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THE PHOTOCHEMICAL CYCLIZATION OF 2-ALKYLAMINO-3-ARYL-2-CYCLOHEXENONES

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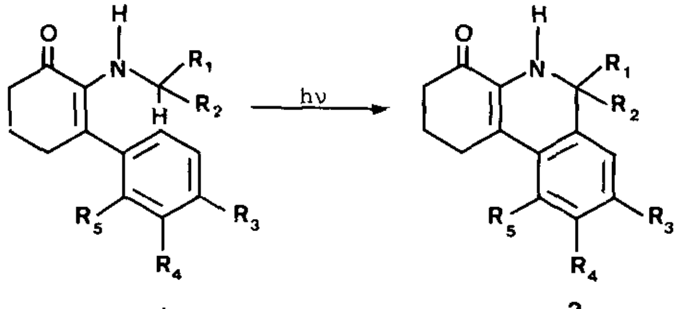
Abstract – The irradiation of 2-alkylamino-3-aryl-2-cyclohexenones gives access to polycyclic heterocycles.

With the purpose of gaining access to polycyclic heterocycles, 2-cyclohexenones compounds (1a-1h) have been prepared and irradiated. These compounds, similar to the aminochalcones previously studied[1], possess both an aryl group β to the carbonyl function, and an abstractable γ-hydrogen on the dialkylamino group. In contrast to the compounds previously studied, the enone portion of these molecules is fixed in an S-trans arrangement.

Cyclohexenones (1a-1h) were prepared by irradiation of the corresponding 2-alkylarylsulfonamido-2-cyclohexenones[2,3]. These compounds were then photolyzed at 366 nm, leading in all cases to the expected products (2). The results are tabulated in Table I.



1 2

The major photoproduct (2) is obtained in yields ranging from 50 to 70% bases on consumed starting material. Total conversion of starting material was not achieved due to the fact that the extinction coefficient of adduct (2) is larger than that of the starting material (1) at 366 nm, leading to an internal filter effect.

1	R_1	R_2	R_3	R_4	R_5	Conversion %	Yield % (a)
a	CH_3	CH_3	CH_3	H	H	20	70
b	CH_3	CH_3	OCH_3	H	H	10	50
c	CH_3	CH_3	H	H	H	10	60
d	CH_3	CH_3	H	$-(CH)_4-$		20	70
e	CH_3	CH_3	$-(CH)_4-$		H	10	50 (b)
f	H	CH_3	CH_3	H	H	20	70
g	H	C_6H_5	CH_3	H	H	15	65
h	H	$CH=CH_2$	CH_3	H	H	20	50

Table I

(a) based on consumed starting material.
(b) mixture of 2 isomers (ca. 1/1).

The structure of (2) is based on a comparison of spectral data with compounds of type (1). The carbonyl frequency in the IR spectrum of (2) is lowered from the 1660 cm^{-1} value observed for (1) to 1650 cm^{-1} due to more efficient conjugation in the cyclized product ; likewise, the U.V. spectrum of (2) exhibits a bathochromic shift. The mass spectrum indicates that two hydrogens, one α to hydrogen and one on the aromatic ring are lost. These observations are in agreement with the suggested photocyclization.

EXPERIMENTAL

The IR spectra were recorded on a Philips SP 2000. UV spectra were recorded in ether on a Beckman Acta III. NMR spectra were recorded on a Varian A 60. Mass spectra were obtained at the UER Pharmacie de Reims.

Photolysis of 2-alkylamino-3-aryl-2-cyclohexenones (1)

A solution of (1) (0.2 g) in ether (100 ml) was irradiated for 6 h at 366 nm[4]. A conversion of (1) from 10 to 20% was usually observed. At longer reaction times no change in reaction mixture composition was observed. The reaction mixture was concentrated in vacuo, leaving a crude product which was subsequently purified by preparative TLC to give (2) in the yields stated in table I.

(2a) : mp 96°C ; NMR (CCl_4) : δ 1.4 (s,6H) ; 2.3 (s,3H) ; 2.0-2.8 (m,6H) ; 4.2 (br.s,1H) ; 7.0 (m,3H) ; IR (CCl_4) : 3320, 1650, 1430, 1115 cm^{-1} ; UV (ether) : λ_{max} = 382 nm, ε = 11700 ; λ_{max} = 242 nm, ε = 14700 ; λ_{max} = 214 nm, ε = 13600 ; mass spectrum m/e 241 (M^+) ; 226 (M-15) ; high resolution mass spectrum m/e 241.1466 ($C_{16}H_{17}NO$ requires 241.1466).

(2b) : mp 82°C ; NMR ($CDCl_3$) : δ 1.4 (s,6H) ; 1.7-2.9 (m,6H) ; 3.8 (s,3H) ; 4.2 (br.s,1H) ; 6.6-7.5 (m, 3H) ; IR ($CHCl_3$) = 3380, 1650, 1565, 1460, 1310, 1115 cm^{-1} ; UV (ether) : λ_{max} = 380 nm, ε = 9100 ; λ_{max} = 244 nm, ε = 11000; λ_{max} = 224 nm, ε = 9500 ; mass spectrum m/e 257 (M^+), 242 (M-15), 199 ; high resolution mass spectrum m/e 257.1410 ($C_{16}H_{19}NO_2$ requires 257.1415).

(2c) : mp 104°C ; NMR ($CDCl_3$) : δ 1.4 (s,6H) ; 1.6-3.0 (m,6H) ; 4.5 (s,1H) ; 7.3 (s,4H) ; IR ($CHCl_3$) : 3300, 1650, 1450, 1350, 1375 cm^{-1} ; UV (ether) : λ_{max}= 340 nm, ε = 3600 ; λ_{max} = 236 nm, ε = 4800 ; mass spectrum m/e 227 (M^+) ; 212 (M-15) ; high resolution mass spectrum m/e 227.1298 ($C_{15}H_{17}NO$ requires 227.1300).

(2d):NMR ($CDCl_3$) : δ 1.3 (s,6H) ; 1.7-3.0 (m,7H) ; 7.2-8.0 (m,6H) ; IR ($CHCl_3$) : 3360, 1660, 1450, 1330, 1200 cm^{-1} ; UV (ether) : λ_{max} = 403 nm, ε = 2100 ; λ_{max} = 290 nm, ε = 6100 ; λ_{max} = 212 nm, ε = 50500 ; mass spectrum m/e 277 (M^+) ; 262 (M-15) ; high resolution mass spectrum m/e 277.1464 ($C_{19}H_{19}NO$ requires 277.1466).

(2e):NMR ($CDCl_3$) : δ 1.4 (s,6H) ; 2.0-3.0 (m,6H) ; 4.5 (br.s,1H) ; 7.2-8.0 (m,6H) ; IR ($CHCl_3$) : 3340, 1675, 1450, 1370, 1340, 1260 cm^{-1} ; UV (ether) : λ_{max} = 400 nm, ε = 3100 ; λ_{max} = 280 nm, ε = 7300 ; λ_{max} = 215 nm, ε = 40800 ; mass spectrum m/e 277 (M^+) ; 262 (M-15).

(2f): mp 84°C ; NMR ($CDCl_3$) : δ 1.3 (d,J=6.5 Hz,3H) ; 1.8-3.0 (m,6H);2.4(s,3H);3.5 (s,1H) ; 4.5 (q,J=6.5 Hz,1H) ; 6.8-7.6 (m,3H) ; IR ($CHCl_3$) : 3380, 1660, 1610, 1450, 1370 cm^{-1} ; UV (ether) : λ_{max} = 384 nm, ε = 4800 ; λ_{max} = 240 nm, ε = 9600 ; λ_{max} = 216 nm, ε = 7700 ; mass spectrum m/e 227 (M^+), 212 (M-15) ; high resolution mass spectrum m/e 227.1298 ($C_{15}H_{17}NO$ requires 227.1300).

(2g):NMR ($CDCl_3$) : δ 1.7-3.0 (m,6H) ; 2.2 (s,1H) ; 7.0-7.5 (m,8H) ; IR ($CHCl_3$) : 3400, 1660, 1610, 1460, 1370, 1335 cm^{-1} ; UV (ether) : λ_{max} = 280 nm, ε = 3400 ; λ_{max} = 240 nm, ε = 12500 ; mass spectrum m/e 289 (M^+), 212, 91 ; high resolution mass spectrum m/e 289.1451 ($C_{20}H_{19}NO$ requires 289.1466).

(2h):NMR ($CDCl_3$) : δ 1.7-3.0 (m,6H) ; 2.3 (s,3H) ; 3.3 (s,1H) ; 4.8 (m,2H) ; 5.1 (m,1H) ; 6.8-7.4 (m,3H) ; IR ($CHCl_3$) : 3380, 1690, 1660, 1410, 1230 cm^{-1} ; UV (ether) : λ_{max} = 376 nm, ε = 1344 ; λ_{max} = 296 nm, ε = 5900 ; λ_{max} = 242 nm, ε = 4929 ; mass spectrum m/e 239 (M^+), 238 (M-1), 213, 212 ; high resolution mass spectrum m/e 239.1290 ($C_{16}H_{17}NO$ requires 239.1310).

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