 68 | 7,1 | 7,4 | 7.3 | 7,8 | 7,4 | |
| | | c | 78,2 | 79,4 | 78,5 | 80,1 | 80,4 | 1,97 | 79,5 | 1.67 | 74,3 | 74,8 | 75,3 | 74,8 | 75,6 | 75,3 | |
| | Empirical formula | | $C_{15}H_{16}O_2$ | $C_1 H_{22}O_2$ | C1-H ₂₀ 02 | $C_{c}H_{c}O_{z}$ | C_{2} , $H_{26}O_{3}$ | $C_{16}H_{>02}$ | C _{lb} II O2 | $C_{18}H_{\odot}O_{2}$ | CleH SO3 | C ₁₇ H ₂ O ₃ | C ₁₈ H-O ₃ | C ₁₈ H O | C_111-03 | C, H, O ₃ | |
| | MR_D | calcu- lated | 66,39 | 75,62 | 75,62 | 84,86 | 84,47 | 71,00 | 80,34 | 80,24 | 72,75 | 77,37 | 1 | | 86,50 | 86,50 | |
| | | found | 66,78 | 75,16 | 75,69 | 84,58 | 84,47 | 71,38 | 80,21 | 79.86 | 73,19 | 78,00 | | | 86,24 | 86,94 | |
| | n_D^{20} | | 1,5458 | 1,5200 | 1,5098 | 1,5090 | 1,5201 | 1,5275 | 1,5180 | 1,5169 | 1,5510 | 1,5480 | | | 1.5298 | 1,5310 | |
| | d, ²⁰ | | 1,0806 | 1,0360 | 1,0106 | 1,0031 | 1,0080 | 1,0430 | 1,0164 | 1,0227 | 1,1251 | 1,1075 | 1 | 1 | 1.0692 | 1,0652 | - |
| | bp, °C (mm) | | 132—133 (2) | 148 - 149 (2) | 141-142 (2) | 168-169 (2) | 179 - 180(2) | 134-135 (1) | 169 - 170 (8) | 148-149 (1) | 155156 (1) | 172-173 (2) | 169—171 (1)* | 165—166 (1) † | 203-204 (4) | 184-185 (1) | |
| | R" | | CH ₃ | CH | CH ₃ | CH ₃ | CH3 | C ₂ H ₅ | C ₂ H ₅ | C_2H_5 | CH3 | CH ₃ | CH ₃ | C_2H_5 | C ₂ H ₅ | C ₂ H ₅ | |
| | Ж | | Н | H | H | H | Н | H | H | Н | OCH3 | OCH3 | OCH, | OCH3 | OCH ₃ | OCH3 | |
| Fury1–Sı | ĸ | | CH ₃ | $n-C_3H_7$ | i-C ₃ H ₇ | n-C ₅ H ₁₁ | $n-C_6H_{13}$ | CH | $n-C_3H_7$ | i-C ₃ H ₇ | CH | $n-C_3H_7$ | i-C _a H ₇ | CH ₃ | $n-C_{3}H_{7}$ | i-C ₃ H ₇ | . |
| TABLE 1. | | Compound | 1 | 11 | III | IV | > | ΛI | VII | VIII | IX | X | XI | XII | XIII | XIV | |

*This compound had mp 61-62° (from hexane). †This compound had mp 65.5-66° (from hexane).

after which the mixture was stirred for 1.5 h and diluted with an equal volume of ether. The ether layer was washed with 2 N sodium carbonate solution and water, dried, with $CaCl_2$, and fractionated.

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