LITERATURE CITED

1. Yu. N. Bubnov, Pure Appl. Chem., 59, No. 7, 895 (1987).
2. M. Dagonneau and J. Vialle, Tetrahedron, 30, No. 3, 415 (1974).

SYNTHESIS OF KETENAMINALS FROM CYCLIC β-DIKETONES AND CYANAMIDES USING NICKEL ACETATE

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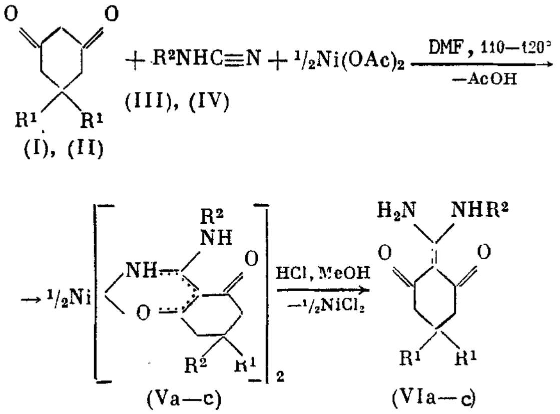
UDC 542.97:547.594.3:547.491.6

The addition of β-dicarbonyl compounds (DCC) at the C≡N bond of the activated nitriles, [1], dicyanogen [2], cyanamides [3], and methyl thiocyanate [4] catalyzed by metal acetylacetonates proceeds through the formation of chelate complexes of the metals with the DCC. Thus, cyclic β-diketones (CDK), which are incapable of chelation, have not been used in these reactions.

We have found that 1,3-cyclohexanedione (I) and dimedone (II) upon heating in DMF with cyanamides (III) and (IV) and $Ni(OAc)_2$ form chelates (V) in 64-75% yield. The smooth acidolysis of (V) gives the corresponding ketenaminals (VI).



R^1 = H (I), Me (II); R^2 = PhCO (III), 4,6-dimethylpyrimidin-2-yl (IV); R^1 = H, R^2 = PhCO (a); R^1 = Me, R^2 = PhCO (b); R^1 = Me, R^2 = 4,6-dimethylpyrimidin-2-yl (c).

$Zn(OAc)_2$ may also be used in the synthesis of (VI), but CDK do not react with (III) and (IV) in the absence of nickel or zinc salts. Reactive enolates are probably formed from CDK and $M(OAc)_2$ as intermediates, which add at the C≡N group of (III) or (IV) to give chelates (V).

A mixture of 9 mmoles (I), 6 mmoles (III), and 5 mmoles $Ni(OAc)_2$ in 14 ml DMF was stirred at 110-120°C under argon for 5 h. The precipitate was filtered off and washed with DMF and ether to give (Va) in 68% yield, dec. >340°C. Mass spectrum (m/z): 572 $[M]^+$. A sample of 3 mmoles (Va) was heated at reflux in 20 ml 0.5 N HCl in methanol for 1 h. Methanol was distilled off and (VIa) was purified by filtration through silica gel using chloroform as the eluent. The yield of (VIa) was 94%, mp 157-158°C (from ethanol). Analogously, (VIb) was obtained in 97% yield, mp 158-159°C and (VIc) was obtained in 99% yield, mp 173-174°C. The structure of (V) and (VI) were supported by IR, PMR, and ^{13}C NMR spectroscopy and mass spectrometry. The elemental analyses of (V) and (VI) agreed with the proposed structures.

LITERATURE CITED

1. A. C. Veronese, C. Talmelli, V. Gandolfi, et al., J. Mol. Catal., 34, No. 2, 195 (1986).
2. M. Basato, B. Corain, A. Marcomini, et al., J. Chem. Soc., Perkin Trans. 2, No. 6, 965 (1984).

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1211-1212, May, 1989. Original article submitted December 27, 1988.

0568-5230/89/3805- 1104$12.50

3. V. A. Dorokhov, M. F. Gordeev, Z. K. Dem'yanets, and V. S. Bogdanov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1683 (1987).
4. V. A. Dorokhov and M. F. Gordeev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 941 (1988).

UNUSUAL SILYLATION OF METHYL β-NITROBUTYRATE BY TRIMETHYLCHLOROSILANE

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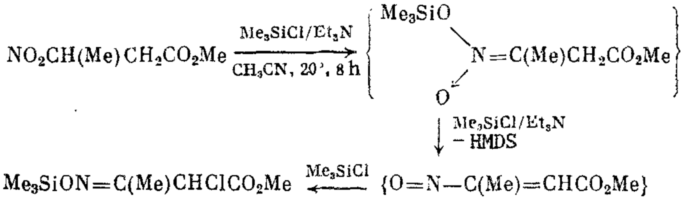
UDC 542.91:547.465.5'261:
547.245'131

Chlorination of the silylated substrate is observed in the silylation of methyl β-nitrobutyrate by excess trimethylchlorosilane in the presence of triethylamine. The methyl ester of α-chloro-β-trimethylsiloxyiminobutyric acid (I) was isolated. The formation of (I) may be represented by the following scheme.



There is no analogy for such a transformation in the chemistry of nitro compounds. The yield of (I) was 50%, bp 55-57°C (0.02 mm). The structure of this product was supported by NMR and mass spectral data. Found: C 41.21; H 6.82; N 6.17; Cl 14.28; Si 11. 13%. Calculated for $C_8H_{16}NO_3SiCl$: C 40.42; H 6.74; N 5.89; Cl 14.95; Si 11.79%. NMR spectra of (I) at 30°C in $CDCl_3$ relative to TMS (δ, ppm): ^1H: 0.21 ($SiMe_3$), 1.98 (C—Me), 3.80 (OMe); 5.04 (CH); ^{13}C: −0.81 ($SiMe_3$), 10.83 (Me, $^1J_{H,^{13}C}$ = 130.2, $^3J_{H,^{13}C}$ = 3.2 Hz), 53.30 (OMe, $^1J_{H,^{13}C}$ = 148.1 Hz), 59.12 (CH, $^1J_{H,^{13}C}$ = 154.4, $^3J_{H,^{13}C}$ = 2.9 Hz), 156.62 (C=N, $^2J_{H,^{13}C}$ = 6.7 Hz, quint), 167.13 (CO, $^2J_{H,^{13}C}$ = 5.3 d, $^2J_{H,^{13}C}$ = 4.2 Hz, q) ; ^{29}Si (INEPT): 27.12; ^{15}N (INEPT, CH_3NO_2 as the standard): −12.7 d. q; ^{17}O (50°C, H_2O as the standard); 139.3, half-width 300 Hz). Mass spectrum: 237, 239 ($M^{+\cdot}$, doublet with 3:1 intensity ratio characteristic for compound with one chlorine atom), 222 $(M - CH_3)^+$, 206 $(M - OCH_3)^+$, 202 $(M - Cl)^+$, 178 $(M - CO_2CH_3)^+$, 177 $(M - CO_2CH_3, H)^{+\cdot}$, 130 $(M - CHClCO_2HC_3, H)^{+\cdot}$, 118 $(M - SiOMe_3, 2CH_3)^{+\cdot}$, 116 $(M - SiOMe_3, OCH_3, H)^+$.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1212-1213, May, 1989. Original article submitted December 29, 1988.

0568-5230/89/3805- 1105$12.50