SYNTHESIS AND IONIC HYDROGENATION OF 1,1-PHTHALOYL-2-PHENYL-3-(p-ALKYLBENZOYL)CYCLOPROPANES

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Continuing our work [1] on the ionic hydrogenation of 1,1-phthaloy1-3-(p-alkylbenzoy1)cyclopropanes (I), which is aimed at clarifying the influence of configuration (cis or trans) on the reactivity of the three-membered ring, we have attached a phenyl substituent to the ring of compounds (I), by preparing cis-1,1-phthaloy1-2-pheny1-3-(p-alkylbenzoy1)cyclopropanes (IIa)-(IIc) and the trans isomers (IIIa)-(IIIc).

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We synthesized compounds (IIa)-(IIc) and (IIIa)-(IIIc) by cyclization of the threo-(IVa)-(IVc) and erythro-dibromides (Va)-(Vc) with KI in acetone [2]



Three-dibromides (IVa)-(IVc) were readily converted to the cis isomers (IIa)-(IIc). The erythro-dibromide (Va) gave the pure trans isomer (IIIa). The cyclization of erythro- (Vb) and (Vc) under the same conditions formed a mixture of the cis- and trans-isomeric cyclopropane compounds in the ratio 1:1, possibly because the original erythro- (Vb) and (Vc) were contaminated by three-dibromides (IVb) and (IVc). An attempt to prepare the pure trans isomers (IIIa)-(IIIc) by acid isomerization of cis isomers (IIa)-(IIc) with HBr/CH₃COOH was unsuccessful, resulting in opening of the three-membered ring to form olefins. The presence of the double bond in these products is supported by their Raman and IR spectra (band at 1650 cm⁻¹). Treatment of the cis isomers (IIa)-(IIC) with CF₃COOH with a compound: CF₃COOH molar ratio of 1:20 at $\sim 20^{\circ}$ C over 6 h resulted in quantitative conversion to the trans isomers (IIIa)-(IIIc). We followed the reaction from the PMR spectra. The spectra of the isomerization products lacked the signal at δ 3.8 ppm typical of the cis isomers (IIa)-(IIC), which was replaced by a signal with δ 4.2 ppm (Table 1). This method is thus a simple and convenient route to pure trans-1,1-phthaloyl-3-(p-alkylbenzoyl)cyclopropanes (IIIa)-(IIIc).

We assigned the configurations of the synthetic cis (IIa)-(IIc) and trans isomers (IIIa)-(IIc) from their ¹³C NMR spectra, since in cis-2,3-disubstituted cyclopropane compounds the signal of the C¹ carbon of the three-membered ring lies 4-7 ppm upfield of its position in the trans isomer [3]. The physical and spectral properties of the synthetic cis and trans isomers (IIa)-(IIc) and (IIIa)-(IIIc) are summarized in Table 1. Having assigned the cis and trans configurations from the ¹³C NMR spectra, we could then assign the PMR signals of these compounds. The protons of the three-membered ring appear as a sharp singlet; the signal of the cis isomer also lies upfield of that of the trans isomer (Table 1).

Under the conditions specified in [1], i.e., when heated at 50° C for 6h with a compound: Et₃SiH: CF₃COOH molar ratio of 1:3:5, the cis and trans isomers did not undergo ionic hy-

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anes [cis-		
)cycloprop		
lkylbenzoy.		
eny1-3-(p-a		
aloy1-2-phe		
f 1,1-Phth		
coperties o		
Spectral Pr	a)-(IIIc)]	
and	III)-	
Physical	c), trans-	
TABLE 1.	(IIa)-(II	

PMR, 6, ppm of cyclopro- pane ring pro- tons		3,80 s (2H)	4,21s (2H)	3,83 s (2H)	4,25s (2H)	3,78s (2H)	4,20 s (2H)
$O_{co} + O_{c} + O_{$	C3	43,27	42,30	43,37	42,38	43,37	42,38
	C ³	41,63	41,04	41,81	41,12	41,81	41,20
13 C NMR, 8, ppm	ū	44,14	47,57	44,15	47,57	44,15	47,65
v, cm ⁻¹		1680 1704 1744	1675 1705 1735	1680 1710 1745	1680 1714 1745	1680 1708 1750	1708 1744 1685
+₩		352	352	366	366	380	380
λ, am in C ₂ H ₅ OH		230 (24 400) 250 (16 900)	232 (25 850) 256 (15 670) 282 (4 240)	228 (40 600) 255 (24 200)	231 (76 000) 260 (29 300)	229 (19 500) 257 (13 600)	260 (25 600) 230 (70 600)
шр, С		191–192	174-175	186–187	192193,5	179–180	172–173
Configu- ration		cis	trans	cis	trans	cis	trans
Compound		(IIa)	(IIIa)	(qII)	(4111)	(IIc)	(IIIc)

Com- pound m					PMR, δ, ppm			
	mp, °C	м+	λ, nm in C ₂ H ₅ OH	v, cm-1	protons of three membered ring	C=C protons	benzyl protons	
(VIa)	128129	338	228 254	1704 1744	Not present	6,53—6,80	4,45	
(VIb)	142-144	352	200 225 255	1710	•	6,51-7,50	4,41	
(VIc)	-		285 -	1745 1708 1750	*	6,40-6,72	4,33.	
(VIIa)	174–175,5	338	226	1705	3,16-3,41	Not present	3,70	
(VIIb)	160161	352	241 225	1735 1714	2,99-3,31		3,55	
(VIIc)	163–163,5	366	243 224 240	1745 1708 1744	3,15–3,33	*	3,61	

TABLE 2. Physical and Spectral Properties of the Products of the Ionic Hydrogenation of Compounds (IIa)-(IIc) and (IIIa)-(IIIc)

drogenation. However, under different conditions — a reactant ratio of 1:6:20 at $\sim 20^{\circ}$ C for 6 h — the reaction gave hydrogenation products in high yield. We established from the spectra of the products that cis isomers (IIa)-(IIc) were hydrogenated to 1,1-phthaloy1-2-pheny1-3-(p-alkylbenzy1)-2-propenes (VIa)-(VIc) while the trans isomers (IIIa)-(IIIc) gave 1,1-phthaloy1-2-pheny1-3-(p-alkylbenzy1)cyclopropanes (VIIa)-(VIIc)



Table 2 summarizes the physical and spectral properties of compounds (VIa)-(VIc) and (VIIa)-(VIIc). Regardless of the configuration of the starting compounds (IIa)-(IIc) and (IIIa)-(IIIc), ionic hydrogenation involves reduction of the benzoyl carbonyl, generating a benzyl group. This is supported by the absence from the IR spectra of reaction products (VIa)-(VIc) and (VIIa)-(VIIc) of the band at 1680 cm⁻¹ (C=0) together with the presence in their PMR spectra of the signals of the methylene protons of the benzyl group at 4.4 ppm (2H) in (VIa)-(VIc) and 3.6 ppm (2H) in (VIIa)-(VIIc).

In cis isomers (IIa)-(IIc) reduction of the carbonyl group is accompanied by opening of the three-membered ring at the C^1-C^3 bond to form (VIa)-(VIc). The structures of these compounds are supported by their Raman spectra, which show a band at 1647-1650 cm⁻¹ (C=C). The PMR spectra have the signals of the double bond protons at δ 6.6 ppm (1H) and lack signals due to the three-membered ring. The proton of the indandione ring is responsible for the signal at δ 3.4 ppm. This assignment is supported by the disappearance of this signal when (VIa)-(VIc) were treated with a 3% pyridine solution of LiOD as a result of keto-enol tautomerism in the phthaloyl fragment. The UV spectra of (VIa)-(VIc) contain intense maxima at 228 and 225 nm with additional absorption due to the double bond at 283 nm. Thinlayer chromatography of (VIa)-(VIc) after alkaline treatment generated an orange coloration characteristic of the enol form of (VIa)-(VIc). Comparison of our work on the ionic hydrogenation of cis isomers (IIa)-(IIc) with our earlier results [1] for compounds (I) (Alk = $CH_3-C_8H_{11}$) reveals that in all cases the three-membered ring is preserved in CF_3COOH in the absence of Et_3SiH . This suggests that under the conditions of the ionic hydrogenation ring opening is preceded by the reduction of benzoyl to benzyl (or alcohol).

The ionic hydrogenation of trans isomers (IIIa)-(IIIc) involves reduction of the benzoyl group and preservation of the three-membered ring. The reaction products were (VIIa)-(VIIc). The presence of the three-membered ring is supported by the PMR spectra which show its signal at δ 3.2 ppm (2H). Compounds (VIIa)-(VIIc) did not give an orange color after alkaline treatment, implying that formation of the enol form is impossible. The UV spectra of compounds (VIIa)-(VIIc) have maxima at 226 and 240 nm. The molecular weights, determined by mass spectrometry, were identical to the calculated values for (VIa)-(VIc) and (VIIa)-(VIIc).

Since cis isomers (IIa)-(IIc) readily isomerized to the trans isomers (IIIa)-(IIIc) in the presence of CF_3COOH , we would have expected the reaction products to be identical and to have structures (VIIa)-(VIIc) regardless of the configuration of the original substituted cyclopropanes. However, hydride reduction of cis and trans isomers (IIa)-(IIc) and (IIIa)-(IIIc) gave products with different structures. Consequently, under the conditions of ionic hydrogenation the isomerization does not proceed like that of 1,2-diphenylcyclopropanes [4]. Thus our results imply that under the conditions of ionic hydrogenation the three-membered ring in cis isomers (IIa)-(IIc) is more reactive than that in the trans isomers (IIIa)-(IIIc). The nature of the p-alkyl substituent in the benzoyl fragment does not affect the course of the reaction in this case.

EXPERIMENTAL

Spectra were recorded on the following instruments: IR, a UR-20 in KBr; PMR, a Varian DA-60IL relative to tetramethylsilane (TMS) in $CDCl_3$; UV, a Specord UV-VIS in C_2H_8OH ; and ¹³C NMR, a Varian XL-100-15 at 25.2 MHz. Mass spectra were obtained with a Varian MATCH-6. Melting points were determined on a Kofler hot stage. Thin-layer chromatography was carried out on silufol, eluent CHCl₃.

<u>Trans-1,1-Phthaloy1-2-pheny1-3-(p-alkylbenzoy1)cyclopropanes (IIIa)-(IIIc).</u> cis Isomer (IIa)-(IIc) or an isomer mixture was treated with CF_3COOH in molar ratio 1:6 and left at 20°C for 6 h. The reaction mixture was poured into water, neutralized with NaHCO₃, and extracted with ether. The crystalline product derived by the usual treatment was recrystallized from CH_3COOH . The yields of (IIIa)-(IIIc) after purification were 80%. The physical constants and spectral parameters of (IIIa)-(IIIc) are summarized in Table 1.

Ionic Hydrogenation of cis- and trans-1,1-Phthaloy1-2-pheny1-3-(p-alkylbenzoy1)cyclopropanes (IIa)-(IIc) and (IIIa)-(IIIc). The reaction was carried out by the procedures of [5], with compound: Et₃SiH: CF₃COOH molar ratio of 1:6:20 at \sim 20°C over 6 h. The yield of the reaction products was 70%.

CONCLUSIONS

1. We have synthesized a series of cis- and trans-1,1-phthaloy1-2-pheny1-3-(p-alky1benzoy1)cyclopropanes and established their configurations.

2. We have suggested a method for preparing trans-1,1-phthaloy1-2-pheny1-3-(p-alky1-benzoy1)cyclopropanes by acid isomerization of the cis isomers in $CF_{3}COOH$.

3. The ionic hydrogenation of cis-1,1-phthaloy1-2-pheny1-3-(p-alkylbenzoy1)cyclopropanes involves reduction of benzoy1 to benzy1 and opening of the three-membered ring to form 1,1phthaloy1-2-pheny1-3-(p-alkylbenzy1)-2-propenes, whereas in the ionic hydrogenation of the trans isomer benzoy1 is again reduced to benzy1 but the three-membered ring is preserved, forming 1,1-phthaloy1-2-pheny1-3-(p-alkylbenzy1)cyclopropanes.

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NITROYLIDES .

5. SYNTHESIS AND SOME REACTIONS OF IODONIUM NITROYLIDES AND α -NITRO-

SUBSTITUTED IODONIUM SALTS*

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Despite the strong destabilizing effect of NO₂ groups on cationoid species, stable sulfonium and selenonium nitro compounds can be prepared in which the onium center and the NO₂ group are attached to the same carbon atom — α -nitro-substituted sulfonium and selenonium salts and their corresponding nitroylides [2-7]. Sulfonium and selenonium compounds are known to be among the most stable onium compounds. We decided to see whether we could prepare α -nitro-substituted representatives of much less stable onium compounds, iodine derivatives: α -nitro-substituted iodonium salts and iodonium nitroylides. Nitro derivatives of this sort are unknown; an earlier attempt to prepare an iodonium nitroylide was unsuccessful [8].

The general method for the synthesis of iodonium ylides is the reaction of iodosoarene diacetates $[ArI(OAc)_2]$ with active methylene compounds [8-10]. We found that iodonium nitroylides, i.e., iodine ylides (I) containing the NO₂ group on the ylidic carbon, can be prepared in 60-70% yield by the reaction of aliphatic nitro compounds with an equimolar quantity of phenyl- or p-nitroiodosobenzene diacetates in ether or ether-benzene (20°C); the crystalline ylides (I) precipitate from solution in analytically pure form

$$\operatorname{ArI}(\operatorname{OAc})_2 + \operatorname{CH}_2(\mathbb{R}')\operatorname{NO}_2 \rightarrow \operatorname{Ar}\overset{\dagger}{\operatorname{I}} - \operatorname{C}(\mathbb{R}')\operatorname{NO}_2^- + 2\operatorname{CH}_3\operatorname{COOH}_{(1)}$$

where Ar = Ph, R' = NO₂ (Ia); Ar = p-NO₂Ph, R' = NO₂ (Ib); COPh (Ic); and CO₂CH₃ (Id). In the case of PhI(OAc)₂ we were able to prepare only dinitroylide (Ia) in the pure form; we could not isolate the mononitroylides (R' = COPh, CO₂CH₃), although their formation was indicated by the UV spectra of solutions derived by mixing the reactants in CH₃CN (λ_{max} 335 and 318 nm, respectively)† and by chemical reactions [11].

We verified the structures of ylides (I) by elemental analysis, IR and UV spectroscopy, and chemical reactions. Like their sulfur and selenium analogs [4, 7], iodonium nitroylides (I) have the nitrocarbanion and consequently the onium structure with delocalization of the negative charge onto the NO₂ group; their IR spectra show intense bands typical of the NO₂ group in nitroalkane salts (Table 1) but not those typical of the uncharged NO₂ group. The UV spectra of dinitroylides (Ia) and (Ib) contain an intense maximum in the 340-nm region, due to the dinitrocarbanion fragment $C(NO_2)^{-2}$, bonded to the electron-accepting group; the spectra also show a bathochromic shift of the maximum relative to the sulfur analog (for Ph₂S-C(NO₂)₂⁻¹ λ_{max} (CH₃CN) is 324 nm [4]), probably because the electron-accepting ability of I⁺ is lower than that of S⁺. This is probably also responsible for the slight shift of the bands of the NO₂ "salt" group in the IR spectra of (Ia) and (Ib) relative to the sulfur and selenium analogs [4, 7] (Table 1), which may imply that the localization of the negative charge on the dinitrocarbanion fragment is greater in ylides (I) than in the sulfur and selenium nitroylides (cf. [12]).

*Preliminary communication [1]. +Compare λ_{max} (CH₃CN) of the selenonium analogs Ph₂ Se-C (R') NO₂: R' = COPh, 339 nm; R' = CO₂CH₃, 314 nm [7].

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