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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713618290

Dithienylthiazines from Dithienylacetylenes

L. I. Belen'kii^a; V. Z. Shirinian^a; G. P. Gromova^a; A. V. Kolotaev^a; M. M. Krayushkin^a N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Russia

To cite this Article Belen'kii, L. I., Shirinian, V. Z., Gromova, G. P., Kolotaev, A. V. and Krayushkin, M. M.(2005) 'Dithienylthiazines from Dithienylacetylenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 5, 1503 — 1504

To link to this Article: DOI: 10.1080/10426500590913393 URL: http://dx.doi.org/10.1080/10426500590913393

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Phosphorus, Sulfur, and Silicon, 180:1503-1504, 2005

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DOI: 10.1080/10426500590913393



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L. I. Belen'kii

V. Z. Shirinian

G. P. Gromova

A. V. Kolotaev

M. M. Krayushkin

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Russia

Keywords Dithienylacetylenes; dithienylthiazines

Recently we studied the Friedel–Crafts acylation of 2-methyl-, 2,4-, and 2,5-dimethylthiophenes with oxalyl chloride in the presence of AlCl₃. The conditions were found to suppress the formation of some side products and to obtain target α -diketones in 50–60% yields. This was attained by adding pyridine or lowering the polarity of the medium because of the use of 1,2-dichloroethane-heptane mixtures as solvents. Dithienylethanediones were transformed to dihydrazones and the latter were readily oxidized by air in the presence of CuCl in pyridine solution to give corresponding dithienylacetylenes. Now the cycloaddition of bis(2,5-dimethyl-3-thienyl)acetylene with thiobenzamide and hetarenecarbaldehydes catalyzed by BF₃ etherate has been shown to afford 4-substituted 5,6-bis(2,5-dimethyl-3-thienyl)-4H-1,3-thiazines (R = 2-thienyl, 3-thienyl, 5-methyl-2-thienyl, 2,5-dimethyl-3-thienyl, 5-methyl-2-furyl), which possess moderate photochromic properties.

Received July 9, 2004; accepted October 5, 2004.

Address correspondence to L. I. Belen'kii, N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Russia.

REFERENCE

[1] L. I. Belen'kii, V. Z. Shirinian, G. P. Gromova, A. V. Kolotaev, Yu. A. Strelenko, S. N. Tandura, A. N. Shumskii, and M. M. Krayushkin, Khim. Geterotsikl. Soed., 1785 (2003).