SUBSTITUTIVE ADDITION REACTIONS OF 2-ALKYLIDENECYCLANONES WITH 2-ALKYLFURANS

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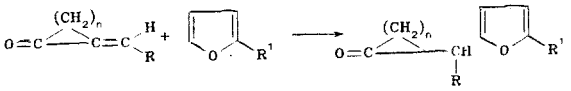
The reaction of 2-alkylidenecyclanones with 2-alkylfurans in an acid medium leads to the formation of substitutive addition products, 1-(2-cyclanon-1-yl)-2-(5-alkylfuryl)alkanes.

The substitutive addition reaction in the furan series has been fairly thoroughly studied [1-6], and is used for the synthesis of various aliphatic derivatives in the furan series. However, no information is available in the literature on the substitutive addition reaction in the series of cyclic unsaturated ketones. The study of this reaction is the subject of the present article.

It was found that in the presence of concentrated sulfuric acid, five- and six-membered 2-alkylidenecyclanones react with 2-alkylfurans according to a substitutive addition scheme.



n=3 (series a): Ia R=CH_3, R^1=H; IIa R=R^1=CH_3; IIIa R=CH_3, R^1=*i*-C_3H_7; IVa R=CH_3, R^1=*n*-C_3H_7; Va R=*n*-C_3H_7, R^1=CH_3; VIa R=*n*-C_3H_7, R^1=*i*-C_3H_7; n=4 (series b): Ib R=R^1=CH_3; IIb R=CH_3, R^1=*i*-C_3H_7; IIIb R=CH_3, R^1=*n*-C_3H_7; IVb R=*n*-C_3H_7, R^1=CH_3

The optimal conditions for the reaction are: temperature 40-50°C, 0.2 ml of 96% sulfuric acid, ratio of 2-alkylidenecyclanone to 2-alkylfuran 0.2:0.2 (mole), duration 4 h 30 min. The physical constants and yields of compounds obtained are listed in Table 1. According to GLC data, the degree of purity of compound Ib is 98.1%. The data of IR and PMR spectroscopy confirm the structure of all the compounds synthesized. For example, the following absorption frequencies appear in the IR spectrum of compound Ib: 2948 (CH_3), 1720 (C=O), 1570 (the furan ring), 1450 cm^{-1} (CH_2). The following set of signals appear in the PMR spectrum of compound Ib: 1.2-2.0 (the $(CH_2)_4$ fragment, m, 9H); 2.3 (R = CH_3, s, 3H); 2.8-3.5 (the CH group of the cyclohexane ring, m, 1H); 5.7-5.9 ppm (the furan ring, s, 2H); the CH_3

TABLE 1. Characteristics of Compounds Obtained

Compound	bp, °C (pressure, mm)	d_4^{20}	n_D^{20}	Found			Empirical formula	Calculated			Yield, %
				C, %	H, %	MR_D		C, %	H, %	MR_D	
Ia	96—97 (5,0)	1,0511	1,4970	74,0	7,9	49,58	$C_{11}H_{14}O_2$	74,1	8,7	49,31	62
IIa	72—73 (0,3)	1,0373	1,4954	75,2	8,3	53,93	$C_{12}H_{16}O_2$	75,0	8,3	54,01	63
IIIa	92—93 (0,1)	1,0029	1,4388	76,9	9,0	63,28	$C_{14}H_{20}O_2$	76,4	9,1	63,17	50
IVa	101—102 (0,1)	1,0021	1,4894	76,5	9,0	63,40	$C_{14}H_{20}O_2$	76,4	9,1	63,17	45
Va	81—82 (0,1)	1,0053	1,4898	76,2	9,1	63,27	$C_{14}H_{20}O_2$	76,4	9,1	63,17	68
VIa	106—107 (0,1)	0,9742	1,4836	77,6	9,6	72,80	$C_{16}H_{24}O_2$	77,4	9,7	72,97	64
Ib	95—96 (0,3)	1,0375	1,5020	76,0	8,3	58,47	$C_{13}H_{18}O_2$	75,7	8,7	58,55	53
IIb	103—104 (0,2)	0,9989	1,4918	72,6	9,3	68,30	$C_{15}H_{22}O_2$	72,6	9,4	67,78	43
IIIb	110—111 (0,1)	1,0133	1,4927	72,4	9,6	67,81	$C_{15}H_{22}O_2$	72,6	9,4	67,78	47
IVb	102—103 (0,2)	1,0032	1,4934	72,1	9,1	67,84	$C_{15}H_{22}O_2$	72,6	9,4	67,78	69
Vb	116—117 (0,1)	0,9733	1,4846	77,7	9,7	77,20	$C_{17}H_{26}O_2$	77,9	9,9	77,58	53

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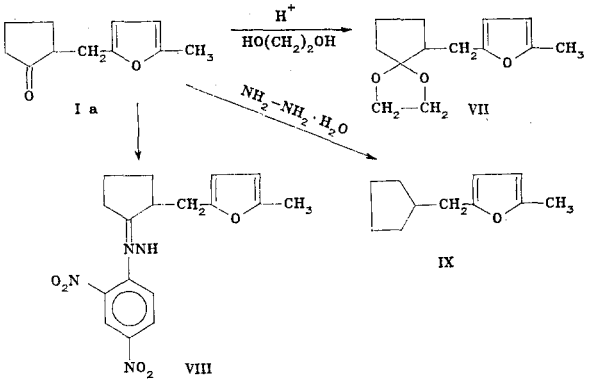
group protons in the CH_3—CH fragment appear in the form of two doublets. We should note that compound Ib is a mixture of two diastereomers.

The following reactions also confirm the structure of compounds obtained:



The reaction of 5-(2-methylfuryl)-2-cyclopentanonylmethane with ethylene glycol in the presence of sulfuric acid leads to ketal VII in a high yield (1100-1355 cm^{-5} — the ether group). In the Kishner reduction of compound Ia, cyclopentyl-5-(2-methylfuryl)methane (IX) was also obtained in a high yield.

EXPERIMENTAL

General Procedure for Substitution-Addition Reactions. Concentrated H_2SO_4 is added, with stirring, to the unsaturated ketone and 0.2 g of hydroquinone at such a rate that the temperature of the mixture does not exceed 7-10°C. Then, 2-alkylfuran is added at 40-50°C, in the course of 3 h, and stirring is continued for another 1 h 30 min. The mixture is diluted with an equal volume of ether, washed with 2 N sodium carbonate and water, dried over $CaCl_2$, and then distilled.

2,4-Dinitrophenylhydrazone of 5-(2-Methylfuryl)-2-cyclopentanonylmethane (IX). A mixture of 0.001 mole of ketone Ia, 0.01 mole of 2,4-dinitrophenylhydrazine, 2 ml of 25% ethanol, and 30 ml of 5% acetic is boiled for 30 min. After the mixture has been left to stand at 20°C, (70%) of hydrazone IX separates out. Mp 136-137°C (from ethanol). Found, %: C 56.5; H 5.0; N 15.7. $C_{17}H_{18}N_4O_5$. Calculated: C 57.0; H 5.0; N 15.6.

Ethylene Ketal of 5-(2-Methylfuryl)-2-cyclopentanonylmethane (VII). A mixture of 0.03 mole of ethylene glycol, 0.02 mole of ketone Ia, 50 ml of benzene, and a drop of H_2SO_4 is boiled until no more water collects in a water separator; the mixture is washed with water, the washings are extracted with benzene (2 × 50 ml), and the benzene extracts are added to the main benzene solution, which is then dried over K_2CO_3. After distillation, 4.04 g (94%) of ethylene ketal VII are obtained. Bp 113-114°C (2 mm), n_D^{20} 1.4958, 1.0870. Found, %: C 70.2; H 8.1. MR_D 59.92. $C_{13}H_{18}O_3$. Calculated, %: C 70.2; H 8.2; MR_D 59.62.

Cyclopentyl-5-(2-methylfuryl)methane (VIII). A 0.08-mole portion of a freshly distilled 80% hydrazine hydrate is added with shaking and water cooling to a mixture of 0.03 mole of ketone Ia and 20 ml of diethylene glycol. The mixture is held for 15 min at 20°C, and after adding 3.8 g of powdered NaOH, it is heated at 110-120°C; when the evolution of nitrogen ceases, the mixture is diluted with an equal volume of water and extracted with ether. The ether extracts are dried over $CaCl_2$ and distilled. Yield 5 g (75%), bp 69-70°C (3 mm), n_D^{20} 1.4280; d_4^{20} 0.9454. Found, %: C 80.7; H 9.8; MR_D 49.30. $C_{11}H_{16}O$. Calculated, %: C 80.7; H 9.9%; MR_D 49.51.

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SYNTHESIS AND BASE-CATALYZED RECYCLIZATION OF 3-ARYLAMINO-CARBONYLANTHRA[1,9-cd]-6-ISOXAZOLONES

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541.127.1'952:543.422.4.6'51

Thermolysis of 1-azido-2-arylaminocarbonylanthraquinones in nonpolar solvents leads to 3-arylaminocarbonylanthra[1,9-cd]-6-isozazolones. By the action of bases, these compounds recyclize in aprotic solvents into 2-arylanthra[1,2-d]-1H-pyrazolin-3,6,11-triones.

It was shown in [1-3] that 3-arylanthra[1,9-cd]-6-isoxazolones isomerize on heating to anthraquinone derivatives containing an angularly condensed six-membered heterocyclic ring at the 1,2-positions. The aim of the present work was to search for new derivatives of anthra[1,9-cd]-6-isoxazolone able to undergo similar isomerizations.

3-Arylaminocarbonylanthra[1,9-cd]-6-isoxazolones (IIIa-i) (Table 1) were synthesized by thermolysis of 1-azido-2-arylaminocarbonylanthraquinones (Ia-i) in boiling toluene. The UV spectra of compounds IIa-i are characterized by the presence of an intense absorption in the 460-480 nm region, characteristic of structurally similar 3-aroylanthra[1,9-cd]-6-isoxazolones

TABLE 1. 3-Arylaminocarbonylanthra[1,9-cd]-6-isoxazolones

Compound	Mp, °C	UV spectrum, λ_{max}, nm (log ε)	Found N, %	Empirical formula	Calculated N, %	Yield, %
IIa	206—208	459 (4,20)	8,4	$C_{21}H_{12}N_2O_3$	8,2	84
IIb	218—220	460 (4,22)	6,8	$C_{21}H_{11}BrN_2O_3$	6,7	79
IIc	210—212	460 (4,22)	6,5	$C_{21}H_{11}BrN_2O_3$	6,7	93
IId	217—219	461 (4,18)	7,7	$C_{21}H_{11}ClN_2O_3$	7,5	75
IIe	209—211	459 (4,19)	7,9	$C_{22}H_{14}N_2O_3$	7,9	89
IIf	217—219	459 (4,19)	8,3	$C_{22}H_{14}N_2O_3$	7,9	78
IIg	214—216	460 (4,22)	8,2	$C_{22}H_{14}N_2O_3$	7,9	84
IIh	202—205	459 (4,09)	7,5	$C_{22}H_{14}N_2O_4$	7,6	75
IIi	216—218	460 (4,23)	7,6	$C_{23}H_{16}N_2O_3$	7,6	66

TABLE 2. 2-Arylanthra[1,2-d]-1H-pyrazoline-3,6,11-triones

Compound	Mp, °C	UV spectrum, λ_{max}, nm (log ε)	Found N, %	Empirical formula	Calculated N, %	Yield, %
IIIa	276—278	462 (3,48)	8,4	$C_{21}H_{12}N_2O_3$	8,2	77
IIIb	310—312	462 (3,39)	7,0	$C_{21}H_{11}BrN_2O_3$	6,7	70
IIIc	251—253	462 (3,47)	7,1	$C_{21}H_{11}BrN_2O_3$	6,7	81
IIId	268—270	475 (3,56)	7,2	$C_{21}H_{11}ClN_2O_3$	7,5	80
IIIe	301—303	480 (3,53)	7,9	$C_{22}H_{14}N_2O_3$	7,9	70
IIIf	310—312	462 (3,42)	8,2	$C_{22}H_{14}N_2O_3$	7,9	70
IIIg	278—280	466 (3,51)	8,2	$C_{22}H_{14}N_2O_3$	7,9	86
IIIh	235—238	466 (3,48)	7,8	$C_{22}H_{14}N_2O_4$	7,6	77
IIIi	290—292	482 (3,53)	7,7	$C_{23}H_{16}N_2O_3$	7,6	83

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