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NEW COMPOUNDS

Aminolysis of Para-Substituted Benzalacetophenones

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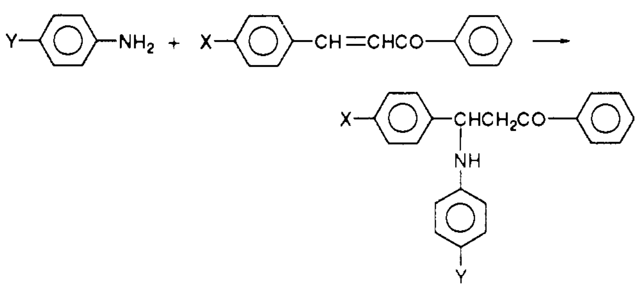
The nucleophilic addition of primary aromatic amines on para-substituted benzalacetophenones was studied in ethanolic solution. The formed adducts were assigned to be β-arylamino-β-(para-substituted phenyl)propiophenones, and their structures were confirmed by elemental analysis and spectroscopic methods.

The nucleophilic attack on carbon–carbon double bonds has been the subject of numerous investigations that were summarized in review articles (*1–3*).

α,β-Unsaturated ketones with addition compounds of heterocyclic amines such as piperazine, morpholine, and piperidine have been described by Pollard and others (*4–6*). Similar addition compounds with aromatic amines instead of heterocyclic amines have now been prepared.



where X = H, Cl, Br, CH_3, or OCH_3 and Y = H, Cl, CH_3, OCH_3, or NO_2

Procedure

The α,β-unsaturated ketone (0.2 mol) prepared as previously described (*7–9*) was dissolved in a minimum amount of boiling methanol under reflux. As soon as the substance completely dissolved, the corresponding anhydrous aromatic amine (0.21 mol) was added and the solution refluxed for 10 h. The use of an excess of amine tended to make the addition more complete and obviated much difficulty in the recrystallization process.

The addition product separated after standing in an icebox for several hours. It was filtered, washed with small amount of alcohol to remove untreated amine, air-dried, and recrystallized from alcohol three times before being subjected to analysis. The yield of the crude product was almost quantitative. The resulting addition products are listed in Table I. They are all stable under ordinary conditions. Similar to the piperazine addition products, but like the addition products of piperidine and morpholine which were reported by Georgy and Schwyzer (*6*), they are decomposed by heating with water, yielding the corresponding starting amine and the α,β-unsaturated ketones. Similarly, dilute hydrochloric acid decomposes them into the hydrochloride of the corresponding amine and the unsaturated ketone, respectively.

The structure of the above-mentioned amino ketones are established by the elemental analysis and their spectral data. Elemental analyses were in excellent agreement with those calculated. The IR spectra showed bands assigned to N–H at 3400–3600 cm^{-1} and C=O at 1650 cm^{-1}-acid. The mass spectra of the produced amino ketones were studied. The relative intensities of the most prominent peaks in their fragmentation patterns are recorded in Table II.

Table I. Physical Data

$XC_6H_4CH(NHC_6H_4Y)CH_2COC_6H_5$

compd no.	X	Y	formula	mp, °C	yield, %
IIa	H	H	$C_{21}H_{19}NO$	161	75
IIb	H	CH_3	$C_{22}H_{21}NO$	159	86
IIc	H	OCH_3	$C_{22}H_{21}NO_2$	139	67
IId	H	Cl	$C_{21}H_{18}NOCl$	167	80
IIe	H	NO_2	$C_{21}H_{18}N_2O_3$	172	88
IIIa	CH_3	NO_2	$C_{22}H_{20}N_2O_3$	192	70
IIIb	CH_3	Cl	$C_{22}H_{20}NOCl$	186	74
IVa	Cl	H	$C_{21}H_{18}NOCl$	235	90
IVb	Cl	Cl	$C_{21}H_{17}NOCl_2$	155	89
Va	Br	H	$C_{21}H_{18}NOBr$	238	83
Vb	Br	NO_2	$C_{21}H_{17}N_2O_3Br$	136	72
VIa	OCH_3	H	$C_{22}H_{21}O_2N$	173	68
VIb	OCH_3	CH_3	$C_{23}H_{23}O_2N$	151	78
VIc	OCH_3	OCH_3	$C_{23}H_{23}O_3N$	182	63
VId	OCH_3	NO_2	$C_{22}H_{20}O_4N_2$	166	87
VIe	OCH_3	Cl	$C_{22}H_{20}O_2NCl$	148	77

Registry No. IIa, 742-43-8; IIb, 37904-94-2; IIc, 802-49-3; IId, 94864-08-1; IIe, 804-20-6; IIIa, 95006-21-6; IIIb, 100410-41-1; IVa, 119948-33-3; IVb, 119948-34-4; Va, 119948-35-5; Vb, 119948-36-6; VIa, 802-48-2; VIb, 119948-37-7; VIc, 119948-38-8; VId, 119948-39-9; VIe, 96171-57-2; $PhNH_2$, 62-53-3; p-$MeC_6H_4NH_2$, 106-49-0; p-$MeOC_6H_4NH_2$, 104-94-9; p-$ClC_6H_4NH_2$, 106-47-8; p-$O_2NC_6H_4NH_2$, 100-01-6; PhCH=CHCOPh, 94-41-7; p-MeC_6H_4CH=CHCOPh, 4224-87-7; p-ClC_6H_4CH=CHCOPh, 956-04-7; p-BrC_6H_4CH=CHCOPh, 1774-66-9; p-$MeOC_6H_4$CH=CHCOPh, 959-33-1.

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Table II. Mass Spectral Patterns and Proposed Fragment Structures[a]

$XC_6H_4CH(NHC_6H_4Y)N_2COC_6H_5$

compd no.	X	Y	M^+	$[XC_6H_4CHCH_2COC_6H_5]^+$	$[XC_6H_4CH_2CH_2COC_6H_5]^+$	$[XC_6H_4CH{=}CHCOC_6H_5]^+$	$[XC_6H_4C{\equiv}CCOC_6H_5]^+$	$[XC_6H_4C{=}CH]^+$	$[XC_6H_4CH{=}CHC_6H_5]^+$	$[XC_6H_4CH{=}NHC_6H_4Y]^+$	$[XC_6H_4CH_2NH_2]^+$	$[XC_6H_4CH—CH{=}CC_6H_5—NC_6H_4Y]^+$ (ring)	$[CH—CH{=}CC_6H_5—NC_6H_4Y]^+$ (ring)	$[CH—CH{=}C—NC_6H_4Y]^+$ (ring)	$[XC_6H_4C{=}CH—CC_6H_5{=}N]^+$ (ring)	$[XC_6H_4C{=}CH—C{=}N]^+$ (ring)	$[XC_6H_4C{=}CH—CH{=}N]^+$ (ring)	$[XC_6H_4CH{=}NH]^+$	$[YC_6H_4NH]^+$
IIa	H	H	301 (10)	209 (5)	210 (5)	208 (3)	206 (4)	102 (7)	180 (20)	182 (100)	107 (2)		206 (8)	129 (7)	205 (4)	128 (9)	129 (7)	105 (70)	092 (6)
IIb	H	CH_3	315 (21)	209 (11)	210 (6)	208 (7)	206 (13)	102 (5)	180 (9)	196 (100)	107 (4)	297 (6)		143 (6)	205 (8)	128 (3)	129 (5)	105 (75)	106 (5)
IIc	H	OCH_3	331 (23)	209 (10)	210 (13)	208 (11)		102 (9)	180 (4)	212 (100)	107 (14)				205 (5)	128 (2)	129 (4)	105 (100)	122 (3)
IId	H	Cl	335 (10)	209 (6)		208 (9)		102 (10)	180 (6)	216 (38)	107 (2)				205 (6)	128 (3)	129 (4)	105 (100)	126 (6)
IIe	H	NO_2	346 (8)	209 (32)	210 (12)	208 (7)	206	102 (5)	180 (14)	227 (50)	107 (2)	328 (6)			205 (4)	128 (2)	129 (2)	105 (100)	137 (2)
IIIa	CH_3	NO_2	360 (6)	223 (17)				116 (74)	194 (4)		121 (17)	342 (2)			219 (1)	142 (6)	143 (5)		137 (26)
IIIb	CH_3	Cl	349 (18)	223 (6)		222 (12)		116 (8)	194 (16)	230 (48)		331 (5)	240 (2)	163 (4)		142 (5)		119 (6)	126 (5)
IVa	Cl	H	335 (3)		244 (100)	242 (60)	240 (32)		214 (8)			317 (3)	206	129 (22)	239 (4)	162 (7)		139 (21)	092 (8)
IVb	Cl	Cl		243 (70)	244 (40)		240 (65)	136 (10)				351 (80)	240 (2)		239 (4)	162 (6)	163 (3)	139 (8)	126 (10)
Va	Br	H	380 (1)		289 (3)	287 (10)	285 (30)	181 (4)			186 (8)	362 (40)		129 (24)		207 (70)	208 (27)		092 (7)
Vb	Br	NO_2		288 (20)	289 (10)		285 (1)	181 (2)	259 (10)			407 (12)	251 (25)	174 (21)	284 (70)	207 (13)	208 (19)		137 (8)
VId	CH_3O	NO_2		239 (3)		238 (25)	236 (25)	132 (4)	210 (5)	257 (25)	137 (4)	358 (7)		174 (21)	235 (3)	158 (30)	159 (70)	135 (20)	137 (4)

[a] The data in parentheses are the intensities of the fragments relative to the base peak.

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