

SHORT
COMMUNICATIONS

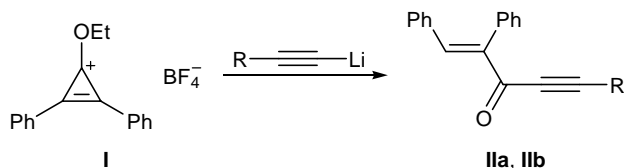
New Synthesis of Conjugated Ethynyl Vinyl Ketones

Yu. V. Skorniyakov, N. A. Lozinskaya, M. V. Proskurnina, and N. S. Zefirov

Faculty of Chemistry, Lomonosov Moscow State University, Vorob'evy gory 1, Moscow, 119992 Russia

Received May 5, 2004

We have found that lithium acetylides react with 1-ethoxy-2,3-diphenylcyclopropenylium tetrafluoroborate (**I**) [1] via opening of the three-membered ring to give the corresponding unsaturated acetylenic ketones **IIa** and **IIb** in 85 and 87% yield, respectively. The structure of compounds **IIa** and **IIb** was proved by the ^1H and ^{13}C NMR spectra and elemental analysis.



R = Ph (**a**), *t*-Bu (**b**).

1,2,5-Triphenyl-1-penten-4-yn-3-one (IIa). To a solution of 2.5 mmol of phenylacetylene in 10 ml of anhydrous tetrahydrofuran, cooled to -70°C , we added dropwise under argon an equivalent amount of butyllithium in hexane. The mixture was stirred for 30 min at -70°C , allowed to warm up to 0°C , stirred for 5 min, and added under argon to a suspension of

2.5 mmol of 1-ethoxy-2,3-diphenylcyclopropenylium tetrafluoroborate in 10 ml of THF, stirred at -70°C . The mixture was stirred for 1 h at that temperature, allowed to warm up to room temperature, filtered from lithium tetrafluoroborate, and evaporated. The crystalline product was purified by chromatography on silica gel (35–70 mesh) using chloroform as eluent. Yield of **IIa** 78%, colorless crystals. IR spectrum, ν , cm^{-1} : 2050 ($\text{C}\equiv\text{C}$), 1720 ($\text{C}=\text{O}$). ^1H NMR spectrum (CDCl_3), δ , ppm: 8.1–8.3 m, 7.0–7.7 m, 6.6 s.

6,6-Dimethyl-1,2-diphenyl-1-hepten-4-yn-3-one (IIb) was synthesized in a similar way. Yield 85%. IR spectrum, ν , cm^{-1} : 2050 ($\text{C}\equiv\text{C}$), 1720 ($\text{C}=\text{O}$). ^1H NMR spectrum (CDCl_3), δ , ppm: 7.1–7.9 m (10H), 6.1 s (1H), 0.8 s (9H). ^{13}C NMR spectrum, δ_{C} , ppm: 196.17, 150.66, 137.94, 137.12, 133.57, 130.52, 129.55, 129.31, 129.19, 126.73, 110.05, 108.15, 77.83, 31.30, 28.90.

REFERENCE

1. Yoshida, H., Kinoshita, H., Kato, T., Kamauta, N., Ogata, T., and Matsumoto, K., *Synthesis*, 1987, p. 393.