CONCLUSIONS

A preparation is reported for o-benzoquinones and catechols containing tertiary alkyl substituents in the ortho position.

LITERATURE CITED

1. US Patent No. 2,198,374 (1940); Chem. Abstr., 34, 4231 (1940).
2. H. A. Bruson and J. W. Kroeger, J. Am. Chem. Soc., 62, 36 (1940).

REACTION OF TRIMETHYLSILYLPROPYNAL WITH DIALKYLAMINES

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

UDC 542.91:547.1'128:547.233.2

Trimethylsilylpropynal (I) adds piperidine and morpholine regioselectively at the C=O bond with the formation of organosilicon acetylenic hemiaminals and aminals [1]. The reaction of tert-butylpropynal with secondary amines may proceed both at the triple bond and at the aldehyde group [2].

In the present work, we studied the reaction of propynal (I) with dialkylamines (II). The reaction was carried out with equimolar amounts at from −10 to 0°C with subsequent warming to about 20°C in the absence of solvent or in hexane. β-Aminoacroleins (III) were obtained under these conditions. The IR spectra of enaminoaldehydes (III) show strong bands at 1590-1605 cm^{-1} characteristic for N—C=C—C=O pentads [3]. The PMR spectra show signals for the α- and β-olefinic protons and signals for the carbonyl proton (Table 1).

$$\underset{(I)}{Me_3SiC{\equiv}CCHO} + \underset{(IIa-d)}{HNR_2} \rightarrow \underset{(IIIa-d)}{R_2NCH{=}CHCHO}$$

$$R = C_6H_{11}\ (a),\ i\text{-}Pr\ (b),\ Et\ (c),\ n\text{-}Bu\ (d).$$

The results confirm the ease of heterloysis of the Si—C_{sp} bond in (I) upon reaction with sterically hindered dialkylamines. The proposal for the initial addition of the nucleophile at the triple bond with the intermediate formation of silicon-containing aminoacroleins

TABLE 1. PMR Spectra of β-Aminoacroleins $R_2N—CH=CH—CHO$ (δ, ppm, ^3J, Hz)

Compound	R	NCH=	CCH=	HC=O	R
(IIIa)	C_6H_{11}	7.14 d (13,1)	5,29 d.d (13,1) (8,3)	9,03 d.d (8,3)	1,71 m 1,31 m
(IIIb)	*i*-Pr	7,10 d (13,5)	5,23 d.d (7,8) (13,5)	9,07 d (7,8)	1,27 d 4,03 m
(IIIc)	Et	6,97 d (12,2)	5,05 d.d (8,3) (12,2)	8,98 d.d (8,3)	3,28 m 0,99 m
(IIId)	*n*-Bu	7.02 d (12,7)	5.07 d.d (12,7) (8,0)	9.04 d (8,0)	3,19 m 2,57 m 0,97 m

---

Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1866-1868, August, 1987. Original article submitted September 11, 1986.

0568-5230/87/3608-1730$12.50

$Me_3Si{-}C(N\langle)$ =CHCHO and subsequent heterolysis of the Si–C bond was not supported. A PMR spectral study did not reveal signals for the aldehyde group of silicon-substituted enaminoaldehydes at 9.5-9.8 ppm observed in the case of their tert-butyl analogs [2]. This indicates the inertness of the triple bond in silicoacetylenic carbonyl compounds relative to nucleophilic reagents [1, 4].

EXPERIMENTAL

The IR spectra were taken neat and in KBr pellets on a UR-20 spectrophotometer. The PMR spectra were taken in a Tesla BS-487C spectrometer at 80 MHz and a Jeol FX-90Q relative to HMDS in $CDCl_3$ or DMSO-d_6.

β-Diethylaminoacrolein (IIIc). The reaction of 2.5 g (I) and 1.4 g Et_2NH at 0°C gave 1.0 g (83%) (IIIc), bp 98-102 (1 mm), n_D^{20} 1.5526 [5]. IR spectrum (ν, cm^{-1}): 1595 (NC=CC=O). Found, %: C 66.14, H 10.27, N 10.87. $C_7H_{13}NO$. Calculated, %: C 66.10, H 10.30, N 11.01.

β-Dibutylaminoacrolein (IIId) was obtained under analogous conditions from 1.3 g (I) and 1.3 g Bu_2NH. The yield was 0.7 g (96%), bp 158-162°C (2 mm), n_D^{20} 1.5077 [6]. IR spectrum (ν, cm^{-1}): 1600 (NC=CC=O). Found, %: C 72.22, H 11.58, N 7.55. $C_{11}H_{21}NO$. Calculated, %: C 72.08, H 11.55, N 7.64.

β-Dicyclohexylaminoacrolein (IIIa). A solution of 1.81 g dicyclohexylamine in 5 ml hexane was added dropwise to a solution of 1.26 g (I) in 2 ml dry hexane at from −5 to −10°C and the mixture was stirred for 1 h at −5°C. After removal of the solvent, the precipitate was washed with hexane to give 2.05 g (87%) crystalline (IIIa), mp 125-126°C [7]. IR spectrum (ν, cm^{-1}): 1590 (NC=CC=O). Found, %: C 76.56, H 10.69, N 5.75. $C_{15}H_{25}NO$. Calculated, %: C 76.54, H 10.70, N 5.94.

CONCLUSIONS

The reaction of trimethylsilylpropynal with dialkylamines is accompanied by heterolysis of the $Si{-}C_{sp}$ bond and formation of β-aminoacroleins.

LITERATURE CITED

1. A. S. Medvedeva, A. I. Borisova, M. M. Demina, et al., Zh. Obshch. Khim., 52, 2554 (1982).
2. A. I. Borisova, A. S. Medvedeva, I. D. Kalikhman, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2640 (1985).
3. Ya. F. Freimanis, Zinatne, Riga (1974).
4. M. F. Shostakovskii, N. V. Komarov, and V. B. Pukhnarevich, Zh. Obshch. Khim., 38, 1172 (1968).
5. S. M. Makin, Abla Akhmed Ismail, V. V. Yastrebov, and K. I. Petrov, Zh. Org. Khim., 7, 210 (1971).
6. H. Amschler and W. Schoetensak, West German Patent No. 2,640,186 (1977); Chem. Abstr., 87, 85030d (1977).
7. C. Jutz, West German Patent No. 2,135,584 (1972); Chem. Abstr., 76, 98554a (1972).