extracts, 1 g (70%) of 90% pure (according to the PMR spectrum) N-methyl-N-(2-hydroxyethyl)diazoacetamide (IVa) was obtained (see Table 1).

N-Ethyl-N-(2-hydroxyethyl)diazoacetamide (IVb) and compound (IIa) were obtained in a similar manner (see Table 1).

CONCLUSIONS

1. Reaction of 2-bromoethyldiazoacetate with free secondary amines or primary amine chlorohydrates in the presence of anhydrous K_2CO_3 in acetonitrile at 20°C affords the correponding aminoethyldiazoacetates in a yield of up to 80%.

2. Reaction of 2-bromoethyldiazoacetate with free primary amines in the presence of K_2CO_3 is accompanied by ammonolysis of the diazoester and affords previously unknown N-alkyl-N-(2-hydroxyethyl)diazoacetamides in yields of up to 70%.

LITERATURE CITED

- 1. E. A. Shapiro, T. N. Romanova, I. E. Dolgii, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 2029 (1986).
- E. A. Shapiro, T. N. Romanova, I. E. Dolgii, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 2655 (1984).
- 3. U. S. Pat. No. 3846112 (1974).
- 4. H. Chaimovich, R. J. Vaughan, and F. H. Westheimer, J. Am. Chem. Soc., <u>90</u>, 4088 (1968).
- 5. L. A. Verbolovich, T. Ya. Polosukhina, and Z. N. Kannova, A Practical Course in Organic, Physical, Colloid, and Biological Chemistry [in Russian], Akad. Nauk KazSSR, Alma-Ata (1963), p. 109.

REACTIONS OF TERT-BUTYLPROPYNAL WITH AMINES

UDC 542.91:547.382.1:547.233.2

A. S. Medvedeva, A. I. Borisova, I. D. Kalikhman, and N. S. Vyazankin

In previous work it has been shown that tert-butylpropynal (I) shows a dual reactivity towards dialkylamines [1]. Alicyclic amines (IIa, b) add at the C=O bond to form aminals (IIIa, b) while diethylamine adds to the C=C bond. In this work we have studied a wider range of amines (II) with differences in basicity and steric demand. Reactions were carried out at $\sim 20^{\circ}$ C without solvent (or in benzene in the case of diethylamine). The reactions were monitored by PMR spectroscopy. It has been shown that diphenyl- and dibenzylamine (as diethylamine) add only at the acetylenic bond of I.



 $R_2N = (CH_2)_5N$ (a), $O(CH_2CH_2)_2N$ (b), Et_2N (c), Ph_2N (d), $(PhCH_2)_2N$ (e).

The PMR spectra of the initially formed β -aminoacroleins (IV) showed doublet signals for the olefinic (5.40-5.96) and formyl (9.53-9.80 ppm) protons with J = 7 Hz. Isomerization to enaminoketones(V) occurred at $\sim 20^{\circ}$ C as evidenced by the gradual disappearance of the aldehyde signals and the appearance of doublets at 5.27-5.48 and 7.55-7.91 ppm (J = 13 Hz) for the CH=CH fragment.

IR spectra of IV showed characteristic frequencies at 1550-1570 (C=C) and 1640-1670 cm^{-1} (C=O) and the isomerization products V showed the conjugated double bond and carbonyl group absorptions at 1550-1575 and 1640-1655 cm^{-1} respectively. The structures of V were

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1347-1351, June, 1987. Original article submitted September 26, 1985.

والمتحافظ والمحافظ والمستعم والمحافظ			N DJ		н	H_C.=	(1)	
Compound		MegC	[CHN]	11-6-0	່ ອີສ		្រែលៀ	[NH]dq
Meach-Cheno Nris	IVC	1,23 s	3,50 q (7,0)	9,55 d (7,0)	5,46 d (7,0)	1	1,13 t (7,0)	ł
Me ₃ CCOCH=CHNEt ₂ *	Vc	1,23 s	3,23 q (7,0)	1	5,29 d (13,0)	7,55 d (13,0)	1,13 t (7,0)	ł
MesCC=CHCHO NBus	IVg	1,28 s	3,11 t	9,53 d (7,0)	5,42 d (7,0)	l	1,20 t [0,89 m]	
MegGCOCH =CHNBu2	Vg .	1,28 s	3,36 t	Ţ	5,27 d (13,0)	7,57 d (13,0)	1,20 t [0,89 m]	
Mescht=CCHO [NBus	VIg	1,28 s	3,36 t	$^{8,86}_{8,70 s} ^{s} (Z)_{8,70 s} (E)$	[$ \begin{array}{c} 6,18 \\ 6,47 \\ 6,47 \\ 8\end{array} $	1,20 t [0,89 m]	
MeaCCOCH=CHN(CH2Ph)2 †	Ve	1,07 s	4,30 s	[5,53 d (12,9)	7,98 d (12,9)	!	7,21 m
Me3CC=CHCHO NPh2	IVd	1,19 s		9,75 d (7,5)	6,10 d (7,5)			7,15 m
Me ₃ CCOCH=CHNPh ₂	ΡΛ	1,00 s		I	5,46 d (11,2)	8,24 d (11,2)	Į	7,15 m
Me ₃ CC=CHCHO N(i-Pr) ₃	IVf	1,29 s	[2,83 m]	9,80 d (7,2)	5,72 d (7,2)	l	1,00 d (7,0)	ł
$Me_3CCOCH=CHN(i-Pr)_3$	νf	1,29 s	[2,83 m]	1	5,40 d (12,7)	7,77 d (12,7)	1,00 d (7,0)	1
$Me_{s}CCH=CCHO$ $(i-Pr)_{s}N$	VIF	1,29 s	[2,83 m]	$^{8,88}_{8,75} $ s $^{(Z)}_{(E)}$	5,08 d (8,1)	$6,20 \le (Z) \\ 6,70 \le (E)$	1,00 d (7,0)	ł
Me ₃ CCOCH=CHNHPr-i	νh	1,15 s	[3,70 m]	I	7,30 s	6,75d (8,1)	1,10 m	[9,80 br s]
Mc ₃ CC≔CCH==NPr-i	\ IIA	1,15 s	[3,70 m]		7,45 s	1	1,10 m	

TABLE 1. PMR Spectra of Obtained Compounds, §, ppm (J, Hz)

 $\frac{*^{13}C}{(Cf. [2] for Me_{3}C-CO-CH=CHN(CH_{3}), 27.46 (CH)_{3}, 41.60 (NCH_{2}), 89.66 (=CH), 150.98 (=CH), 203.15 (C=0). (Cf. [2] for Me_{3}C-CO-CH=CHN(CH_{3})_{2} (\delta, ppm): 91.2 (=CH) (C^{2}), 154.4 (=CH) (C^{3}), 202.2 (C=0) (C^{1})). \\ +^{13}C NMR (Ve) (\delta, ppm)^{2}: {}^{3}26.11 (CH_{3})_{3}, 40.75 (NCH_{2}), 90.62 (=CH), 152.79 (=CH), 135.89, 128.80, 127.89, 127.63 (C_{6H_{5}}), 204.04 (C=0). \\ \end{array}$

also confirmed by UV [1] and ¹³C NMR spectra (Table 1; compare the similar structure $Me_3CCOCH=CHNMe_2$ [2]), and the value of the free energy of activation for hindered rotation about the C-N bond. In the case of $Me_3CCOCH=CHNEt_2$ (Vc) the ΔG^{\neq} (determined from a coalesc-ence temperature of -10°C) was 13.5 kcal/mole and this can be compared with a value [3] of 13.12 kcal/mole for $Me_3CCOCH=CHNMe_2$. This evidence excludes the possibility of acrylamides $Me_3CCH=CHCONR_2$ [4] as alternative β -enaminoacrolein isomerization products. In agreement with studies [3] of the effect of substituents at the carbonyl carbon of enaminoketones of type V on the S-cis:S-trans conformer ratio, the ketones $Me_3CCOCH=CHNR_2$ were found to be in the trans-S-cis configuration.



In the absence of a catalyst, the isomer conversion was complete within three weeks while the addition of p-toluenesulfonic acid catalyst (PTSA) noticeably accelerated both the addition of amine to the propynal and the IV \rightarrow V isomerization. Thus, whereas the propynal (I)/diethylamine reaction mixture still contains 20% of I after 1 day, the mixture with PTSA contains only the desired product Vc (by PMR) after 5 h. The catalytic role of protic reagents in the isomerization of β -amino and β -thioacroleins has been discussed in [4, 5].

Dialkylamines with bulky substituents (i-Pr, n-Bu) added to both the β - and α -positions of propynal I. Diisopropylamine and di-n-butylamine gave 50 and 10% respectively of the α -aminoacroleins VIe and VIg.

(I) + HNR₂ \rightarrow Me₃CCOCH=CHNR₂ + Z, *E*-Me₃CCH=C(NR₂)CHO Vf, g VIf, g R = *i*-Pr (f), *n*-Bu (g).

The PMR spectra of the α -aminoacroleins VI showed singlet formyl proton signals at 8.86-8.88 (Z) and 8.70-8.75 (E) and olefinic protons at 6.18-6.20 (Z) and 6.47-6.70 (E) ppm with J = 7 Hz.

The α -orientation of the amine reactions for tert-butylpropynal is no doubt of steric origin. Previously the addition of amines to the α -carbon of acetylenic aldehydes had been noted only for dimethylaminopropynal (a representative of the push-pull acetylenes [6, 7]). Substituted propynals with primary amines usually formed the corresponding aldimines [8, 9]. However, PMR data (see Table 1) of the reaction of I with sterically hindered iso-propylamine showed a mixture of azomethine VII and enaminoketone Vh (ratio 1:1).

(I) +
$$H_2N$$
-Pr- $i \rightarrow Me_3CC \equiv CCH \equiv NPr-i + Me_3CCOCH = CHNHR$
(VII) Vh

It is known that propynal reacts with NH_3 , depending on solvent, to form adducts at the C=O or C=C bonds [10]. Acetylenic γ -hydroxyaldehydes give Michael adducts [11] with NH_3 and in the case of triethylgermylpropynal the corresponding aldimine [12]. Tert-butylpropynal in ether reacted to form a viscous product, elemental analysis of which was in agreement with $C_{14}H_{21}NO$. Its IR spectrum showed bands at 1580-1600 (C=N), 2240 (strong, C=C), and 3200 cm⁻¹ (broad, OH). This data is in agreement with a product of reaction of two moles of propynal with one of NH_3 apparently $Me_3CC=CCH=NCH(OH)C=CCMe_3$, which was unstable and readily converted to a glassy polymer.

Thus the mode of addition of amines to tertbutylpropynal was determined by steric rather than basicity parameters.

EXPERIMENTAL

IR spectra were recorded for KBr tablets or thin layers on a UR-20 instrument, $^{13}\mathrm{C}$ NMR spectra on a Jeol FX-90Q and PMR spectra on a Tesla BS-487C (80 MHz, CDCl₃ solvent, referenced to TMS and HMDS).

<u>Reaction of 4,4-dimethyl-pent-2-yn-1-al (I) with Diisopropylamine</u>. The amine (0.3 g, 3 mmole) was added to the propynal I (0.33 g, 3 mmole) at $\sim 20^{\circ}$ C. An exotherm was observed. Standing for 3 days and evacuation gave 0.55 g (87%) of viscous, dark orange product. Found: C 74.38; H 11.15; N 5.59%. C₁₃H₂₅NO. Calculated: C 73.88; H 11.92; N 6.63%. According to PMR data the product was a 15:50:35 mixture of β -aminoacrolein (IVf), α -aminoacrolein (VIf), and aminoketone (Vf). After 2 weeks IVf had completely isomerized to Vf.

Addition of Dibutylamine to I. Dibutylamine (0.13 g, 1 mmole) was added to I (0.11 g, 1 mmole) at $\sim 20^{\circ}$ C. Standing for 2 weeks and evacuation gave a mixture of the isomers IVg, Vg, and VIg in the ratio 35:55:10 and in overall yield of 0.15 g (62%). Found: C 74.59; H 12.31; N 5.59%. C₁₅H₂₉NO. Calculated: C 75.25; H 12.21; N 5.85%.

 $\frac{4,4-\text{Dimethyl-1-dibenzylamino-pent-1-en-3-one (Ve)}{\text{with mp 106-107°C (from hexane) and M⁺ m/z 307. Found: C 82.04; H 8.04; N 5.09%.}$ $C_{21}H_{25}NO.$ Calculated: C 82.04; H 8.20; N 5.20%.

Reaction of I with Diphenylamine. A mixture of I (0.11 g, 1 mmole) and diphenylamine (0.17 g, 1 mmole) in CCl₄ (3 ml) was held for 3 weeks at \sim 20°C to give 0.22 g (78.5%) of a mixture of 4,4-dimethyl-3-diphenylamino-pent-2-en-1-al (IVd) and 4,4-dimethyl-1-diphenyl-amino-pent-1-en-3-one (Vd) in the ratio 1:1. Found: C 81.88; H 7.52; N 5.20%. C₁₉H₂₁NO. Calculated: C 81.68; H 7.58; N 5.01%.

<u>Reaction of I with Isopropylamine</u>. Isopropylamine (0.12 g, 2 mmole) was added to I (0.2 g, 1 mmole) at $\sim 20^{\circ}$ C. Standing for 3 days and evacuation gave a viscous orange product (0.1 g). PMR showed it to be a 1:1 mixture of Vh and VII.

<u>Reaction of I with Ammonia</u>. A stream of dry NH_3 was passed through a solution of I (0.95 g) in ether at -30 to -40°C. An immediate white, crystalline precipitate redissolved upon further passage of ammonia. Drying (MgSO₄) and removal of solvent gave a viscous yellow product (0.98 g). Found: C 77.05; H 9.52; N 6.54%. C₁₄H₂₁NO. Calculated: C 76.64; H 9.64; N 6.35%. After 1 day it was converted to a glassy polymer.

CONCLUSIONS

1. It has been shown that, depending on structure, secondary amines react with tertbutylpropynal at the C=C or C=O bonds to form acetylenic aminals or Michael adducts.

2. Acyclic and aromatic secondary amines add to tert-butylpropynal only at the triple bond. Dialkylamines with bulky substituents (i-Pr, n-Bu) add to both the β - and α -positions of the acetylenic fragment.

3. β -Aminoacroleins, containing tertiary and secondary amino groups, spontaneously isomerize to enaminoketones.

LITERATURE CITED

- 1. A. I. Borisova, A. S. Medvedeva, I. D. Kalikhman et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2640 (1985).
- 2. L. Kozerski and J. Dabrowski, Org. Magn. Reson., <u>5</u>, 459 (1973).
- 3. J. Dabrowski and L. Kozerski, Org. Magn. Reson., 4, 137 (1972).
- 4. A. Niederhauser and M. Neuenschwander, Helv. Chim. Acta, 56, 1318 (1973).
- 5. N. A. Keiko, L. G. Stepanova, I. D. Kalikhman, and M. G. Voronkov, Zh. Org. Khim., 20, 1802 (1984).
- 6. A. Niederhauser, A. Frey, and M. Neuenschwander, Helv. Chim. Acta, <u>56</u>, 944 (1973).
- 7. M. Neuenschwander and P. Bigler, Helv. Chim. Acta, 56, 959 (1973).
- 8. A. S. Medvedeva, L. P. Safronova, G. G. Chichkareva, and M. G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., 121 (1976).
- 9. I. V. Suvorova and M. D. Stadnichuk, Zh. Obshch. Khim., <u>54</u>, 132 (1984).
- A. P. Arendaruk, T. M. Godzhello, V. N. Mel'yantseva et al., Khim.-Farm. Zh., <u>7</u>, No. 9, 6 (1973).
- A. S. Medvedeva, L. P. Safronova, and É. I. Kositsyna, Izv. Akad. Nauk SSSR, Ser. Khim., 1153 (1980).
- 12. A. I. Borisova, M. M. Demina, A. S. Medvedeva et al., Zh. Obshch. Khim., <u>53</u>, 1310 (1983).