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SYNTHESIS OF 3,4,6-TRIARYL-2-PYRONES

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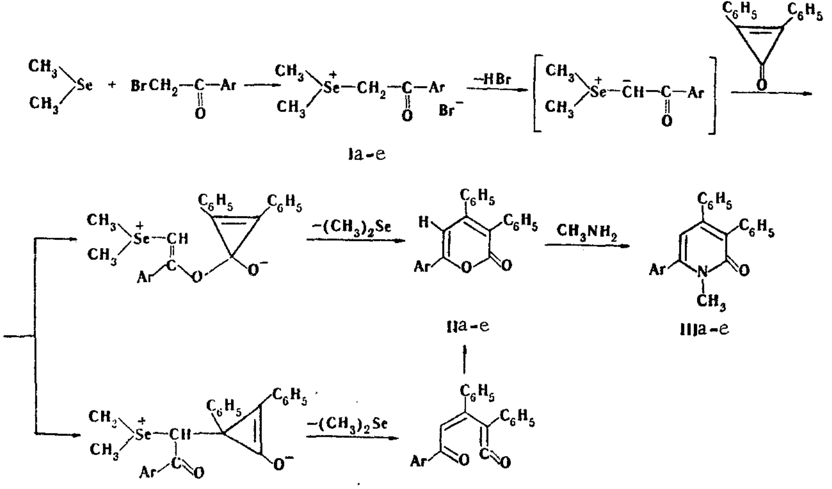
A preparative method was worked out for the synthesis of 3,4,6-triaryl-2-pyrones by 1,3-dipolar cycloaddition of selenium arylacylmethylides to diphenylcyclopropenone.

It is known that the reaction of stable selenonium ylides with acetylenedicarboxylic acid esters is a convenient preparative method for the synthesis of tetrasubstituted furans [1]. In the present research selenium ylides were used in the synthesis of α-pyrones. It is shown that 1,3-dipolar cycloaddition of reactive selenium carbonylylides to an active dipolarophile – diphenylcyclopropenone [2] – is a convenient preparative method for the synthesis of 3,4,6-triaryl-2-pyrones.

Since selenium monocarbonylylides are unstable under ordinary conditions and decompose readily to give carbenes and, subsequently, the corresponding cyclopropanes [3], stable selenonium salts – aracyldimethylselenonium bromides – were used as the starting compounds for the synthesis of the 2-pyrones. These salts were deprotonated by a methanolic solution of potassium hydroxide and underwent smooth conversion to the corresponding monocarbonylylides, which were subjected, without isolation, to reaction with diphenylcyclopropene.

1,3-Dipolar cycloaddition may begin with attack by the dipolarophile either at the ylide carbon atom or the oxygen atom. Since it is known [4] that the negative charge in phenacylmethylides is shifted to a considerable extent to the oxygen atom, it may be assumed that attack by the dipolarophile at the oxygen atom with subsequent ring closure will be the most likely pathway:



I, II, IIIa Ar=C_6H_5; b Ar=2-thienyl; c Ar=2-selenienyl; d Ar= 2-furyl; e Ar= = 1-methyl-2-pyrrolyl

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TABLE 1. Physical Constants and Spectral Data for 3,4,6-Triaryl-2-pyrones

Compound	mp, °C	Found, %		Empirical formula	Calc., %		IR spectrum, cm^{-1}		PMR spectrum, δ, ppm ($CDCl_3$)	UV spectrum ($CHCl_3$)		Yield, %
		C	H		C	H	C=O	C=C		λ_{max}	(ε)	
IIa	182—183	85,6	5,1	$C_{23}H_{16}O_2$	85,2	5,0	1717	1635, 1545	6,71 s 1H (pyrone ring) 7,10 s 10H [phenyl (3 and 4 positions)] 7,30 m 3H 7,75 m 2H } phenyl (6 position)	358 257 245	(7200), (9850) sh.	95
IIb	211—212	76,7	4,5	$C_{21}H_{14}O_2S$	76,4	4,2	1717	1628, 1545	6,59 s 1H (pyrone ring) 7,19 s 10H [phenyl (3 and 4 positions)] 7,47 m 1H 7,65 m 2H } (thiophene ring)	377 270 246	(8150) (5420) sh.	85
IIc	210—211	66,4	3,8	$C_{21}H_{14}O_2Se$	66,8	3,7	1716	1628, 1545	6,54 s 1H (pyrone ring) 7,14s 10H [phenyl (3 and 4 positions)] 7,36m 7,72m 3H } (selenophene ring)	383 277 252	(9650) (5900) sh.	80
Id	191—192	79,9	4,7	$C_{21}H_{14}O_3$	80,2	4,5	1717	1635, 1540	6,56m 1H (furan ring) 6,64s 1H (pyrone ring) 7,12m 10H [phenyl (3 and 4 positions)] 7,48m 2H (furan ring)	273 265 241	(9300) (2150) sh.	80
IIe	132—133	80,4	4,8	$C_{22}H_{17}O_2N$	80,7	5,2	1715	1625, 1538	3,83s 3H (methyl) 6,50s 1H (pyrone ring) 6,73m 2H (pyrrole ring) 7,23s 10H [phenyl (3 and 4 positions)] 7,60m 1H (pyrrole ring)	389 261 245	(4650) (1490) sh.	80

TABLE 2. Physical Constants and Spectral Data for 3,4,6-Triaryl-2-pyridones

Compound	mp, °C	Found, %		Empirical formula	Calc., %		IR spectrum, cm^{-1}		PMR spectrum, δ, ppm (HMDS)*	Yield, %
		C	H		C	H	C=C	C=O		
IIIa	170—171	85,5	5,6	$C_{24}H_{19}ON$	85,5	5,7	1635 1545	1585	3,33 s 3H (methyl) 6,07 s 1H (pyridone ring) 7,05 s 5H 7,07 s 5H (phenyl) 7,36 s 5H	85
IIIb	165—166	76,9	5,3	$C_{22}H_{17}ONS$	77,0	5,0	1638, 1545	1590	3,50 s 3H (methyl) 6,23 s 1H (pyridone ring) 7,10 s 10H [phenyl (3 and 4 positions)] 7,52 m, 7,78 m 3H (thiophene ring)	70
IIIc	185—186	67,9	4,4	$C_{22}H_{17}ONSe$	67,7	4,4	1640, 1545	1595	3,52 s 3H (methyl) 6,24 s 1H (pyridone ring) 7,06 m 10H [phenyl (3 and 4 positions)] 7,00 m, 7,30 m 3H (selenophene ring)	65
IIIe	186—188	81,4	6,0	$C_{23}H_{20}ON_2$	81,2	5,9	1638, 1545	1590	3,33 s 3H (N-methyl groups of pyrrole) 3,50 s 3H (N-methyl groups of pyridone 6,33 s 1H (pyridone ring) 7,16 s 10H [phenyl (3 and 4 positions)] 6,73 m, 8,10 m 3H (pyrrole ring)	90

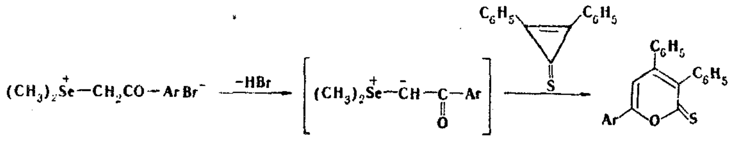
*Hexamethyldisiloxane.

The aracyldimethylselenonium bromides were synthesized by reaction of dimethyl selenide with the appropriate ω-bromomethyl aryl ketones (see [5, 6] for the synthesis).

Intense absorption at 1715-1717 (C=O) and 1625-1635 and 1540-1545 cm^{-1} (C=C) was observed in the IR spectra of all of the 2-pyrones obtained in this research; a 5-H singlet of the pyrone ring was observed in the PMR spectra at 6.5-6.59 ppm.

The triaryl-2-pyrones were converted to the corresponding N-methyl-2-pyrones by heating with an aqueous alcohol solution of methylamine for 12-23 h (see Table 2).

The reaction of aracyldimethylselenonium bromides with another active dipolarophile — diphenylcyclopropenethione [10] — leads to the formation of the corresponding trisubstituted pyran-2-thiones:



IVa, b

IV a Ar=2-selenienyl; b Ar=2-thienyl

The spectral characteristics of the trisubstituted 2-pyrones, 2-pyridones, and pyran-2-thiones obtained in this research are in good agreement with the data in [7-9] from the spectra of 2-pyrones, 2-pyridones, and pyran-2-thiones that do not have substituents in the 5 position.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with IKS-22 and UR-10 spectrometers. The PMR spectra of $(CD_3)_2SO$ and $CDCl_3$ solutions of the compounds were recorded with Varian

T-60 and XL-100 spectrometers with hexamethyldisiloxane as the internal standard. The UV spectra were recorded with a Cary-15 spectrophotometer.

2-Furacyldimethylselenonium Bromide. A 0.1-mole sample of dimethyl selenide was added with stirring to a solution of 0.1 mole of ω-bromomethyl 2-furyl ketone in 50 ml of nitromethane. After 5-10 min, white crystals began to form rapidly. The mixture was stirred for 30 min, after which it was cooled with ice water and filtered. The salt thus obtained was washed with ether and recrystallized from methanol–ether (1 : 2) to give 26 g (90%) of a product with mp 159-160 deg C. IR spectrum: 1670 cm^{-1}. PMR spectrum, δ: 2.4-2.8 (q, 6H, CH_3), 5.1 (s, 2H, CH_2), 6.8 (m) and 7.79 ppm (m, 3H). Found: C 32.3; H 3.9%. $C_8H_{11}BrO_2Se$. Calculated: C 32.2; H 3.7%.

N-Methyl-2-pyrracyldimethylselenonium Bromide. This compound was obtained by the method described above from 0.04 mole of ω-bromomethyl N-methyl-2-pyrryl ketone and 0.04 mole of dimethyl selenide. Workup gave 10 g (80%) of a product with mp 172-173 deg C (from methanol). IR spectrum: 1645 cm^{-1}. PMR spectrum, δ: 2.33-2.65 (q, 6H, CH_3), 4.93 (s, 2H, CH_2), 6.7 and 7.8 ppm (m, 3H). Found: C 34.8; H 4.6%. $C_9H_{14}BrNOSe$. Calculated: C 34.8; H 4.5%.

3,4,6-Triaryl-2-pyrones (II). A solution of 0.02 mole of potassium hydroxide in 20 ml of alcohol was added with stirring to 0.01 mole of aracyldimethylselenonium bromide and 0.01 mole of diphenylcyclopropenone in 40 ml of absolute methanol. The reaction mixture become clear, and a precipitate formed after 10-30 min. Stirring was continued at 20 deg C for another 30 min, after which the precipitate was removed by filtration, washed with cold methanol, and recrystallized from isopropyl alcohol (see Table 1).

3,4,6-Triaryl-N-methyl-2-pyridones (III). A mixture of 0.02 mole of 3,4,6-triaryl-2-pyrone, 25 ml of 25% aqueous methylamine solution, and 35 ml of ethanol was refluxed for 2 h, after which 25 ml of methylamine and 15 ml of alcohol were added, and refluxing was continued for ~25 h. The solvent was then removed by vacuum evaporation to a volume of ~10 ml, and the precipitated crystals were removed by filtration and recrystallized from isopropyl alcohol (see Table 2).

3,4-Dipehnyl-6-(2-selenienyl)pyran-2-thione (IVa). A solution of 0.1 mole of potassium hydroxide in 20 ml of alcohol was added with stirring to 0.05 mole of 2-selenacyldimethylselenonium bromide [3], 0.05 mole of diphenylcyclopropenethione, and 50 ml of absolute methanol. The resulting solution became clear and turned red, and a red precipitate formed after 2-3 min. Stirring was continued at 20 deg C for another 30 min. The precipitate was removed by filtration and washed with cold methanol to give 1 g (50%) of red plates with mp 199-200 deg C (from isopropyl alcohol). IR spectrum: 1660 (C=C) and 1120 cm^{-1} (C=S). PMR spectrum, δ ($CDCl_3$): 6.79 (s, 1H), 7.11 (s, 10H), 7.79 (m, 1H), and 8.13 ppm (m, 2H). Found: C 63.8; H 3.6%. $C_{21}H_{14}OSSe$. Calculated: C 64.1; H 3.6%.

3,4-Diphenyl-6-(2-thienyl)pyran-2-thione (IVb). This compound was obtained by the method described above from 0.01 mole of 2-thienacyldimethylselenonium bromide [3] and 0.01 mole of diphenylcyclopropenethiol in the presence of a solution of 0.02 mole of potassium hydroxide in 20 ml of methanol. Workup gave 2.7 g (80%) of a product with mp 179-180 deg C (from propyl alcohol). IR spectrum: 1610 (C=C) and 1120 cm^{-1} (C=S). PMR spectrum, δ ($CDCl_3$): 6.85 (s, 1H), 7.13 (s, 10H), 7.63 (m, 2H), and 7.73 ppm (m, 1H). Found: C 72.8; H 4.2%. $C_{21}H_{14}OS_2$. Calculated: C 72.8; H 4.0%.

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