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Reaction of N-Arylcitraconisoimidium Perchlorates with Aromatic Hydrocarbons Under Friedel-Crafts' Conditions, a New and Convenient One-Step Method for the Synthesis of β-Aroyl-α-aryl-N-arylbutyramides

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Reaction of N-Arylcitraconisoimidium Perchlorates with Aromatic Hydrocarbons Under Friedel-Crafts' Conditions, a New and Convenient One-Step Method for the Synthesis of β-Aroyl-α-aryl-N-arylbutyramides

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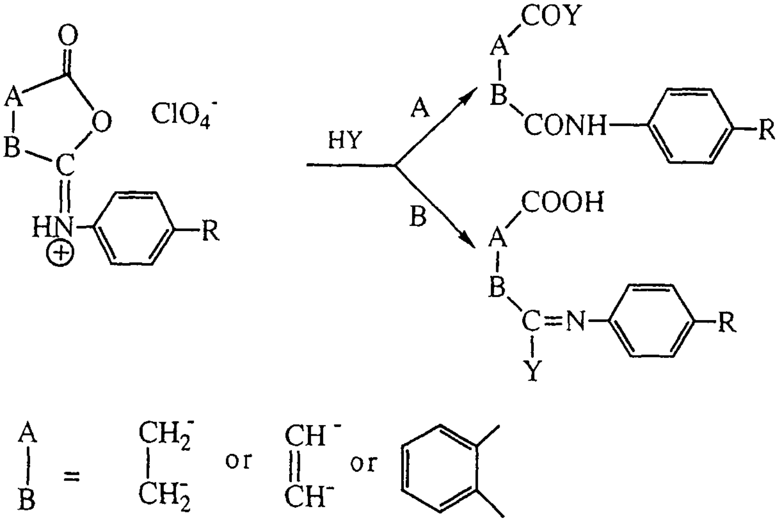
Abstract : A number of β-Aroyl-α-aryl-N-arylbutyramides (4a-h) have been synthesized using a new methodology involving arylation at the α,β-unsaturated ketonic systems of N-aryl-citraconisoimidium perchlorates (2a-c), followed by a subsequent ring opening via addition on the carbonyl group to give the title compounds (4a-h).

The previously reported$^{(1,2)}$ reactions of N-Arylcitraconisoimidium perchlorates show that ring opening of these salts takes place via attack on the carbonyl group in all cases studied. (Scheme 1, pathway A). It was of interest to study the mode of ring opening of some N-Arylcitraconisoimidium perchlorates of general formula (2) in which the electron releasing effect of the methyl group is expected to reduce the electrophilicity of the adjacent carbonyl group and consequently may lead to the alternative attack on the $-\overset{|}{C}=\overset{+}{N}H-$ group (Scheme 1 - pathway B).



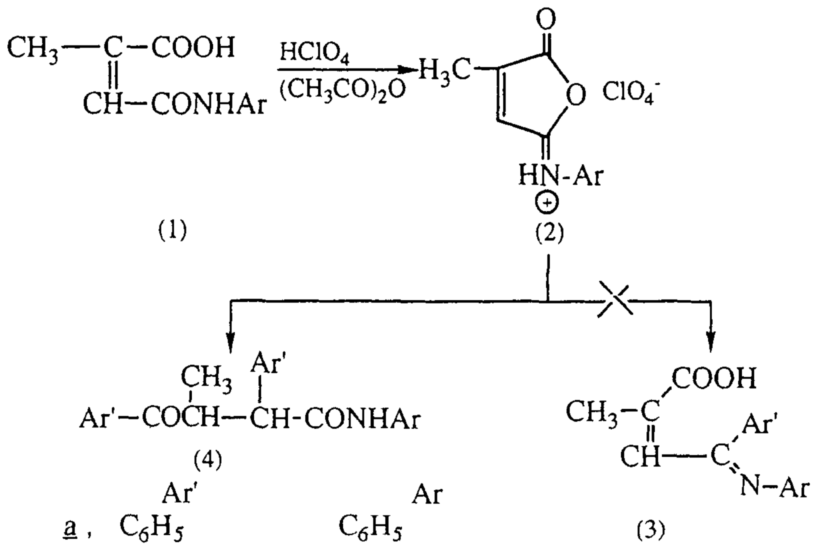
R = H or CH_3 or Cl

Scheme 1

A few studies dealing with the mode of reaction of different cyclic isoimidium perchlorates can be found in the literature$^{(1,2,4,5)}$ but none explores the use of citraconisoimidium salts in simple studies. These salts (2) are easily prepared by $^{(1,2)}$ the action of perchloric acid on N-arylcitraconamic acids (1) in acetic anhydride. Similar to other citraconamic acids (1a&c) (3), the acid (1b) is prepared by the reaction of p-toluidine with citraconic anhydride.

The structure of (2a-c) is supported by I.R. spectra (cf. Experimental Section) and by the ready hydrolysis to the amic acids (1a-c) upon treatment with water.

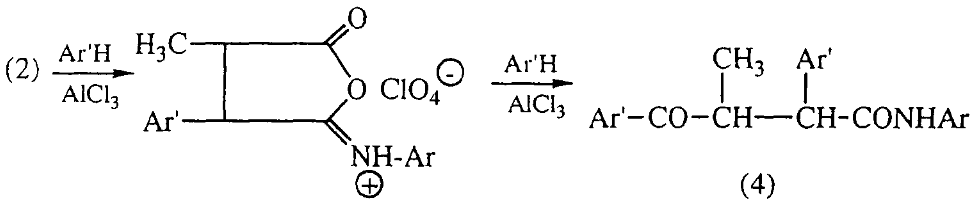
Initially we assumed that the reactivity of salts (2a-c) would follow the pattern reported for N-arylmaleisoimidium salts namely to react solely at the carbonyl group (1,2,4,5). Interestingly, these



	Ar'	Ar
a,	C_6H_5	C_6H_5
b,	$C_6H_4CH_3(p)$	C_6H_5
c,	$C_6H_3(CH_3)_2$-3,4	C_6H_5
d,	C_6H_5	$C_6H_4CH_3(p)$
e,	$C_6H_4CH_3(p)$	$C_6H_4CH_3(p)$
f,	$C_6H_3(CH_3)_2$-3,4	$C_6H_4CH_3(p)$
g,	$C_6H_4CH_3(p)$	$C_6H_4Cl(p)$
h,	$C_6H_3(CH_3)_2$-3,4	$C_6H_4Cl(p)$

isoimidium salts behaved differently. Thus when N-arylcitraconisoimidium salts (2) reacted with benzene, toluene and o-xylene in the presence of anhydrous aluminium chloride, products (4) corresponding to attack on the α,β-unsaturated ketonic systems followed by incorporation of another unit of the hydrocarbon on the carbonyl group (Scheme 2), are obtained in good yields. No acidic products of the type (3) arising from attack on the alternative sit $-\overset{|}{C}=\overset{+}{N}H-$ were isolated. The structure of compound (4) is based on their analytical data and the Infrared spectra which show close similarity to that of β-aroyl-N-aryl-propionamides$^{(3)}$.

Specifically the structure of (4a-h) finds support by a study of ^1H NMR spectra of some selected compounds (c.f Experimental Section) which lack the characteristic signals of a CH_2 group at δ 2.3 ppm$^{(6)}$. This excludes isomeric structure with the second Ar' next to the ketone functionality. Scheme (2) suggests a possible pathway for the formation of (4).



Scheme 2

Experimental

All melting points are uncorrected. Elemental analyses were carried out at the microanalytical units, Ain Shams and Cairo Universities. I.R. spectra in KBr were run on a Pye-Unicam SP 1200 spectrophotometer. ^{1}H NMR spectra were recorded using a Bruker 200 MHz instrument using $CDCl_3$ as a solvent. Electronic spectra were obtained on a Perkin-Elmer Lambda 4 BUV-vis. Spectrophotometer using ethanol as a solvent.

N-p-Tolylcitraconamic acid 1b.

An ethereal solution of citraconic anhydride (1.13g, 0.01mol) was added to a stirred solution of p-toluidine (1.07g, 0.01mol) in ether (25mL). The solid product was filtered off and recrystallised from ethanol to give N-p-tolylcitraconamic acid (1b) as pale yellow crystals, m.p. 178-9 °C, yield 85%. ν_{max} (KBr) 1620, 1685, 3240, 3310 cm^{-1}. (Found : C, 65.50; H, 5.80; N, 6.80; $C_{12}H_{13}NO_3$ requires : 65.75; H, 5.93; N, 6.39).

N-Arylcitraconisoimidium Perchlorates (2a-c).

Perchloric acid (2mL) was added dropwise to a suspension of N-arylcitraconamic acids (0.02mol) in acetic anhydride (20mL). The solution deposited the title compounds (2a-c) as yellow crystals. (cf. Table 1).

Hydrolysis of N-Arylcitraconisoimidium Perchlorates

N-Arylcitraconisoimidium Perchlorates (1g) were treated with water (25mL) whereupon N-arylcitraconamic acids (1a-c, 0.6g) were obtained. The product showed no melting point depression on admixture

Table 1

Compd.	M.P. °C	yield %	Molecular Formula	Analysis % Found / Calc. C	H	N	Cl	I.R. Spectra cm^{-1} $\nu_{C=O}$	$\nu_{C=N^+}$
2a	120-1	65	$C_{11}H_9NO_6Cl$	45.50	3.50	4.90		1882	1735
				46.07	3.14	4.88			
2b	95-6	73	$C_{12}H_{11}NO_6Cl$	47.30	3.70	4.60		1890	1705
				47.92	3.66	4.66			
2c	116-7	68	$C_{11}H_9NO_6Cl$	40.99	2.49		22.50	1882	1695
				41.12	2.80		21.81		

with authentic samples prepared by the action of amines on citraconic anhydride.

Reaction of N-Arylcitraconisoimidium perchlorates with aromatic hydrocarbons under Friedel-Craft's conditions formation of β-aroyl-α-aryl-N-arylbutyramides (4a-h).

Anhydrous aluminium chloride (3.34g, 0.025mol) was added portionwise to a stirred cold (ice - bath) solution of N-Arylcitraconisoimidium Perchlorate (0.01mol) in the aromatic hydrocarbon (50mL). The reaction mixture was stirred for 5 hrs. at room temperature, left overnight, and then hydrolysed by the addition of ice and concentrated hydrochloric acid. The resulting mixture was then steam distilled to remove the excess solvent and the residual organic product was filtered off, washed with aqueous sodium hydrogen carbonate and recrystallized from a suitable solvent to give the title compound (4a-h).

β-Benzoyl-α-phenyl-N-phenylbutyramide (4a), m.p. 177-8 °C (benzene), yield 60%, I.R. (ν_{NH} 3260, $\nu_{C=O}$ 1640, 1650) cm^{-1}. ^{1}H NMR δ 2.18 (d, 3H, γ CH_3), 4.42 (d, 1H , αCH), 6.7 (s, 1H , NH), 7.25-7.75 (m, 15 ar-H's) ppm. Found : C, 81.37; H, 6.49; N, 4.09; $C_{23}H_{21}NO_2$ requires : C,80.47; H 6.12; N, 4.08%.

β-p-Toluoyl-α-N-phenylbutyramide (4b), m.p. 208-9 °C (benzene, yield 68%, λ_{max} 240.3 n.m. (log ε 4.51), I.R. (ν_{NH} 3265, $\nu_{C=O}$ 1645, 1655) cm^{-1}. Found : C, 81.46; H, 6.78; N, 3.96; $C_{25}H_{25}NO_2$ requires : C, 80.86; H, 6.74; N, 3.77%.

β-3,4-Dimethylbenzoyl-α-3,4-dimethylphenyl-N-phenyl-butyramide, (4c), m.p. 199-200 °C, (benzene), yield 71%; I.R. (ν_{NH} 3242, $\nu_{C=O}$ 1645, 1655) cm^{-1}. Found : C, 82.08; H, 7.11; N, 3.52; $C_{27}H_{29}NO_2$ requires : C, 81.20; H, 7.27; N, 3.51%.

β-p-Toluoyl-α-p-tolyl-N-phenylbutyramide (4d), m.p. 186-7 °C, (ethanol), yield 69%, I.R. (ν_{NH} 3320, $\nu_{C=O}$ 1655, 1672) cm^{-1}. ^{1}H NMR δ 2.20 (d, 3H, γ CH_3), 2.27 (s, 3H, CH_3), 4.40 (d, 1H, αCH), 6.73 (s, 1H, NH), 7.25-7.47 (m, 14H) ppm. Found : C, 81.65; H, 6.11; N, 4.00; $C_{24}H_{23}NO_2$ requires : C, 80.67; H, 6.44; N, 3.92%.

β-p-Toluoyl-α-p-tolyl-N-p-tolylbutyramide (4e), m.p. 190-1 °C. (ethanol), yield 65%, I.R. (ν_{NH} 3320, $\nu_{C=O}$ 1675,1680) cm^{-1}

^{1}H NMR δ 2.16 (d, 3H, γ CH_3), 2.27 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 4.33 (d, 1H, αCH), 6.74 (s,1H, NH), 7.14-7.39 (m, ar-H's) ppm. Found : C, 81.36; H, 6.82; $C_{26}H_{27}NO_2$ requires : C, 81.04; H, 7.01%.

β-3,4-Dimethylbenzoyl-α-3,4-dimethylphenyl-N-p-tolyl-butyramide (4f), m.p. 199-200 °C. (ethanol), yield 72%, I.R. (ν_{NH} 3305, $\nu_{C=O}$ 1655, 1660) cm^{-1}. Found : C, 81.32; H, 7.54; N, 3.71; $C_{28}H_{31}NO_2$ requires : C, 81.36; H, 7.51; N, 3.39%.

β-p-Toluoyl-α-tolyl-N-p-chlorophenylbutyramide (4g), m.p. 208-9 °C. (ethanol), yield 78%, λ_{max} 240.8 n.m (log ε 4.49), I.R. (ν_{NH} 3265, $\nu_{C=O}$ 1650, 1660) cm^{-1}, ^{1}H NMR (DMSO; 300 MHz) δ 1.99 (d,3H, γ CH_3), 2.28 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 3.27-3.32 (m, 1H, βCH), 4.40 (d, 1H, αCH), 7.01-7.67 (m, 12H), 11.1 (s, 1H, NH) ppm. Found : C, 74.34; H, 5.99; N, 3.60; Cl, 8.90; $C_{25}H_{24}NO_2Cl$ requires : C, 74.07; H, 5.92; N, 3.46; Cl, 8.64%.

β-3,4-Dimethylphenyl-α-3,4-dimethylphenyl-N-p-chloro-phenylbutyramide (4h), m.p. 187-8 °C (ethanol), yield 70%, I.R. (ν_{NH} 3282, $\nu_{C=O}$ 1655, 1660) cm^{-1}. Found : N, 3.32; Cl, 8.90, $C_{27}H_{28}NO_2Cl$ requires : N, 3.23; Cl, 8.28%.

References :

1. M.F. Ismail, E.I. Enayat, F.A. EL-Bassiouny and H.A. Younes, Acta Chim. Hung. 128, 365 (1991); Chem. Abst., 115, 158859 q (1991).

2. G.V. Boyd and R.L. Monteil, J. Chem. Soc., Perkin Trans. 1, 1978, 1338.
3. A.E. Baydar and G.V. Boyd, J. Chem. Soc., Perkin Trans. 1, 2890, (1981).
4. M.F. Ismail, E.I. Enayat, F.A. EL-Bassiouny and H.A. Younes, Acta Chim. Hung. 128, 103 (1991); Chem. Abst., 115, 71289 e (1991).
5. A.E. Baydar and G.V. Boyd, J. Chem. Soc., Perkin Trans. 1, 2871, (1981).
6. R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectroscopic Identification of Organic Compounds, (John Wiley & Sons), Vol. 4, 224 (1981).

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