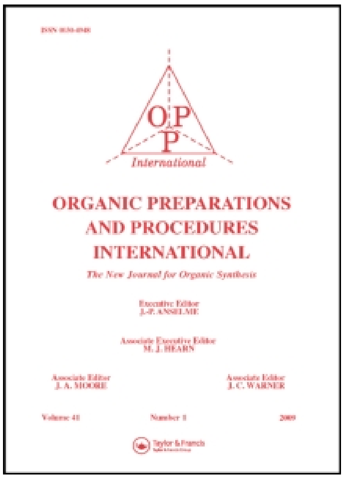

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CONJUGATED AZOALKENES. PART I SYNTHESIS OF SOME AROYLAZOALKENES

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CONJUGATED AZOALKENES. PART I

SYNTHESIS OF SOME AROYLAZOALKENES

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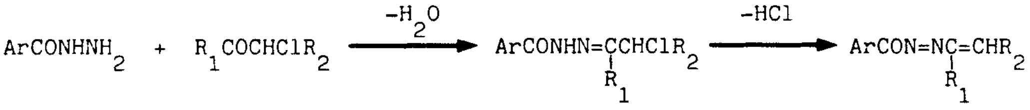
Conjugated azoalkene derivatives have been demonstrated to be important synthetic objectives and useful intermediates in organic chemistry by several authors, and especially by Caglioti and his coworkers.[1-4] In particular we have reported interesting 1,4-conjugate additions of some nucleophiles to the azo-ene system of azoalkenes, producing hydrazone derivatives with simultaneous C-functionalization.[1,2] Furthermore, we have described the synthesis of new 1-aminopyrrole derivatives by reaction of some azoalkenes with compounds containing activated methylene groups.[1,3]

The synthetic utility shown by some conjugated azoalkenes encouraged us to intensify the investigations for the synthesis of unknown derivatives of this type.[2,3] This paper describes the synthesis of some aroylazoalkenes obtained by dehydrohalogenation of the parent 2-chlorohydrazone derivatives.

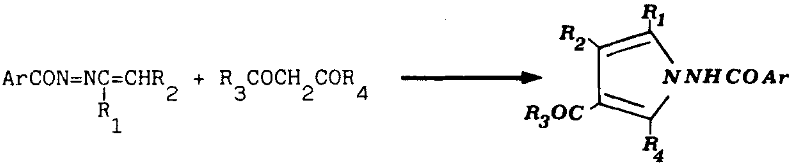


$$ArCONHNH_2 + R_1COCHClR_2 \xrightarrow{-H_2O} ArCONHN{=}\underset{R_1}{C}CHClR_2 \xrightarrow{-HCl} ArCON{=}N\underset{R_1}{C}{=}CHR_2$$

1 **2** **3** **4**

a) Ar = C_6H_5 $R_1 = CH_3$, $R_2 = CO_2CH_3$
b) Ar = $3\text{-}ClC_6H_4$ $R_1 = CH_3$, $R_2 = CO_2C_2H_5$
c) Ar = $3\text{-}CH_3C_6H_4$
d) Ar = $C_6H_5CH_2$

These compounds were necessary to our research aims since the synthesis of new 1-aroylamino-3-aminocarbonylpyrroles, 1-aroylamino-3-carbonylpyrroles and 1-aroylamino-3-carboxypyrroles by reaction of the aroylazoalkenes **4** with ß-ketoamides, ß-diketones and ß-ketoesters, respectively, are currently in progress in our laboratories.



$ArCON{=}N\underset{\displaystyle R_1}{\underset{|}{C}}{=}CHR_2 + R_3COCH_2COR_4$

R_3=N<, alkyl, aryl, alkoxy, aryloxy R_4=alkyl, aryl

2-Chlorohydrazones (3). General Procedure.- The aroylhydrazine **1** (0.02 mol) was slowly added to a stirred solution of the 2-chloroketone **2** (0.02 mol) in diethyl ether (100 ml). The mixture was stirred at room temperature until the reaction was complete (monitored by t.l.c. on silica gel; elution with cyclohexane-ethyl acetate mixture 60/40 (v/v); R_f: **3a**=0.32; **3b**=0.41; **3c**=0.38; **3d**=0.49; **3e**=0.36; **3f**=0.44; **3g**=0.38; **3h**=0.48). The reaction mixture was then concentrated to a small volume (10 ml) under reduced pressure with gentle heating. Addition of n-pentane (5°), gave the product **3** in satisfactory purity and in high yields (70-90 %).

Aroylazoalkenes (4). General Procedure.- The 2-chlorohydrazone **3** (3 mmol) dissolved in acetone (15 ml) is poured into a large separatory funnel containing n-pentane (285 ml) and saturated aqueous sodium carbonate (or 1% aqueous sodium hydroxide for **3g** and **3h**) (50 ml). The mixture is vigorously shaken until the reaction is complete (monitored by t.l.c. on silica gel; elution with cyclohexane-ethyl acetate mixture 60/40 (v/v); R_f: **4a**=0.69; **4b**=0.73; **4c**=0.71; **4d**=0.76; **4e**=0.71; **4f**=0.76; **4g**=0.70; **4h**=0.76). The organic layer is separated, washed with saturated aqueous sodium chloride, dried with sodium sulfate, and evaporated under reduced pressure with very mild heating, affording the product **4** in satisfactory purity. The product **4** is

Table 1. Physical Properties and Spectral Data of Compounds **3a-h**

Reagents 1	2	Hydrazone 3	mp[a] (°C)	IR (nujol) ν(cm^{-1})	^{1}H-NMR (CDCl$_3$/TMS$_{int}$) δ(ppm)
1a	**2a**	**3a**	96-97	3160 1770 1650	2.13 (s, 3H, Me); 3.77 (s, 3H, COOMe); 5.13 (s, 1H, CH); 7.2-8.06 (m, 5H, Ar); 9.43 (s, 1H, NH, D$_2$O exchange)
	2b	**3b**	100-102	3320 1750 1675	1.3 (t, 3H, COOEt); 2.13 (s, 3H, Me); 4.2 (q, 2H, COOEt); 5.17 (s, 1H, CH); 7.23-8.07 (m, 5H, Ar); 9.33 (s, 1H, NH, D$_2$O exchange)
1b	**2a**	**3c**	88-89	3200 1770 1660	2.17 (s, 3H, Me); 3.8 (s, 3H, COOMe); 5.13 (s, 1H, CH); 7.17-8.03 (m, 4H, Ar); 9.43 (s, 1H, NH, D$_2$O exchange)
	2b	**3d**	75-76	3200 1770 1665	1.27 (t, 3H, COOEt); 2.2 (s, 3H, Me); 4.23 (q, 2H, COOEt); 5.1 (s, 1H, CH); 7.23-7.97 (m, 4H, Ar); 9.83 (s, 1H, NH, D$_2$O exchange)
1c	**2a**	**3e**	78-79	3160 1750 1660	2.13 (s, 3H, Me); 2.33 (s, 3H, ArMe); 3.77 (s, 3H, COOMe); 5.13 (s, 1H, CH); 7.13-7.77 (m, 4H, Ar); 9.6 (s, 1H, NH, D$_2$O exchange)
	2b	**3f**	87-88	3170 1760 1655	1.27 (t, 3H, COOEt); 2.17 (s, 3H, Me); 2.37 (s, 3H, ArMe); 4.23 (q, 2H, COOEt); 5.15 (s, 1H, CH); 7.13-7.87 (m, 4H, Ar); 9.23 (s, 1H, NH, D$_2$O exchange)
1d	**2a**	**3g**	112-115	3200 1760 1670	2.0 (s, 3H, Me); 3.8 (s, 3H, COOMe); 3.97 (s, 2H, PhCH$_2$); 5.07 (s, 1H, CH); 7.3 (s, 5H, Ar); 10.0 (s, 1H, NH, D$_2$O exchange)
	2b	**3h**	90-93	3220 1740 1685	1.3 (t, 3H, COOEt); 1.97 (s, 3H, Me); 3.97 (s, 2H, PhCH$_2$); 4.28 (q, 2H, COOEt); 5.03 (s, 1H, CH); 7.33 (s, 5H, Ar); 9.73 (s, 1H, NH, D$_2$O exchange)

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[a] Melting points are uncorrected. With decomposition.

The microanalyses were in satisfactory agreement with the calculated values.

Table 2. Yields, Physical Properties and Spectral Data of Compounds **4a-h**

Azoalkene **4**	Yield[a] (%)	mp[b] (°C)	IR (neat) ν(cm^{-1})	^{1}H-NMR (CDCl$_3$/TMS$_{int}$) δ(ppm)
4a	70	24	1730 1655	2.4 (s, 3H, Me); 3.86 (s, 3H, COOMe); 7.07 (s, 1H, CH); 7.3-8.13 (m, 5H, Ar)
4b	77	oil	1730 1655	1.3 (t, 3H, COOEt); 2.37 (s, 3H, Me); 4.25 (q, 2H, COOEt); 7.0 (s, 1H, CH); 7.23-8.13 (m, 5H, Ar)
4c	43	66-67	1730 1655	2.4 (s, 3H, Me); 3.86 (s, 3H, COOMe); 7.07 (s, 1H, CH); 7.3-8.13 (m, 4H, Ar)
4d	59	42	1725 1650	1.35 (t, 3H, COOEt); 2.4 (s, 3H, Me); 4.33 (q, 2H, COOEt); 7.07 (s, 1H, CH); 7.27-8.07 (m, 4H, Ar)
4e	68	32-33	1730 1655	2.4 (s, 6H, Me and ArMe); 3.83 (s, 3H, COOMe); 7.0 (s, 1H, CH); 7.23-7.87 (m, 4H, Ar)
4f	55	oil	1720 1650	1.33 (t, 3H, COOEt); 2.4 (s, 6H, Me and ArMe); 4.3 (q, 2H, COOEt); 7.02 (s, 1H, CH); 7.13-7.92 (m, 4H, Ar)
4g	45	oil	1735 1675	2.23 (s, 3H, Me); 3.83 (s, 3H, COOMe); 3.97 (s, 2H, PhCH$_2$); 6.93 (s, 1H, CH); 7.3 (s, 5H, Ar)
4h	47	oil	1735 1680	1.33 (t, 3H, COOEt); 2.23 (s, 3H, Me); 3.97 (s, 2H, PhCH$_2$); 4.3 (q, 2H, COOEt); 6.93 (s, 1H, CH); 7.33 (s, 5H, Ar)

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[a] Yield of pure isolated product.
[b] Melting points are uncorrected. With decomposition.
The microanalyses were in satisfactory agreement with the calculated values.

stored in the refrigerator (at -20 °C) without appreciable decomposition for several days.

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