UNUSUAL REACTIONS OF α-NITRO-β-DIMETHYLAMINOACROLEIN

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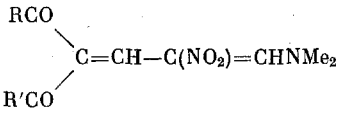
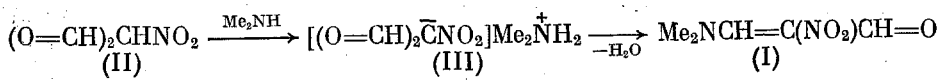
In continuing researches into the valence isomerization δ-aminodienone ⇄ 2-amino-2H-pyran [1-3], we have examined the synthesis of δ-aminodienones containing a γ-nitro-group



Examples are known of the synthesis of δ-aminonitrobutadienes by the condensation of α-nitro-β-dimethylaminoacrolein (I) with compounds containing a reactive methylene group [4]. Attempts were therefore made to obtain γ-nitro-δ-dimethylaminodienones by condensing (I) with β-dicarbonyl compounds. However, we encountered some unusual reactions, both in the preparation of (I) and in its subsequent reactions. It has been found that the literature method for the synthesis of (I) from nitromalonaldehyde (II) by reaction with ethereal dimethylamine [5] gives quantitative yields of the dimethylammonium salt of nitromalonaldehyde, the structure of which was proved by its ^1H and ^{13}C NMR spectra (Table 1) and its UV spectra as compared with the sodium salt of nitromalonaldehyde, and confirmed by its elemental analysis



On brief heating in absolute methanol, the salt (III) was converted into the aldehyde (I), the structure of which was confirmed by its ^1H and ^{13}C spectra (Table 1) and its UV spectrum.

The aldehyde (I) and salt (III) are readily interconvertible. In aprotic solvents (chloroform and dioxane), (I) is stable, but in alcohol containing even traces of moisture it is hydrolyzed to (III). Thus, in 99.5% methanol (C 0.15 mole/liter), (I) affords 60% of (III) after seven days. The reaction is considerably accelerated when the concentration of water is increased, 75% of (III) being obtained from (I) in 85% methanol after 0.5 h.

On the other hand, (III) is stable in alcohols containing water, but is rapidly converted into the aldehyde (I) in nonaqueous solvents, 66% of (I) being obtained after one day from (III) in chloroform, and a quantitative yield after the same length of time in dioxane.*

These reactions appear to provide an explanation for the previously observed [5] changes in the UV spectrum of (I) with time, which were erroneously attributed to conformational changes. The results reported in [5] for the changes in the UV spectrum of (I) in dioxane are in complete agreement with the conversion of the salt (III) (λ_{max} 275 and 318 nm) into the aldehyde (I) (λ_{max} 285 and 340 nm). The UV and IR spectra of (I) in dioxane, and the ^1H NMR spectrum of (I) in $CDCl_3$, do not change with time.

When the aldehyde (I) is condensed with dimedone in the presence of catalytic amounts of triethylamine in absolute methanol at ∿20°C, instead of the expected γ-nitro-δ-aminodienone (IV), 22% of a bright yellow crystalline product was obtained which was the dimethylammonium salt of 2-nitroethylidenedimedone (V), the structure of which was established from its ^1H and ^{13}C NMR spectra (Table 2), its UV spectrum, the electrical conductivity of its solution in

*In view of the low solubility of (III) in chloroform and dioxane, this reaction was followed in dilute solution (C ∿0.05 mole/liter).

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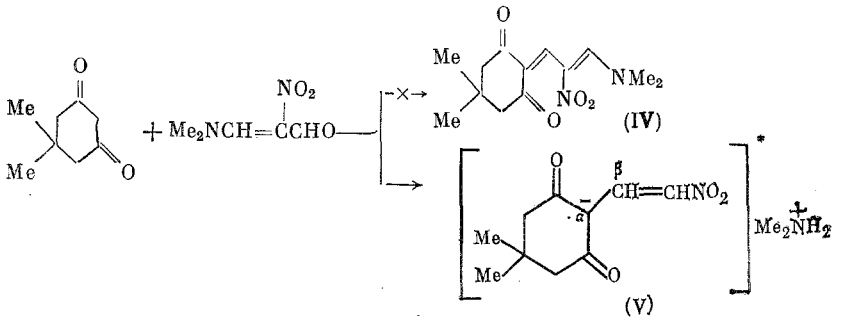
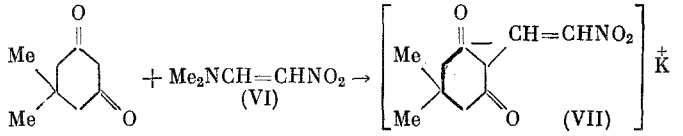
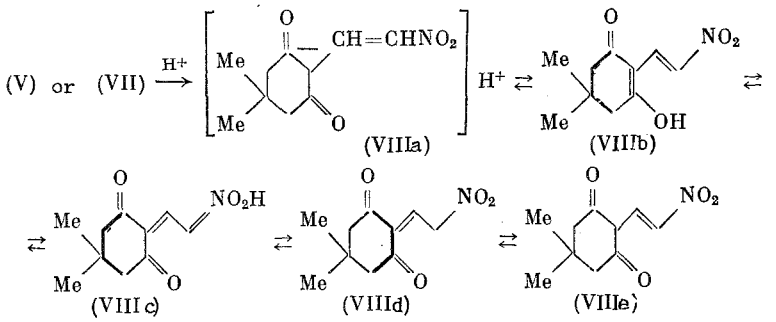


methanol, its elemental analysis, and by direct synthesis using the reaction of nitrovinylated CH-acids with nitroenamines [6-8].

Reaction of 1-dimethylamino-2-nitroethylene (VI) with dimedone in the presence of potassium ethoxide under the conditions described in [7] gave the potassium salt (VII), the ^{1}H NMR and UV spectra of which corresponded to the spectra of the salt (V)



Treatment of (V) or (VII) with hydrochloric acid afforded the same nitro-compound (VIII), which can exist either in the anionic (VIIIa) or the protonated (VIIIb-e) forms



In the UV spectra, the long-wavelength band at 435-440 nm corresponding to (V) and (VII) is assigned to (VIIIa), and that at 328-345 nm to (VIIIb). This assignment was confirmed by the ^{1}H NMR spectra (Table 2), obtained with solutions of approximately the same concentration. According to the UV spectra (Table 3), the position of the equilibrium between (VIIIa) and (VIIIb)† is dependent on the solvent and the concentration.

In highly dilute alcoholic solutions, (VIIIa) predominates, but as the concentration is increased the equilibrium shifts towards (VIIIb). Similar behavior is seen in acetone.

In water, only (VIIIa) was found, and the addition of water to organic solvents also shifted the equilibrium towards (VIIIa).

In chloroform and dichloromethane, even in highly dilute solution (C $2\cdot10^{-5}$ mole/liter), only (VIIIb) was observed (λ_{max} 255 and 328 nm (in chloroform), 265 and 335 nm in (dichloromethane)), but the addition of trace amounts of water resulted in the appearance in the UV spectrum of absorption with λ_{max} 435 nm, corresponding to (VIIIa). In 50% methanol and 50% acetone, only (VIIIa) was present.

*This designation is arbitrary, since the negative charge is delocalized over the whole molecule.

†According to the UV and PMR spectra, (VIIId) and (VIIIe) are not present in appreciable amounts. The relatively low value of λ_{max} (328-345 nm), which differs by ~100 nm from λ_{max} for (VIIIa), corresponds to the form (VIIIb) rather than to (VIIIc), since it is known that absorption in nitronic acids is shifted by only 10-20 nm to shorter wavelengths as compared with the absorptions of the corresponding anions [9].

TABLE 1. ^1H and ^{13}C NMR Spectra of (I) and (III)

	^1H NMR spectrum (δ, ppm) from TMS			^{13}C NMR spectrum (δ, ppm) from TMS ($J_{^{13}C,\ ^1H}$, Hz)			
			NO_2 | $Me_2NCH=CCH=O$ (I)				
solvent	CHO	CH	Me_2N	CHO	CH	CNO_2	Me_2N
CD_3OD	9,93 (1H)	8,50 (1H)	3,29and58 (6H)	183 (185,0)	157,9 (175,7)	126,9 (20,3)	45,5 (139,6)
$CDCl_3$	10,15 (1H)	8,32 (1H)	3,35and53 (6H)				
			$[(O=CH)_2\bar{C}NO_2]Me\overset{+}{N}H_2$ (III)				
	CHO	NMe_2		CHO	$\bar{C}-NO_2$	Me_2N	
CD_3OD	9,73 (2H)	2,71 (6H)		183,87 (177,5)	133,3	35,6 (142,4)	
$CDCl_3$	9,83 (2H)	2,87 (6H)					
			$(O=CH)_2\bar{C}NO_2Na^+$				
	CHO						
$CD_3OD : D_2O$, 5 : 1	9,65						

TABLE 2. ^1H NMR Spectrum of (V), (VII), and (VIII), and the ^{13}C Spectrum of (V)

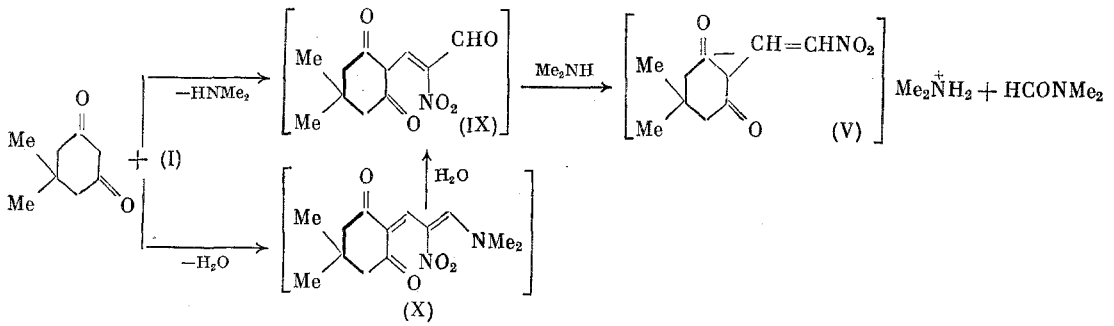
Compound	Solvent	^1H NMR spectrum (δ, ppm) from TMS, $J_{\beta,\gamma}$, Hz						^{13}C NMR spectrum (δ, ppm) from TMS ($J_{^{13}C\ ^1H}$, Hz)							
		Me	CH_2	Me_2N	H_β	H_γ		C^2 and C^4	C^3	Me	Me_2N	C_α	C_β	C_γ	O || C
(V)	CD_3COCD_3	0,98 (6H)	2,20 (4H)	2,98 (6H)	8,45 (1H)	8,33 (1H)	12,8								
	CD_3OD *	1,03 (6H)	2,27 (4H)	2,65 (6H)	8,45 (1H)	8,28 (1H)	12,8	52,5 (125,8)	31,9	28,8 (126,7)	35,6 (143,3)	109,5	137,4 (151,0)	128,8	198,3
	CD_3OH							52,5 (125,8)	31,9	28,8 (126,7)	35,5 143,3	109,5	137,4 (151)	129,14	198,3
(VII)	CD_3OD	1,03 (6H)	2,27 (4H)		8,45 (1H)	8,30 (1H)	12,8								
(VIIIa)	$CD_3OH : H_2O$, 1 : 1	1,13 (6H)	2,53 (4H)		8,33 (1H)	8,22 (1H)	12,8								
(VIIIb)	CD_3COCD_3	1,09 (6H)	2,53 (4H)		8,15 (2H)										
(VIIIb)	CD_3OH	1,06 (6H)	2,47 (4H)		8,08 (2H)										

*After one day, H_γ was replaced by D, the signal for H_β became a singlet, and the signal for C_γ a triplet, $J_{C_\gamma\ D}$ = 29.6 Hz.

TABLE 3. UV Spectral Data for (VIII) in Dilute Solutions

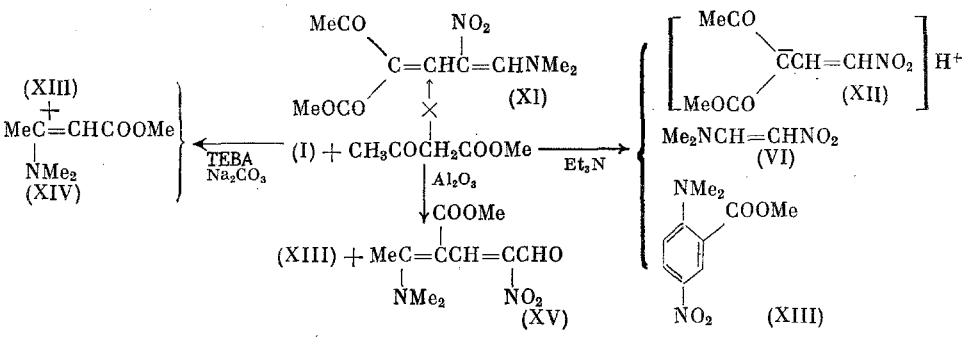
Solvent	C, mole/liter	λ_{max}, nm (ε)	Solvent	C, mole/liter	λ_{max}, nm (ε)
EtOH	$2{,}4\cdot10^{-5}$	287 (11816) 435 (19834)	MeOH : H_2O, 1 : 1	$1{,}75\cdot10^{-3}$	285 (11400) 440 (19200)
	$2{,}4\cdot10^{-4}$	282 (8440) 345 (7342) 435 (10296)	Me_2CO	$2\cdot10^{-5}$	340 (8820) 440 (15190)
				$2\cdot10^{-4}$	340 (13149) 440 (2159)
	$2{,}4\cdot10^{-3}$	278 (8448) 345 (9216) 435 (3840)		$2\cdot10^{-3}$	340 (14995) 440 (441)
MeOH	$3{,}5\cdot10^{-5}$	285 (14300) 435 (21700)	Me_2CO : H_2O, 1 : 1	$1\cdot10^{-3}$	285 (11760) 440 (21840)
	$3{,}5\cdot10^{-4}$	280 (9700) 340 (10000) 435 (4840)	H_2O	$1{,}9\cdot10^{-4}$	285 (7400) 440 (14500)
	$3{,}5\cdot10^{-3}$	270 (10200) 340 (12600)			

The formation of (V) from dimedone and (I) can be rationalized either by the deformylation of (I) in the course of the reaction to give (VI),* followed by condensation of (VI) with dimedone, or by deformylation of the initially formed α-nitroaldehyde (IX)



The possibility of the formation of (V) from (VI) was confirmed by the observation (PMR and UV spectra) of (VI) in the reaction products of (I) with dimedone, and furthermore, (VI) and dimedone gave, under the conditions of the condensation of (I) with dimedone, a small yield of (V). Since the yield of (V) from (VI) is low, it is possible that (V) is formed by the deformylation of (IX).

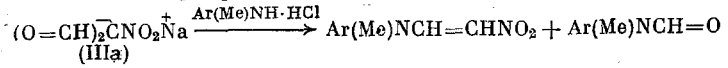
Attempts to obtain the γ-nitro-δ-dimethylaminodienone (XI) from (I) and ethyl acetoacetate were likewise unsuccessful



Treatment with triethylamine gave a mixture of products, which was subjected to preparative TLC to give the nitroethylidene derivative of ethyl acetoacetate (XII), (VI), and methyl o-dimethylamino-m-nitrobenzoate (XIII).

Phase transfer catalysis with TEBA and sodium carbonate in benzene gave (XIII) and the β-dimethylaminocrotonate (XIV). Condensation of ethyl acetoacetate with (I) in the presence of alumina also gave a low yield of (XIII) and the aldehyde (XV). The structures of (IV),

*It has been shown above that the aldehyde (I) readily affords the dimethylammonium salt of nitromalonaldehyde (III). An example is known of the deformylation of the salt (IIIa) on treatment with aromatic amines [10]



(VI), (XIII), and (XV) were confirmed by their PMR and UV spectra, and of (XII) by comparison with an authentic sample [8].

For the synthesis of γ-nitro-δ-dimethylaminodienones we had intended to use the hitherto unknown aminal and acetal of α-nitro-β-dimethylaminoacrolein $Me_2NCH{=}CCH(NO_2)(Y)_2$ (Y = Me_2N, MeO). We were, however, unable to obtain the aminals. Under the conditions previously established for the synthesis of aminals of α-substituted β-dimethylaminoacroleins $Me_2NCH{=}CCH(R)(NMe_2)_2$ where R = Me, Ph, and Cl, from the appropriate substituted trimethine salts [3, 11, 12], 2-nitro-3-dimethylamino-2-propenylidenedimethylammonium perchlorate was converted into (I). We were likewise unable to obtain the acetal (Y = MeO) or 1,1,3-trimethoxy-3-dimethylamino-3-nitropropane, since (I) did not afford the compound $[Me_2\overset{+}{N}{=}CHC(NO_2){=}CHOMe]MeSO_4^-$ required for it synthesis on treatment with dimethyl sulfate.

EXPERIMENTAL

UV spectra were obtained on a Specord UV-VIS, and PMR spectra on Bruker WM-250 (^1H, 250 MHz; ^{13}C, 62.89 MHz) and Tesla BS-467 (^1H, 60 MHz) instruments.

Dimethylammonium Salt of Nitromalonaldehyde (III) and α-Nitro-β-dimethylaminoacrolein. To 11 g of nitromalonaldehyde [5] in 50 ml of dry ether was added with stirring and cooling at 0°C 10 ml of dimethylamine in 25 ml of dry ether. The resulting solid was isolated and washed with ether to give 15 g (98%) of (III), mp 96-98°C (after reprecipitation from the methanol solution with hexane). UV spectrum (λ_{max}, nm, in EtOH): 227 (ε 9990), 273 (ε 14080) and 327 (ε 13214). Found: C 37.16; H 6.28; N 16.97%. $C_5H_{10}N_2O_4$. Calculated: C 37.03; H 6.22; N 17.28%. Electrical conductivity in methanol (C 10^{-3} mole/liter, 22°C) $0.39 \cdot 10^{-3}$ ohm^{-1}.

Fifteen grams of (III) was dissolved in 50 ml of 99.9% methanol and boiled for 10 min. There was obtained 8.7 g (65%) of (I), mp 79-80°C (from abs. methanol). UV spectrum (λ_{max}, nm, in EtOH): 220 (ε 5120), 290 (ε 15360), 340 (ε 17280). IR spectrum (in dioxane, ν, cm^{-1}): 1670 s, 1605 s, 1505 s, 1300 s, 1280 pl.

On TLC on Silufol (acetone–chloroform–ethanol, 56:12:1) with visualization in UV, (III) gave a spot at the origin, and (I) a spot with R_f 0.5.

Condensation of (I) with Dimedone. Dimethylammonium Salt of 2-Nitroethylidenedimedone (V). A mixture of 1 g of dimedone, 1 g of (I), and two drops of triethylamine in 4 ml of abs. methanol was heated at 35°C until the solid had dissolved completely, then kept for three days at 20°C. The UV spectrum of the reaction mixture showed bands at 263, 290, 340, 355, and 435 nm. The mixture was evaporated, 1 ml of a mixture of acetone and ether (1:1) added, cooled to -30°C and 0.4 g (22%) of bright yellow product (IV) isolated. This was reprecipitated, dissolved in 3 ml of abs. methanol, and poured with cooling at 0°C into hexane (100 ml), mp 152-154°C, UV spectrum (λ_{max}, nm, in EtOH): 285 (e 25400), 435 (e 42400). Found: C 56.04; H 8.01; N 10.89%. $C_{12}H_{20}N_2O_4$. Calculated: C 56.23; H 7.87; N 10.93%. Electrical conductivity of (V) in methanol (10^{-3} mole/liter, 22°C) $0.39 \cdot 10^{-3}$ ohm^{-1}. The PMR spectrum of the evaporated mother liquors following removal of (V) showed signals for (VI) (CD_3OD, δ, ppm): 3.25 (Me_2N), 6.62 (H^2), 8.15 (H^1), $J_{1,2}$ = 11 Hz.

Treatment of (V) with Acid. Compound (V) (0.2 g) was dissolved in 2 ml of water, cooled to 2-3°C, and a few drops of hydrochloric acid were added. There was obtained 0.14 g of (VIII) as a bright yellow solid, which was isolated and washed several times with water. MP 132-135°C. Found: C 57.43; H 6.18; N 6.63%. $C_{16}H_{13}NO_4$. Calculated: C 56.86; H 6.20; N 6.63%. Mass spectrum (m/z): 165 M^+. For UV spectrum see Table 3, and PMR spectrum Table 2.

Condensation of 1-Dimethylamino-2-nitroethylene (VI) with Dimedone. a) To a boiling solution of 0.7 g of dimedone in 10 ml of acetonitrile were added simultaneously 0.6 g of (VI) in 5 ml of acetonitrile and 5 ml of EtOK (from 0.2 g of potassium and 5 ml of abs. ethanol). The mixture was boiled for 10 min, then cooled to 0°C and dry ether added until a solid separated, to give 0.5 g (40%) of the potassium salt of 2-nitroethylenedimedone (VII), λ_{max} (EtOH) 285 and 435 nm, for PMR spectrum see Table 2. The salt (VII)

contained dimedone potassium salt as impurity; λ_{max} (EtOH) 285 nm; PMR spectrum (CD_3OD, δ, ppm): 1.0 (Me), 2.05 (CH_2). Treatment of (VII) with HCl as described above gave (VIII). PMR spectrum (CD_3COCD_3, δ, ppm): 1.03 (6H, Me), 2.48 (4H, CH_2), 8.08 (2H. Hβ and H_γ).

b) A mixture of 0.7 g of dimedone, 0.6 g of (VI), and two drops of triethylamine in 3 ml of abs. methanol was warmed to 35°C, until the solid had dissolved, and kept for seven days at 20°C. The UV spectrum of the reaction mixture showed bands at 285 and 435 nm characteristic of (V), in addition to a band at 355 nm for (VI). Removal of (VI) left a pasty product containing (V). PMR spectrum (CD_3OD, δ, ppm): 1.03 (6H, Me), 2.2 (4H, CH_2), 2.63 (6H, MeN), 8.4 (1H, Hβ), 8.23 (1H, H_γ), $J_{\beta,\gamma}$ = 12.8 Hz. The yield of (V), according to the UV spectral data, was not greater than 8%.

Condensation of Ethyl Acetoacetate with (I). a) A mixture of 0.33 g of ethyl acetoacetate, 0.4 g of (I), and two drops of triethylamine in 20 ml of abs. methanol was kept for four days at 20°C. Following evaporation, the residue was submitted to preparative TLC in silica gel (chloroform–methanol, 50:1, elution with methanol and chloroform) to give 0.15 g of (XIII) as a yellow solid, mp 81-83°C, R_f 0.6 (Silufol, acetone–hexane, 1:1), UV spectrum (in ethanol): 382 nm (ε 15640). PMR spectrum ($CDCl_3$, δ, ppm): 2.96 (6H, Me_2N), 3.86 (3H, CO_2Me), 6.78 (1H, H^6, D), 8.08 (1H, H^5, DD), 8.45 (1H, H^3, D), $J_{5,3}$ = 3 Hz. Mass spectrum (m/z): 224 M^+ Found: C 53.64; H 5.32; N 12.32%. $C_{10}H_{12}N_2O_4$. Calculated: C 53.6; H 5.35; N 12.5%. Also isolated was 0.1 g of (XII) as a viscous yellow oil, R_f 0.3 (Silufol, chloroform–methanol, 50:1, yellow spot). UV spectrum 440 nm (EtOH), 340 nm ($CHCl_3$). From its UV spectrum and TLC (XII) was identical with (XII) isolated following treatment of the potassium salt of the nitroethylidene derivative of ethyl acetoacetate with hydrochloric acid [8]. In solution, (XII) was unstable, decomposing to products with λ_{max} 200-250 nm. In addition to (XII) and (XIIII), preparative TLC afforded 0.08 g of (VI), λ_{max} 355 nm (EtOH). PMR spectrum ($CDCl_3$, δ, ppm): 2.88 and 3.06 (6H, Me_2N), 8.15 (1H, H^1), 6.64 (1H, H^2), J_{H^1,H^2} = 11 Hz, R_f 0.35 (Silufol, acetone–hexane, 1:1, visualized in UV).

b) A mixture of 0.58 g of ethyl acetoacetate, 0.72 g of (I), 0.5 g of sodium carbonate, 0.02 g of TEBA, and 2 ml of benzene was heated with stirring for 6 h at 40°C. The solid was isolated, washed with benzene, chloroform, and ether. Evaporation gave 0.15 g of (XIII) as a crystalline solid, mp 81-83°C. The residue following removal of (XIII) was distilled in vacuo (0.5 mm) (bath temperature 120-125°C) to give 0.1 g of (XIV) as an oil, n_D^{20} 1.5330, λ_{max} 282 nm (EtOH). PMR spectrum ($CDCl_3$, δ, ppm): 2.48 (3H, Me), 2.87 (6H, Me_2N), 3.55 (3H, CO_2Me), 4.49 (1H, CH).

c) A mixture of 0.25 g of ethyl acetoacetate, 0.3 g of (I), and 0.6 g of alumina was kept for two days. Preparative TLC on silica, chloroform–acetone–ethanol (6:12:0.1) with elution with chloroform and methanol gave 0.15 g of (XIII), mp 80-82°C (R_f 0.8) and 0.1 g of 2-nitro-4-methoxycarbonyl-5-dimethylaminohexa-2,4-dienal (XV) as a yellow oil (R_f 0.2), λ_{max} 385 and 335 nm (EtOH). PMR spectrum ($CDCl_3$, δ, ppm): 2.3 (3H, Me), 2.7 (6H, Me_2N), 3.7 (3H, MeO), 7.82 (1H, CH), 9.84 (1H, CHO).

2-Nitro-3-dimethylamino-2-propenylidenedimethylammonium perchlorate was obtained as described in [13]. PMR spectrum (CD_3CN, δ, ppm): 3.16 and 3.53 (6H, Me_2N), 8.4. (2H, H^1 and H^3).

CONCLUSIONS

1. α-Nitro-β-dimethylaminoacrolein and the dimethylammonium salt of nitromalonaldehyde are readily interconvertible.

2. Condensation of α-nitro-β-dimethylaminoacrolein with dimedone in the presence of triethylamine is accompanied by deformylation with the formation of the dimethylammonium salt of nitroethylidenedimedone.

3. Condensation of α-nitro-β-dimethylaminoacrolein with ethyl acetoacetate in the presence of triethylamine, TEBA, or alumina gives methyl o-dimethylamino-m-nitrobenzoate together with the nitroethylidene derivative of ethyl acetoacetate, β-dimethylaminocrotonic ester, and 2-nitro-4-methoxy-carbonyl-5-dimethylaminohexa-2,4-dienal.

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SYNTHESIS OF 1,3-DIAZACYCLANES BY THE BENZOYLATION OF BIS-SCHIFFS BASES

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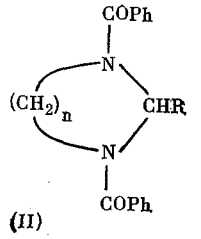
We have previously reported [1] that the acylation of bis-Schiffs bases of ethylenediamines with aromatic acid chlorides in polar media is anomalous, resulting in the formation of NN'-diaroyl-2-substituted imidazolines. We here extend this reaction to Schiffs bases with more remote azomethine groups.

As substrates for acylation we took the compounds RCH = $N(CH_2)_n$ N = CHR(I), where n and R are respectively 3, i-Pr (a); 3, Ph (b); 4, i-Pr (c); 4, Ph (d); 5, i-Pr (e); 5, Ph (f); 6, i-Pr (g); 6, Ph (h); 8, i-Pr (i); and 8, Ph (j), together with NN'-bisisobutylidene-2-methyl-1,4-diaminobutane (Ik). The acylating agent used was benzoyl chloride, the reactions with (Id, f, h, and j) being carried out in benzene and acetonitrile, and with (Ia-c, g, i, and k) in acetonitrile only. Under these conditions, the azomethines (I) (n = 3) selectively afforded the NN'-dibenzoylhexahydropyrimidines (IIa and b), but (I, $n \geqslant 4$) gave principally the noncyclic amides (III)-(V) (Table 1). Using the procedure described in [1], the Schiffs



(II)

$PhCONH(CH_2)_nNHCOPh$ (III)

$Me_2C{=}CHN(CH_2)_nNHCOPh$ (IV)
COPh

$Me_2C{=}CHN(CH_2)_nNCH{=}CMe_2$ (V)
COPh COPh

base was acylated in the presence of triethylamine, but in the case of the seven-membered heterocycles (Ic and k) it was found that the yields of cyclic products (II) were substantially increased if no triethylamine was present. For example, benzoylation of (Ic) as described in [1] afforded the diazacyclopentane (IIc) in 9% yield, whereas in the absence of triethylamine the yield was 22%. Similar variations in yield were found in the case of (IIi), and only the cyclization of (Ia and b) and the bisazomethines RCH = $N(CH_2)_2N$ = CHR was independent of the addition of triethylamine.

As will be seen from Table 1, the reaction has features similar to those of the carbon-chain compounds, since cyclization to 5- and 6-membered heterocycles was the most efficient,

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