SYNTHESIS OF 3-ARYL-3a-PHENYLINDANO[2,1-d]-OXAZOLIDINE-2,4-DIONES

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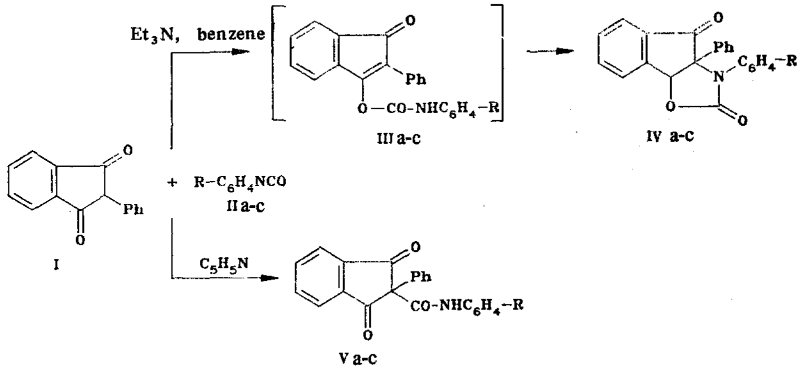
2-Phenylindan-1,3-dione reacts with aryl isocyanates in benzene in the presence of catalytic amounts of triethylamine with the formation of 3-aryl-3a-phenylindano-[2,1-d]oxazolidine-2,4-diones. In pyridine, this reaction leads to 2-arylcarbamoyl-2-phenylindan-1,3-dione.

In the indan-1,3-dione series [1] and among carbamic acid derivatives [2] there are compounds that have found practical use as raticides (2-phenyl- and 2-diphenylacetylindan-1,3-diones), herbicides, fungicides, and insecticides (esters of 2-aryl-3-hydroxyinden-1-ones, isopropyl N-(3-chlorophenyl)carbamate, N-aryl-N',N'-dimethylureas). At the same time, there is no information relating to carbamoyl derivatives of indan-1,3-dione. In view of this we have performed the reaction of 2-phenylindan-1,3-dione (I) with the isothiocyanates (IIa-c) with the aim of obtaining the corresponding 2-phenyl-3-(R-phenylcarbamoyloxy)inden-1-ones (III) and testing their pesticidal activity.

It is known that, depending on the conditions of performing the synthesis, β-dicarbonyl compounds, which include (I), can react with isocyanates either by the O—H bond (enolic form) or by the C—H bond (diketo form) [3].

We have shown that in benzene in the presence of catalytic amounts of triethylamine at room temprature, instead of the expected carbamates (III) the 3-(R-phenyl)-3a-phenylindan-[2,1-d]oxazolidine-2,4-diones (IV) were obtained (Table 1). Raising the temperature of the reaction led to resinification of the reaction mixture.



II→V a R=H, b R=3-Cl, c R=4-Cl

In the IR spectra of compounds (IV) (Table 1), two bands of the stretching vibrations of carbonyl groups were obtained at about 1725-1726 and 1745-1751 cm^{-1}. The presence of ester groups in the molecules was shown by two strong bands of the vibrations of C—O—C bonds in the 1127-1130 and 1228-1230 cm^{-1} regions. At the same time, there were no bands of the stretching vibrations of NH and C═C bonds conjugated with aromatic rings, as should be characteristic for compound (III). The absence of the latter was confirmed by the absence from the ESP of absorption bands at about 400 nm that are characteristic for the

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TABLE 1. 3-(R-Phenyl)-3a-phenylindano[2,1-d]oxazolidine-2,4-diones (IVa-c) and 2-(R-Phenylcarbamoyl)-2-phenylindan-1,3-diones (Va-c)

Compound	mp, °C	IR spectrum (KBr), cm^{-1}					Found, %				Empirical formula	Calculated, %				Yield, %
		C=O	COC	NH	amide I	amide II	C	H	N	Cl		C	H	N	Cl	
IVa	219—220	1725 1745	1127 1230	—	—	—	77,3	4,3	4,0	—	$C_{22}H_{15}NO_3$	77,4	4,4	4,1	—	60
IVb	185—186	1726 1750	1127 1228	—	—	—	70,2	3,7	3,7	9,3	$C_{22}H_{14}ClNO_3$	70,3	3,8	3,7	9,4	42
IVc	214—215	1725 1751	1130 1230	—	—	—	70,2	3,7	3,6	9,3	$C_{22}H_{14}ClNO_3$	70,3	3,8	3,7	9,4	59
Va	176—177	1700 1740	—	3390	1682	1515	77,3	4,4	4,0	—	$C_{22}H_{15}NO_3$	77,4	4,4	4,1	—	30
Vb	186—187	1700 1741	—	3370	1683	1520	70,2	3,7	3,6	9,3	$C_{22}H_{14}ClNO_3$	70,3	3,8	3,7	9,4	48
Vc	192—193	1700 1741	—	3390	1683	1545	70,3	3,7	3,6	9,4	$C_{22}H_{14}ClNO_3$	70,3	3,8	3,7	9,4	47

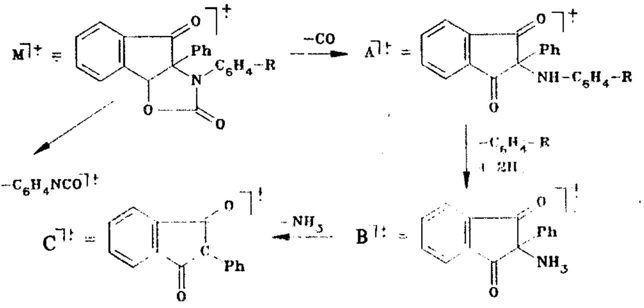
TABLE 2. Mass Spectra of Compounds (IVa, c) and (Va)

Compound	m/z values (relative intensities of the peaks of the ions in % of the maximum peak)
IVa	341, $M]^{+\cdot}$ (2,4)*, 313, $A]^{+\cdot}$ (5,5), 240 (1,9), 239 (18,1), 238, $B]^{+\cdot}$ (100), 223 (3,2), 222 (21,4), 221, $C]^{+\cdot}$ (36), 206 (3,0), 205 (9,4), 194 (2,4), 193 (6,4), 178 (2,5), 177 (13,9), 166 (4,5), 164 (3,3), 163 (4,1), 153 (7,1), 152 (8,6), 151 (2,7), 133 (7,5), 132 (14,0), 120 (7,1), 119 (54,9), 106 (5,6), 105 (24,6), 104 (90,8), 93 (17,9), 92 (5,9), 91 (21,7), 90 (3,3), 89 (3,6), 78 (12,7), 77 (18,7), 76 (67,8), 75 (3,7)
IVc	377 (1,1), 375, $M]^{+\cdot}$ (3,2), 350 (2,0), 348, $A]^{+\cdot}$ (6,2), 240 (1,4). 239 (13,5), 238, $B]^{+\cdot}$ (75,3), 223 (1,8), 222 (16,2), 221, $C]^{+\cdot}$ (26,4), 206 (2,6), 205 (9,1), 194 (2,2), 193 (6,3), 178 (3,8), 177 (16,7), 166 (2,4), 164 (3,0), 156 (2,6), 155 (25,5), 154 (7,9), 153 (83,7), 152 (9,7), 133 (12,2), 132 (13,1), 128 (4,1), 127 (27,6), 126 (4,5), 125 (29,4), 106 (8,0), 105 (27,8), 104 (100), 90 (22,3), 89 (8,1), 78 (4,9), 77 (20,5), 76 (73,8), 75 (7,1)
Va	341, $M]^{+\cdot}$ (2,3), 250 (3,8), 249, $A]^{+\cdot}$ (28,0), 223 (1,5), 222 (19,6), 221, $B]^{+\cdot}$ (100), 205 (28,2), 194 (4,8), 193 (7,3), 177 (7,0), 166 (7,4), 164 (5,0), 163 (3,8), 155 (7,7), 127 (5,9), 126 (2,7), 105 (4,4), 104 (3,5), 92 (23,3), 91 (1,6), 89 (9,4), 77 (4,5), 76 (11,1), 75 (4,1)

*(IVa) — 3,3a-diphenylindano[2,1-d]oxazolidine-2,4-dione; (IVc) 3-(4-chlorophenyl)-3a-phenylindano[2,1-d]oxazolidine-2,3-dione; (Va) 2-phenyl-2-(phenylcarbamoyl)indan-1,3-dione.

enolic forms of derivatives of the β-diketone (I) [4]. In the PMR spectra, the singlet of a methine proton was observed at about 3.31 ppm.

The mass spectra (Table 2) contained weak (2-3%) peaks of the molecular ions, which showed the instability of the given structures in the form of radical ions. Fragmentation under the action of electron impact took place either with the cleavage of the C—O and C—N bonds and the formation of the particles $(C + H)]^{+\cdot}$ with m/z = 222 and $RC_6H_4NCO]^{+\cdot}$ (55-84%),* or with splitting out of the particle CO and the formation of the radical ion $A]^{+\cdot}$ (5-6%) and the even more stable fragment $B]^{+\cdot}$ with m/z = 238 (75-100%). In the latter, the bond between the nitrogen atom and the carbon atom in position 2 of the indan-1-one ring was preserved, which confirms the structure of compounds (IVa-c).



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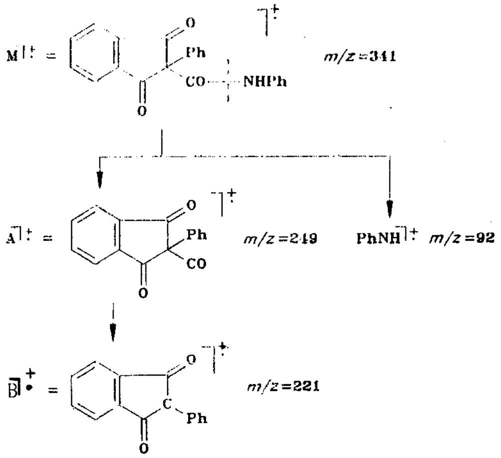
*This pathway does not give an obvious confirmation of structures (IVa-c).

Since in nonpolar solvents in the presence of tertiary amines compound (I) reacts with the formation of enolic derivatives [5], the reaction under consideration apparently takes place with the formation of the carbamate (III) followed by the closure of the oxazoline ring. Under the conditions studied, the reaction did not take place with the feebly active methyl, ethyl, and butyl isocyanates.

The reaction of the diketone (I) with aryl isocyanates in a polar solvent — dry pyridine — took place at the C—H bond with the formation of the corresponding 2-(R-phenylcarbamoyl)-2-phenylindan-1,3-diones (Va-c) (Table 1). A rise in the temperature of the reaction led to pronounced resinification.

In the IR spectra of compounds (V) (Table 1) there were two strong absorption bands at about 1700 and 1740-1741 cm^{-1} which, according to [6], belong to the stretching vibrations of the NH bond (3370-3390 cm^{-1}) and by "amide I" absorption bands at about 1682-1683 and "amide II" bands at about 1515-1545 cm^{-1} which were absent from the spectrum of the initial β-diketone (I). At the same time, there were no bands of the stretching vibrations of ester groupings and of a C═C bond conjugated with aromatic rings and a carbonyl group. In the ESP there was no absorption band at about 400 nm that is characteristic for enolic derivatives of the diketone (I).

In the PMR spectra no signal of a methine proton was observed, and, at room temperature, the NH signal fell into the region of signals of the aryl protons (6.80-8.02 ppm) but with a rise in the temperature to 60°C it shifted upfield and appeared at 6.32 ppm.



The mass spectrum of the 2-phenylcarbamoyl derivative (Va) (Table 2) contained the weak peak of the molecular ions with m/z = 341 (2%). Under the action of electron impact, cleavage of the C—N bond in the carbamoyl grouping took place primarily with the formation of the particles $C_6H_5NH]^{+\cdot}$ with m/z = 92 (23%) and $A]^{+\cdot}$ with m/z = 249 (28%), which confirmed the structure of compound (Va).

Compounds (IV) and (V) prove to be weakly and moderately active herbicides, fungicides, and insecticides.

EXPERIMENTAL

IR spectra were obtained on a Perkin—Elmer 457 instrument in KBr tablets, ESPs on a Specord UV-vis instrument in solution in 95% ethanol, and PMR spectra on a Varian CFT-20 (80 MHz) instrument in CDCl$_3$ with TMS as internal standard. Mass spectra were taken on a Varian MAT CH 7A instrument with a SS-100 data processing system; energy of the ionizing electrons was 70 eV; direct introduction of the samples into the ion source; temperature 250°C.

Confirmation of the individuality of the compounds and a check on the course of the reactions were carried out by the TLC method on Silufol UV-254 plates with a fixed layer of silica gel in the benzene—ethyl acetate (3:1) system, the spots being revealed with iodine vapor.

The 3-(R-Phenyl)-3a-phenylindano[2,1-d]oxazolidine-2,4-diones (IVa-c). With stirring, an equimolar amount of the appropriate isocyanate and one drop of triethylamine were added to a solution of 4.5 mmole of the β-diketone (I) in 50 ml of absolute benzene. After 8 days, the precipitate that had deposited was filtered off and was washed successively with benzene and hexane. Compounds (IVa-c) were white crystalline substances readily soluble in chloroform and acetone and soluble with heating in benzene and ethanol.

The 2-(R-Phenylcarbamoyl)-2-phenylindan-1,3-diones (Va-c). With stirring, an equimolar amount of the appropriate isocyanate was added to a solution of 4.4 mmole of the β-diketone (I) in 10 ml of dry pyridine. After 5 days, the mixture was poured into cold water. The oil that separated out was extracted twice with methylene chloride, and the extract was dried over magnesium sulfate. The crystals that deposited from the filtrate on standing were filtered off and washed with cold methylene chloride. Compounds (Va-c) were pale yellow crystalline substances readily soluble in chloroform and acetone and soluble on heating in benzene.

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