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Reaction Products of 2,7-Diaroyl-4,5-Fulvenotropones with Hydrazine Hydrate

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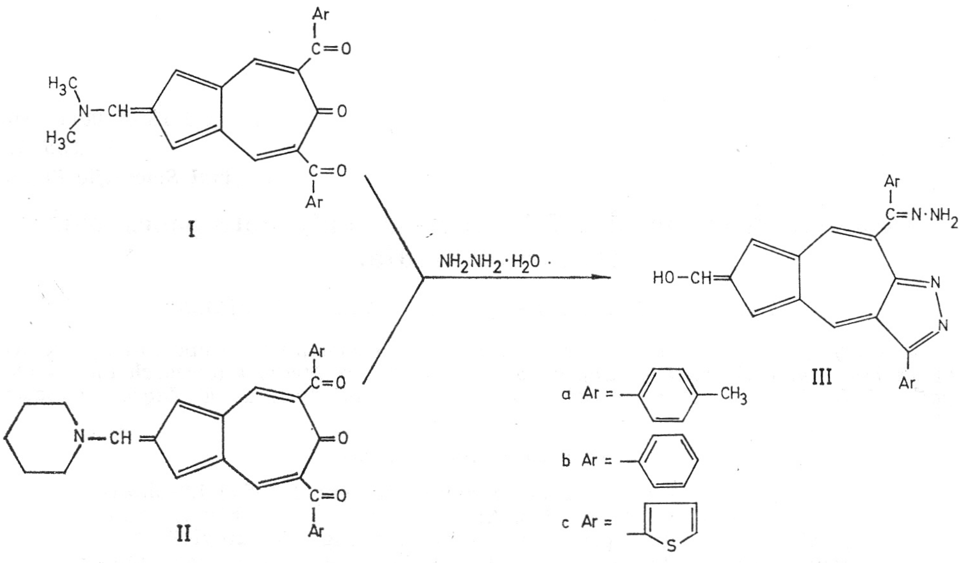
6′-Hydroxy-8-(α-hydrazonoarylmethyl)fulveno(2′,3′-5,6)-1,2-diazaazulenes (IIIa, Ar=tolyl; IIIb, Ar=phenyl; IIIc, Ar=thienyl) were obtained as reaction products of corresponding 2,7-diaroyl-4,5-fulvenotropones with hydrazine hydrate. The structure of the obtained compounds are discussed on the basis of their infrared, mass and ^{1}H nuclear magnetic resonance spectra.

INTRODUCTION

Several ways are known to lead to 1,2-diazaazulenes from cycloheptanones[1,2], pyrazole-3,4-dicarbaldehyde[3] and tropone or tropolone derivatives[4a], while pyrazoloazulene was obtained from 5- and 6-acetylazulene derivatives[5]. In this paper the investigations focused on the reactivity of 2,7-diaroyl-4,5-fulvenotropones were described which afforded heterocyclic azulenes of 1,2-diazaazulene type.

For the tropone molecule which is not condensed with benzenoid or with the heteroaromatic ring, the reaction with hydrazine and the subsequent formation of the corresponding 2-amino derivative is characteristic[6,7]. The substituents or annulated ring system influence the reactivity of the tropone carbonyl group effectuating in some cases a complete indifference to ketonic reagents[4b,8,9]. It was found that 2,6-disubstituted tropones, although having a vacant position next to the carbonyl group, underwent an abnormal reaction when treated with hydrazine giving products of rearrangement instead of the expected 2-aminotropone derivatives[10]. In the case of 6′-*N*,*N*-dimethylamino-2,7-diaroylfulveno(2′,3′-4,5)tropones[11] the carbon atoms next to the tropone carbonyl bear aroyl groups as substituents. During the reaction of the tropone carbonyl and one of the aroyl carbonyls with hydrazine hydrate, an isopyrazolic ring is formed. Simultaneously the other aroyl carbonyl is converted to hydrazone and an *N*,*N*-dimethylamino group on the exocyclic fulvene carbon exchanged for hydroxyl. The prepared 6′-hydroxyfulveno (2′,3′-5,6)-1,2-diazaazulenes are shown on Scheme 1.

Compound IIIa was obtained by the reaction of hydrazine hydrate with 6′-piperidino-2,7-di(*p*-toluyl)fulveno(2′,3′-4,5)tropone (IIa). Compound IIIb was obtained by the reaction of hydrazine hydrate with 6′-piperidino-2,7-dibenzoylfulveno(2′,3′-4,5)tropone (IIb). With excess hydrazine hydrate, 6′-*N*,*N*-di-



methylamino- (Ia, b, c), as well as 6′-piperidino-2,7-diaroylfulveno(2′,3′-4,5) tropones (IIa, b), provided identical products: 6′-hydroxy-fulveno(2′,3′-5,6)-1,2-diazaazulenes (IIIa, b, c). All obtained compounds were identified by mass, ^{1}H-NMR and ir. spectral data.

DISCUSSION

Products only slightly soluble or insoluble in most organic solvents were obtained in the reaction of hydrazine hydrate with 6′-*N,N*-dimethylamino-2,7-bis(*p*-tolyl)-4,5-fulvenotropone (Ia). During the optimization of reaction conditions it was found that excess hydrazine hydrate resulted in the formation of a product with the formula $C_{27}H_{22}ON_4$ (M. W. 418). The comparison of the ir spectrum with that of the starting compound showed that the absorption bands characteristic for tropone and aroyl carbonyl groups were missing. Instead, the absorption bands of the isopyrazolic ring were present accompanied by absorption bands indicating the hydrazone amino group. In the ^{1}H-NMR spectrum of the product no signals of *N*-methyl protons could be found, but the signal of the exocyclic fulvene proton was present. The mass spectrum was also in agreement with the structure proposed. These data confirmed the presumption that 6′-hydroxy-8-[α-hydrazono-(*p*-methylbenzyl)]-3-(*p*-tolyl)fulveno(2′,3′-5,6)-1,2-diazaazulene (IIIa) was obtained. Corresponding products were also obtained with other fulvenotropone derivatives (Scheme 1). In all cases the 6′-*N,N*-dimethylamino was exchanged for a hydroxyl group. For additional proof the same reaction was performed with 6′-piperidino-2,7-bis(*p*-toluyl)-4,5-fulvenotropone (IIa). In fact, the product was identical with the one obtained by the condensation of 6′-*N,N*-dimethylamino compound with excess hydrazine hydrate .These findings are compatible with the results obtained by Hafner *et al.* in the case of some other tropone derivatives[12].

The tautomeric form, originating from the structure postulated as a reactive transition state which is not fulvenic, could be detected in equilibrium mixture only with adequately hetero substituted benzofulvene derivatives[13]. Recently it has been shown that 2-hydroxyazulene exists in enolic form in methanol, and in azulanone form in chloroform or in water[6]. In our case, because of the lack of the carbonyl absorption band in the ir. spectra of the obtained products and signals with chemical shifts corresponding to alicyclic methylene protons, tautomerism was not taken into consideration.

The reaction of azaazulene IIIa with acetone afforded the asymmetrical azine. The molecular peak ($M^+ = 458$) was accompanied by signals indicating the fragmentation of methyl, *iso*-propylidene and imino-*iso*-propylidene groups. Moreover, in the ir. spectrum, the absorption bands characteristic for the primary amino group were absent. Thus the original monohydrazone formation with the participation of one aroyl carbonyl was confirmed.

Ir. spectra

Several distinct absorption bands in the area 3500—3200 cm^{-1} in the ir. spectra indicate the presence of hydroxy and amino groups[14a,15]. The stretching of CH on the C=C double bonds in aromatic and aliphatic molecules originates the absorption bands at 3100—2800 cm^{-1} [16,17]. By comparing the 1700—1200 cm^{-1} range of ir. spectra of the starting tropones with the obtained hydrazones it is evident that the broad strong band at 1610—1530 cm^{-1} is characteristic of the tropone[18-21] and that the aroyl carbonyl stretching and strong multiple band at 1500 cm^{-1}, originated by three β-carbonyls[12], are not present in the spectra of the products. Strong absorption bands at 1620—1605 cm^{-1} and 1570—1565 cm^{-1} are found instead.

As shown by I. I. Grandberg *et al.*[22], the absorption of the C=N group of isopyrazoles results in a strong band at 1600 cm^{-1} differentiating this ring from the pyrazolic, where two weak bands are found. This is particularly evident in the case of the rearrangement of 3,4,4,5-tetramethylisopyrazole to 1,3,4,5-tetramethylpyrazole. In the ir. spectra of the tetrasubstituted isopyrazole rings, intensive bands at 1390, 1275 and 1250—1240 cm^{-1} are also present and these can also be seen in the spectra of compounds IIIa, b, and c. The fulvene exocylic double bond stretching frequencies[12,17,23] are in the range 1660—1630 cm^{-1} as shoulders on the C=N stretching band at about 1600 cm^{-1}. Only the ir. spectrum of compound IIIa shows these shoulders distinctly at 1630 cm^{-1} while in other cases they are weakly expressed. The absorption bands at 1605, 1615 and 1610 cm^{-1} are assigned to the C=N stretching in compounds IIIa, b, and c congruent with Gubelt and Warkentin[24] who assigned the band at 1610 cm^{-1} to the C=N stretching of tris-isopyrazole.

The C=C stretching modes of aromatic, sevenmembered and fulvene rings[17,25] are also present in this area. The conjugation of C=N with C=C leads to multiple frequencies: those near 1640 cm^{-1} and 1570 cm^{-1} are attributed to the asymmetric and symmetric stretching frequencies of the system —C=C—C=N—[14b]. The strong absorption band present in all recorded ir. spectra might be assigned in this way. Other absorption bands are caused by the in-plane and out-of-plane deformations of aromatic hydrogen atoms and amino groups and, in compound IIIc, by the thiophene nucleus hydrogen atoms.

Mass spectra of 5,6-fulveno-1,2-diazaazulenes

The molecular weights of compounds IIIa, b and c are taken from the mass spectra (Fig. 1). The *m/e* values of the parent ions are 418, 390 and 402 in agreement with the molecular weights calculated for the proposed molecular formulae. The ions with masses diminished by 28, 27, 18 and 17 mass units correspond to the elimination of N_2, HCN, water and hydroxyl, or to a smaller extent ammonia, conformably with the $M^+ - 16$ and $M^+ - 17$ relative intensities measured in the mass spectrum of benzophenone monohydrazone. Further, fragments with 91 (tolyl), 77 (phenyl) and 39 (cyclopropenyl)[26] mass units are present in the mass spectra of relevant compounds. The masses of ions 119, 105 and 111 correspond to fragments with structures as given[27]:

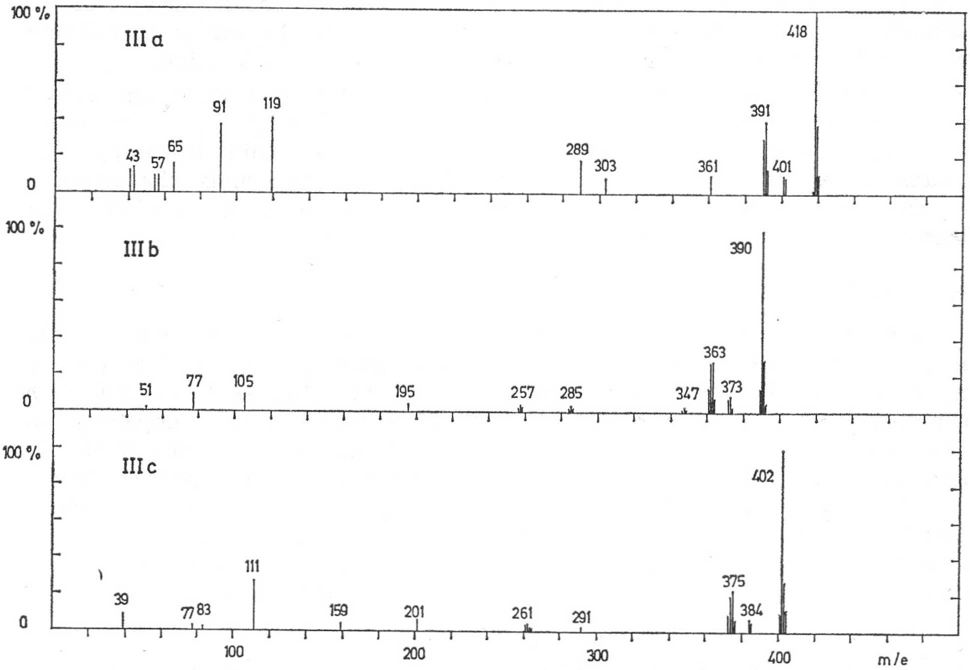
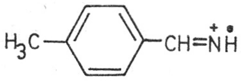
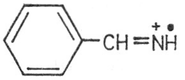
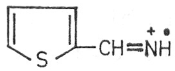


Fig. 1. Mass spectra of 1,2-diazaazulene derivatives IIIa, Ar = tolyl, IIIb, Ar = phenyl, IIIc, Ar = thienyl.







^{1}H-NMR spectra of 5,6-fulveno-1,2-diazaazulenes

The signals corresponding to 6 protons with chemical shift values for $-N(CH_3)_2$ groups in ^{1}H-nmr. spectra of 6′-*N*,*N*-dimethylamino-2,7-diaroylfulveno(2′,3′-4,5)tropones[11] are not present in the spectra of their condensation products with hydrazine hydrate. The methyl protons of *p*-tolyl substituent give a singlet at $\delta = 2.35$ ppm. The signals of the fulvene ring protons are well separated from those of the phenyl protons[28]. There are two signals at

$\delta = 7.9$ and 8.05 ppm in the spectrum of compound IIIa, and two at $\delta = 7.83$ and 7.98 ppm in the case of compound IIIb. The thiophene protons in compound IIIc show two multiplets at $\delta = 6.8$—7.1 ppm and $\delta = 7.25$—8.16 ppm. This second one overlaps with two fulvene protons giving signals at 7.3—8.05 ppm. These data are in agreement with chemical shifts for 6-hydroxy-2,3-diformylfulvene showing the singlet of the fulvene proton at 7.89 ppm[12].

The exocyclic protons of diazaazulenes IIIa, b and c originate signals at $\delta = 8.83$, 8.8 and 9.3 ppm (broad signal) and are separated from the signals of the protons belonging to the sevenmembered ring at $\delta = 8.52$ and 8.56 ppm (compd. IIIa), $\delta = 8.53$ and 8.58 ppm (compd. IIIb) and $\delta = 8.85$—8.83 ppm (compd. IIIc)[29]. The addition of trifluoroacetic acid eliminated the signals of the hydroxy protons.

EXPERIMENTAL

All melting points are uncorrected.

Ir. spectra were recorded with Perkin Elmer Model 257 spectrophotometer in KBr pellets. Mass spectra were taken with instrument CEC 21-110 C, 70eV, 100 μA and temperature 200—250 °C. The proton magnetic resonance spectra were recorded with spectrometer Varian Model A-60. Because of low solubility, a mixture of $CDCl_3$ and CF_3COOH was used as solvent. In the case of compound IIIc TMS was applied as the external reference, and in other cases as the internal reference.

Condensation of fulvenotropones with hydrazine hydrate — General procedure

Condensation resulted in better yields when hydrazine hydrate was added to the boiling suspension of the corresponding tropone in abs. ethanol. The precipitation of the product followed after the initial dissolution of tropone. The precipitate was filtered off the hot reaction mixture, washed with abs. ethanol and dried in vacuum (10^{-2} torr) for several hours. The repeated recrystallization of the products was reduced to a minimum to avoid eventual decomposition.

6′-hydroxy-8-[α-hydrazono(p-methylbenxyl)]-3-(p-tolyl)fulveno(2′,3′-5,6)1,2-diazaazulene (IIIa)

0.22 g (0.5 mmol) of 6′-*N*,*N*-dimethylamino-2,7-bis(*p*-toluyl)fulveno(2′,3′-4,5)tropone (Ia) was condensed with 1.6 ml of 100% hydrazine hydrate. 0.11 g (57.3% yield) of product was obtained, m. p. 242 °C (dec.).

Ir. spectrum: 3430, 3300, 3270, 3210, 3180, 1565, 1391, 1375, 1240, 1250, 1185, 1130, 1150, 1050, 1020, 910, 825, 768, and 722 cm^{-1}.

^{1}H-NMR spectrum, δ values: 2.25 ppm (broad signal, 6H, methyl H); 6.90—7.58 ppm (m,8H,phenyl H); 7.9 and 8.05 ppm (two broad signals, 1H+1H, fulvene ring H); 8.55 and 8.60 ppm (two s, 1H+1H, seven-membered ring H); 8.83 ppm (s,1H, exocyclic fulvenic H).

Anal. $C_{27}H_{22}N_4O$ (418.48) calc'd.: C 77.49; H 5.30; N 13.38%
found: C 77.61; H 5.19; N 13.52%

6′-hydroxy-8-(α-hydrazonobenzyl)-3-phenylfulveno(2′,3′-5,6)-1,2-diazaazulene (IIIb)

By condensation of 0.1 g (0.25 mmol) 6′-*N*,*N*-dimethylamino-2,7-dibenzoylfulveno(2′,3′-4,5)tropone (Ib) with 0.17 ml of hydrazine hydrate, 0.047 g (60.3% yield) of product was obtained m. p. 230 °C (dec.).

Ir. spectrum: 3390, 3280, 3200, 3060, 2890, 1640, 1620, 1615, 1565, 1391, 1240, 1050, 1020, 750, and 700 cm^{-1}.

^{1}H-nmr. spectrum, δ values: 7.43 ppm (broad signal, 10 H, phenyl H); 7.83 and 7.98 ppm (two broad signals, 1H+1H, fulvene ring H); 8.52 and 8.60 ppm (two broad signals, 1H+1H, sevenmembered ring H); 8.80 ppm (broad s, 1H, exocyclic fulvenic H).

Anal. $C_{25}H_{18}N_4O$ (390.426) calc'd.: C 76.90; H 4.65; N 14.35%
found: C 77.26; H 4.77; N 14.21%

6'-Hydroxy-8-(α-hydrazonothenyl)-3-thienylfulveno(2',3'-5,6)-1,2-diazaazulene (IIIc)

0.0965 g (0.23 mmol) of 6'-*N,N*-dimethylamino-2,7-dithenoylfulveno(2',3'-4,5)tropone (III) was condensed with 0.8 ml of 100% hydrazine hydrate yielding 0.056 g (60.2%) of product, m. p. 224 ° (dec.).

Ir. spectrum: 3380, 3280, 3190, 3080, 1610, 1568, 1560, 1410, 1390, 1240, 1140, 1050, 990, 930, 790, 720, and 710 cm^{-1}.

^{1}H-NMR spectrum, δ values: 6.8—7.1 ppm (broad, 2 H, thiophene H); 7.25—8.16 ppm (broad m, 6 H, thiophene H + fulvene ring H); 8.50—8.83 ppm (broad m, 2 H, seven-membered ring H); 9.3 ppm (broad s, 1 H, exocyclic fulvenic H).

Anal. $C_{21}H_{14}N_4OS_2$ (402.29) calc'd.: C 62.69; H 3.50; N 13.91; S 15.93%
found: C 62.92; H 3.63; N 13.61; S 15.78%

Condensation of 6'-piperidino-2,7-diaroylfulveno(2',3'-4,5)tropones with hydrazine hydrate

Compound (IIIa). — By condensation of 6'-piperidino-2,7-(*p*-toluyl)fulveno(2',3'-4,5)tropone (IIa) 0.236 g (0.4 mmol) with 1.6 ml 100% hydrazine hydrate, 0.101 g (57.4% yield) of product was obtained which was shown to be identical with compound IIIa by m. p. 242 °C (dec.), by identical MS, ir. and ^{1}H-NMR spectra and elemental analyses.

Anal. $C_{27}H_{22}N_4O$ (418.48) calc'd.: C 77.49; H 5.30; N 13.38%
found: C 77.63; H 5.80; N 13.57%

Compound (IIIb). — 0.224 g (0.5 mmol) of 6'-piperidino-2,7-dibenzoylfulveno (2',3'-4,5)tropone (IIb) was condensed with 1.6 ml of 100% hydrazine hydrate. 0.085 g (43.6%) yield of product was obtained identical with compound IIIb as shown by m. p. 230 °C (dec.), by identical MS, ir. and ^{1}H-NMR spectra and elemental analyses.

Anal. $C_{25}H_{18}N_4O$ (390.46) calc'd.: C 76.90; H 4.65; N 14.35%
found: C 76.72; H 5.04; N 14.53%

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SAŽETAK

Produkti reakcije 2,7-diaroil-4,5-fulvenotropona s hidrazinhidratom

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6′-hidroksi-8-(α-hidrazonoarilmetil)fulveno(2′,3′-5,6)-1,2-diazaazuleni (IIIa, Ar= =tolil, IIIb, Ar=fenil, IIIc, Ar=tienil) dobiveni su kao produkti reakcije odgovarajućih 2,7-diaroil-4,5-fulvenotropona s hidrazinhidratom. Strukture dobivenih spojeva razmatrane su na temelju njihovih infracrvenih i masenih spektara te spektara ^{1}H-nuklearne magnetske rezonancije.

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