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FIVE-MEMBERED 2,3-DIOXO HETEROCYCLES.

2.* SYNTHESIS AND [1,5]-SIGMATROPIC REARRANGEMENT OF 4-ACYL-3-DIPHENYLMETHOXY-1,5-DIPHENYL-2,5-DIHYDROPYRROL-2-ONES

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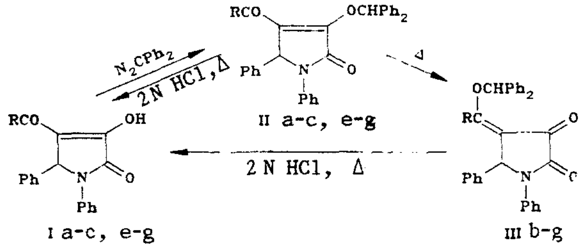
4-Acyl-1,5-diphenyltetrahydropyrrole-2,3-diones react with diphenyldiazomethane to give O-alkylation products, which upon heating undergo [1,5]-sigmatropic suprasurface rearrangement to form 4-[methyl- and 4-[-aryl(diphenylmethoxy)-methylene]-1,5-diphenyltetrahydropyrrole-2,3-diones.

We have previously established that 4-arylsulfonyl-3-diphenylmethoxy-2,5-dihydrofuran-5-ones at 170-175°C undergo [1,3]-sigmatropic rearrangement to 4-arylsulfonyl-4-diphenylmethyltetrahydrofuran-2,3-diones [2]. It seemed of interest to investigate the possibilities and pathways of similar rearrangements among diphenylmethoxy derivatives of other heterocyclic compounds. With this end in mind, in the reaction of diphenyldiazomethane with 4-acyl-1,5-diphenyltetrahydropyrrole-2,3-diones Ia-c, e-g we obtained products of O-alkylation of the enol form of the latter at the keto carbonyl group in the 3 position of the heteroring, viz., 4-acyl-3-diphenylmethoxy-1,5-diphenyl-2,5-dihydropyrrol-2-ones IIa-c, e-g (Table 1). The reaction proceeds in dioxane at 20°C in 4-48 h.



Judging from the time required for disappearance of the characteristic color of diphenyldiazomethane, electron-acceptor substituents in the para position of the aroyl fragment increase the reaction rate; this is evidently associated with an increase in the acidic properties of the enol hydroxy group in starting pyrolediones Ia-g. The effect of electron-donor substituents in the same position is just the opposite.

The IR spectra of pyrrole-2-ones IIa-c, e-g (Table 2) contain intense absorption bands at 1699-1712 (lactam carbonyl) and 1630-1636 cm^{-1} (ketone carbonyl group conjugated with a double bond). In addition to signals of aromatic substituents and the groups bonded to them, the PMR spectra of the compounds in d_6-DMSO contain a singlet of a methylidyne proton in the 5 position of the heteroring at 5.65-6.35 ppm.

When IIa-c, e are heated at 170-195°C for 20-90 min, they undergo quantitative conversion to 4-[aryl(diphenylmethoxy)methylidene]-1,5-diphenyltetrahydropyrrole-2,3-diones IIIb-e.

In the IR spectra of rearrangement products IIIb-g the band of the lactam carbonyl group is shifted to the high-frequency region as compared with starting pyrrolediones Ia-g and is observed at 1760-1764 cm^{-1}; this is evidently a consequence of an increase in the strain

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*See [1] for Communication 1.

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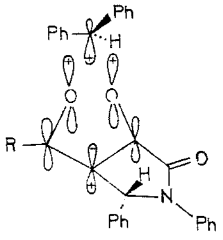
TABLE 1. Reaction Conditions and Characteristics of II and III

Compound	R	Reaction conditions		mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
		Temp., °C	Time, h		C	H	N (Hal)		C	H	N (Hal)	
IIa	C_6H_5	18—22	6	160—162	83,1	5,2	2,7	$C_{36}H_{27}NO_3$	82,9	5,2	2,8	94
IIb	p-$CH_3C_6H_4$	18—22	6	190—191	82,8	5,5	2,7	$C_{37}H_{29}NO_3$	83,0	5,5	2,6	97
IIc	p-ClC_6H_4	18—22	3	167—168	77,9	4,9	2,6 (6,7)	$C_{36}H_{26}ClNO_3$	77,8	4,7	2,5 (6,4)	91
IIe	p-$C_2H_5OC_6H_4$	18—22	48	168—169	80,5	5,5	2,6	$C_{38}H_{31}NO_4$	80,7	5,5	2,5	82
IIf	p-$NO_2C_6H_4$	18—22	3	190—191	76,0	4,8	5,0	$C_{38}H_{26}N_2O_5$	76,3	4,6	4,9	77
IIg	CH_3	18—22	3	154—155	81,2	5,3	3,1	$C_{31}H_{25}NO_3$	81,0	5,5	3,0	92
IIIb	p-$CH_3C_6H_4$	190—195	0,3	234—235	83,3	5,6	2,9	$C_{37}H_{29}NO_3$	83,0	5,5	2,6	—
IIIc	p-ClC_6H_4	170—175	0,3	219—220	77,6	4,5	2,8 (6,1)	$C_{36}H_{26}ClNO_3$	77,8	4,7	2,5 (6,4)	—
IIId	p-BrC_6H_4	190—195	0,4	233—235	72,2	4,6	2,4 (13,4)	$C_{36}H_{26}BrNO_3$	72,0	4,4	2,3 (13,3)	—
IIIe	p-$C_2H_5OC_6H_4$	175—180	1,5	203—205	80,4	5,5	2,6	$C_{38}H_{31}NO_4$	80,7	5.5	2,4	—
IIIg	CH_3	170—175	0,5	235—236	80,9	5,3	3,3	$C_{31}H_{25}NO_3$	81,0	5,5	3,0	—

of the tetrahydropyrroledione ring as a result of the formation of an exocyclic ethylene bond. In addition, bands of a ketone carbonyl group and of an exocyclic double bond at 1711-1724 and 1632-1683 cm^{-1}, respectively, appear in the spectra of the rearrangement products. The PMR spectrum contains a multiplet of 24 aromatic protons centered at 7.45 ppm and a singlet of a methylidyne proton in the 5 position of the heteroring at 6.35 ppm. The spectra of IIIb, d, e are similar.

The absence in the PMR spectra of a signal of a methylidyne proton of the diphenylmethoxy group is explained by its superimposition on the multiplet of aromatic protons. This signal is observed at 8.05 ppm only in the case of 4-acetyl-3-diphenylmethoxy-1,5-diphenyl-2,5-dihydropyrrole-2-one (IIg); it is observed at 6.11 ppm for rearrangement product IIIg. The shift of the latter to strong field is apparently explained by the electron-donor character of the methyl group.

The formation of IIIb-g is evidently a consequence of [1,5]-sigmatropic rearrangement of the diphenylmethyl group. The ease of occurrence of the process and the quantitative yields of the reaction products constitute evidence in favor of this. The mechanism of the reaction is probably similar to that described in [2] and is a suprasurface process with retention of the configuration of the migrating group. At increased temperatures the bond between the oxygen and carbon atoms of the diphenylmethoxy grouping begins to loosen up. Synchronously with this process, a bond between the oxygen atom of the side chain and the carbon atom of the migrating group begins to form; as a result, migration of the diphenylmethyl group occurs:



The [1,5]-sigmatropic rearrangement observed in this case proceeds through a six-membered transition state and is therefore energetically more favorable than the [1,3]-rearrangement previously described for 4-arylsulfonyl-4-diphenylmethyltetrahydrofuran-2,3-diones [2], which is realized through a four-membered transition state.

Compounds IIa-c, e-g and IIIb-g are readily hydrolyzed on heating in dioxane—2 N HCl (3:1) to give starting pyrolediones Ia-g. In the case of III facile hydrolysis is additional evidence for the occurrence of a [1,5]-sigmatropic shift, since the products of a [1,3]-sigmatropic shift are not capable of undergoing hydrolysis with splitting out of a diphenylmethyl group. In the investigation of the hydrolysis of IIIb-g it was observed that the rate of hydrolysis increases with an increase in the electron-acceptor properties of the para substituents in the aroyl fragment. Thus IIIc is hydrolyzed completely by air moisture

TABLE 2. Spectral Characteristics of IIa-c, e-g

Comp.	IR spectrum, ν, cm^{-1}		PMR spectrum, δ, ppm		
	CO_{lact}	CO_{ket}	Ar—H	1H, CH	CH_3, C_2H_5
IIa	1700	1636	7,31m	5,98s	—
IIb	1708	1631	7,38m	6,31s	2,35s
IIc	1705	1635	7,38m	6,15s	—
IIe	1712	1630	7,28m	6,35s	4,11q ; 1,35t
IIf	1705	1635	7,55m	6,35s	—
IIg	1699	1669, 1635	7,35m	5,65s; 8,05s	2,41s

TABLE 3. Spectral Data for 4-[Methyl- and 4-[Aryl(diphenylmethoxy)methylidene]-1,5-diphenyltetrahydropyrrole-2,3-diones (IIIb-e, g)

Compound	IR spectrum, ν, cm^{-1}			PMR spectrum, δ, ppm		
	CO_{lact}	CO_{ket}	$C{=}C_{exo}$	Ar—H	1H, CH	CH_3
IIIb	1761	1718	1634	—	—	—
IIIc	1760	1724	1666	7,45m	6,35s	—
IIId	1760	1719	1683	—	—	—
IIIe	1764	1715	1632	—	—	—
IIIg	1763	1712	—	7,35m	6,11s;5,48s	1,55 s

at 230°C in 20 min. The extremely facile hydrolysis of the rearrangement product in the case of IIf (R = NO_2) is evidently the reason that pyrroledione If was isolated as the only product in this case.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were recorded with a UR-20 spectrometer. The PMR spectra were recorded with an RS-60 spectrometer (60 MHz) with hexamethyldisiloxane (HMDS) as the internal standard.

4-Acyl-3-diphenylmethoxy-1,5-diphenyl-2,5-dihydropyrrole-2-ones IIa-c, e, g. An 11-mmole sample of diphenyldiazomethane dissolved in 10 ml of dioxane was added to a solution of 10 mmole of 4-acyl-1,5-diphenyltetrahydropyrrole-2,3-dione in 50 ml of dioxane, and the mixture was maintained at 20°C for 3-48 h until the solution became colorless. The solvent was evaporated, and the precipitate was recrystallized from butanol to give the IIa-c, e, g.

4-[Methyl- and 4-[Aryl(diphenylmethoxy)methylidene]-1,5-diphenyltetrahydropyrrole-2,3-diones IIIa-e, g. A 1-mmole sample of IIa-c, e, g was maintained at 170-195°C for 15-90 min, after which ether was added, and the crystals were removed by filtration to give the IIIa-e, g.

4-(p-Methylbenzoyl)-1,5-diphenyltetrahydropyrrole-2,3-dione (Ib). A 0.7-g (1.3 mmole) sample of IIb or IIIb in a solution of 10 ml of dioxane and 3 ml of 2 N HCl was heated for 3 h, after which the solvent was evaporated, and the residue was recrystallized from butanol to give 0.43 g (91%) of Ib with mp 247-248°C (dec.) [3].

4-(p-Chlorobenzoyl)-1,5-diphenyltetrahydropyrrole-2,3-dione (Ic). A 0.45-g (0.8 mmole) sample of IIIc was heated for 30 min at 230°C, after which the reaction mass was cooled to give 0.2 g (62%) of Ic with mp 254-255°C (dec.) [3].

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