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REACTION OF AMMONIA WITH β,β' -DITHIOALKYL- α,α' -DIVINYL KETONES

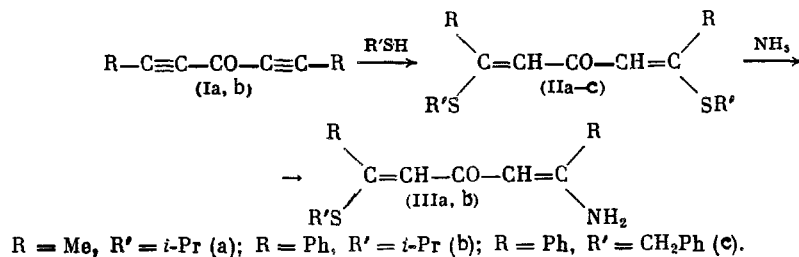
Kh. T. Shamurzaev, G. N. Bondarev,
and S. A. Grachev

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Divinyl ketones, $RR'C=CH-CO-CH=CRR'$, are used to prepare $\alpha,\alpha,\alpha',\alpha'$ -tetrasubstituted piperidines [1-4], which are precursors of stable nitroxyl radicals commonly employed in chemical and biological investigations as spin labels and probes.

One of the methods for the synthesis of substituted divinyl ketones $RR'C=CH-CO-CH=CRR'$ is the addition of various nucleophilic reagents to diacetylenic ketones $RC\equiv C-CO-C\equiv CR$. Such ketones react with thiols, alcohols, and phenols to form the products of addition at one or both acetylenic bonds depending on the reaction conditions [5, 6]. There have been no reports of the reaction of such divinyl ketones with ammonia. We would expect that the products of this reaction should be 2,2,6,6-tetrasubstituted γ -piperidones.

The starting divinyl ketones were synthesized according to Nazarov and Prostakov [2] at about 20°C in the presence of basic catalysts.



The expected γ -piperidones were not found after treatment of divinyl ketones obtained (II) with ethanolic ammonia in a sealed ampul at 100-120°C. Ammonia enters into an N-keto-vinylation reaction [7] with divinyl ketones (IIa) and (IIb): one thioalkyl group at a vinyl carbon atom is replaced by an amino group to give aminothioalkyldivinyl ketones (IIIa) and (IIIb). Ketone (IIc) does not react with ammonia under these conditions. The formation of aminodivinyl ketones (IIIa) and (IIIb) is indicated by IR and PMR spectroscopy. The replacement of the second thioalkyl group in ketones (IIa) and (IIb) does not occur under the conditions selected.

EXPERIMENTAL

The PMR spectra were taken on a Tesla BS-487 spectrometer at 60 MHz, while the IR spectra were taken on a Specord IR-71 spectrometer for 10% solutions in $CHCl_3$. The optical path-length was 0.1 mm.

The synthesis of 1,5-diphenyl-1,4-pentadiyn-3-one (Ib) and 2,5-heptadiyn-4-one (Ia) was described by Chauvelier [8].

1,5-Dithiobenzyl-1,5-diphenyl-1,4-pentadien-3-one (IIc). A sample of 1 g (4.3 mmoles) (Ib) in 20 ml absolute ethanol was added over 0.5 h to a stirred solution of PhCH_2SNa prepared from 1.2 g (9.6 mmoles) PhCH_2SH and 0.1 g (4.3 mmoles) sodium in 20 ml absolute ethanol with water cooling. After 2 h, 20 ml water was added and the mixture was extracted with ether. The residue after removal of the solvent was subjected to chromatography on a 30 × 2-cm column packed with grade-II silica gel using 1:1 benzene-ether as the eluent to give 1.33 g (65%) (IIc) as a thick brown oil. Found: C 78.01; H 5.94%. Calculated for $\text{C}_{31}\text{H}_{24}\text{OS}_2$: C 77.78; H 5.48%. PMR spectrum (δ , ppm): 3.5 m (CH_2 , 4H), 5.7 s, 6.3 s (CH= , 2H), 7.3 m (C_6H_5 , 20H). IR spectrum (ν , cm^{-1}): 1609 (CO), 1550, 1490 (CH=CH).

1,5-Dithioisopropyl-1,5-diphenyl-1,4-pentadien-3-one (IIb). A solution of 1.16 ml (12.6 mmoles) $i\text{-PrSH}$ and 0.1 g (0.98 mmole) Et_3N in 20 ml ether was added to 1.45 g (6.3 mmoles) (Ib) in 50 ml ether. The reaction mixture was stirred at about 20°C for 3 h. After removal of the solvent in vacuum, the residue was subjected to chromatography on a 30 × 2-cm column packed with grade-II silica gel using 3:1 benzene-ether as the eluent to give 1.6 g (71.4%) (IIb) as a thick red-brown oil. Found: C 72.41; H 6.82%. Calculated for $\text{C}_{23}\text{H}_{26}\text{OS}_2$: C 72.21; H 6.85%. PMR spectrum (δ , ppm): 1.16 d, 1.33 d (CH_3 , 12H), 2.9-3.3 m (CH , 2H), 6.3 s, 6.5 s (CH= , 2H), 7.34 m (C_6H_5 , 10H).

1,5-Dithioisopropyl-2,5-heptadien-4-one (IIa). A solution of 2.89 g (37.9 mmoles) $i\text{-PrSH}$ and 0.1 g (0.98 mmole) Et_3N was added dropwise to a solution of 2 g (18.8 mmoles) (IIa) in 30 ml absolute ethanol. After stirring for 2 h at about 20°C the solvent was removed in vacuum. The residue was recrystallized from ethanol to give 2.29 g (47%) (IIa), mp 76°C. Found: C 60.67; H 8.67; S 24.72%. Calculated for $\text{C}_{13}\text{H}_{22}\text{OS}_2$: C 60.41; H 8.58; S 24.81%. PMR spectrum (δ , ppm): 1.3 d (CH_3 , 12H), 2.38 s ($=\text{CCH}_3$, 6H), 3-3.4 pent (CH , 2H), 5.93 s (CH= , 2H).

1-Amino-1,5-diphenyl-5-thioisopropyl-1,4-pentadien-3-one (IIIb). A solution of 1.4 g (3.6 mmoles) (IIb) and 0.3 g (18 mmoles) ammonia in 10 ml ethanol was heated at 100°C in a sealed ampul for 8 h. The solvent was removed and the residue was subjected to chromatography on a 30 × 2-cm column packed with grade-II silica gel; the eluent was 3:1 benzene-ether. The yield was 0.72 g (66.6%) (IIIb) as a thick oil. Found: C 74.87; H 6.67; S 9.72; N 4.20%. Calculated for $\text{C}_{20}\text{H}_{21}\text{NSO}$: C 74.27; H 6.54; S 9.91; N 4.33%. PMR spectrum (δ , ppm): 1.2-1.33 d (CH_3 , 12H), 2.8-3.1 m (CH , 2H), 5.4 s (CH=CN , 1H), 6.2 s (CH=CS , 1H), 7.28 m (C_6H_5 , 10H). IR spectrum (ν , cm^{-1}): 3480, 3400, 1590 (NH_2), 1610 (CO), 1560, 1490 (C=C).

2-Amino-6-thioisopropyl-2,5-heptadien-4-one (IIIa). A solution of 1.3 g (5.7 mmoles) (IIa) and 1.15 g (67 mmoles) NH_3 in 20 ml ethanol was heated in a sealed ampul for 2 h at 120°C. The solvent was removed and the residue was recrystallized from ethanol to give 0.82 g (72.4%) (IIIa), mp 65°C. Found: C 60.56; H 8.86; S 15.92%. Calculated for $\text{C}_{10}\text{H}_{17}\text{ONS}$: C 60.26; H 8.60; S 16.09%. PMR spectrum (δ , ppm): 1.2-1.3 d ($(\text{CH}_3)_2\text{CH}$, 6H), 1.9 s (CH_3CN , 3H), 2.35 s (CH_3CS , 3H), 3.0-3.4 m (CH , 1H), 4.9 s (CH=CN , 1H), 5.85 s (CH=CS , 1H). IR spectrum (ν , cm^{-1}): 3490, 3400, 1598 (NH_2), 1630 (CO), 1565 (C=C).

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CONCLUSIONS

Syntheses are reported for β, β' -dithioalkyldivinyl ketones, which react with ammonia to give β -amino- β' -thioalkyldivinyl ketones.

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