STABLE FULVENES OF THE FURAN SERIES

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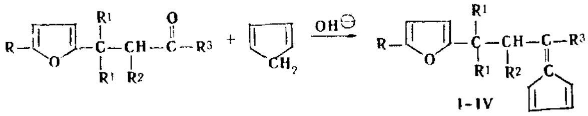
Relatively stable fulvenes were obtained by the reaction of cyclopentadiene with furan compounds containing unconjugated carbonyl groups.

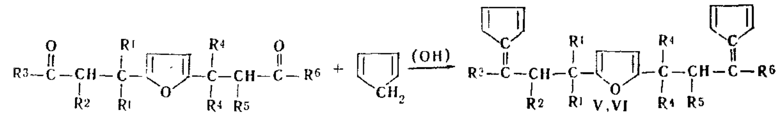
Fulvenes that contain a furan ring in conjugation with cyclopentadienyl double bonds are extremely unstable and are readily oxidized and polymerized [1, 2]. In connection with the fact that fulvenes can serve as monomers for the preparation of high-molecular-weight polymers and copolymers and as crosslinking agents for unsaturated polyesters [3-5], it seemed of interest to synthesize sufficiently storage-stable fulvenes containing five-membered cyclic ethers.

We found that fulvenes (I-IV) of this sort are formed in the reaction of cyclopentadiene (CPD) in the presence of an alkaline catalyst with furan compounds in which the furan ring is not conjugated with the carbonyl group via the scheme



I R = R¹ = R² = H, R³ = CH$_3$; II R = CH$_3$, R¹ = R² = R³ = H; III R = R¹ = R³ = H, R² = C$_2$H$_5$; IV R = R¹ = R³ = CH$_3$, R² = H

If the furan compound contains two isolated carbonyl groups, the corresponding bisfulvenes are formed in the reaction with CPD:



V R¹ = R² = R³ = R⁴ = R⁶ = H, R⁵ = C$_2$H$_5$; VI R¹ = R³ = R⁶ = CH$_3$, R² = R⁴ = R⁵ = H

The UV spectra of these compounds contain an absorption band at λ_{max} 270 nm, which is characteristic for fulvenes [2]. The synthesized fulvenes are colored liquids and, according to gas-liquid chromatography (GLC), are pure substances.

The starting furan compounds with ring-conjugated carbonyl groups were obtained by hydrogenation of the corresponding compounds with conjugated carbonyl groups or by the addition of α,β-unsaturated carbonyl compounds to furan derivatives in acid media [6]. Polymers with considerable heat stability were obtained by polymerization of the synthesized fulvenes [7, 8].

EXPERIMENTAL

Fulvene from 2-(3-Oxobutyl)furan (I). A total of 22 ml of a 10% alcohol solution of potassium hydroxide was added with stirring and cooling to 20° in the course of 20 min to a mixture of 27.6 g (0.2 mole) of 2-(3-oxobutyl)furan and 14.5 g (0.22 mole) of freshly distilled CPD in 50 ml of ethanol, and the reaction mixture was stirred for 1 h and extracted with ether. The ether extracts were washed with water and dried with

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TABLE 1. Synthesized Fulvenes

Fulvene	Starting carbonyl compounds	n_D^{20}	Empirical formula	Found, %		Calc., %		Yield, %
				C	H	C	H	
I	2-(3-Oxobutyl)furan	1,5669	$C_{13}H_{14}O$	83,58	7,55	83,87	7,53	59
II	2-Methyl-5-(3-oxopropyl)furan	1,5440	$C_{13}H_{14}O$	83,82	7,50	83,87	7,53	49
III	2-(2-Ethyl-3-oxopropyl)-furan	1,5306	$C_{14}H_{16}O$	83,68	7,93	83,95	8,05	60
IV	2-Methyl-5-(1,1-dimethyl-3-oxobutyl)furan	1,5402	$C_{16}H_{20}O$	84,19	8,72	84,21	8,77	87
V	2-(3-Oxopropyl)-5-(2-ethyl-3-oxopropyl)furan	1,5570	$C_{22}H_{24}O$	86,82	7,87	86,84	7,90	45
VI	2-(1,1-Dimethyl-3-oxobutyl)-5-(3-oxobutyl)-furan	1,5582	$C_{24}H_{28}O$	86,75	8,41	86,70	8,43	40

calcined magnesium sulfate. The ether was removed by distillation, and the fulvene was purified by chromatography on aluminum oxide with benzene as the solvent and alcohol as the eluent to give 21.9 g of I. Compounds II-IV were similarly obtained.

Fulvene from 2-(1,1-Dimethyl-3-oxobutyl)-5-(3-oxobutyl)furan (VI). This compound (26.4 g) was similarly synthesized from 47 g (0.2 mole) of 2-(1,1-dimethyl-3-oxobutyl)-5-(3-oxobutyl)furan and 29 g (0.44 mole) of freshly distilled CPD in 30 ml of ethanol in the presence of 13 ml of 10% alcoholic potassium hydroxide. Compound V was similarly obtained. The properties of the newly synthesized fulvenes are presented in Table 1.

The UV spectra of the compounds were recorded with an SF-4A spectrometer, and the IR spectra of thin layers of the compounds were recorded with an IKS-14 spectrophotometer. The chromatograms were recorded with an LKhM-8M chromatograph with a 2-m-long column; the stationary phases were 10% polyethylene glycol sebacate (PEGS) on Chromosorb W and 10% SiSS silicone on Chromosorb W.

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