NEW METHOD FOR THE SYNTHESIS OF 1,4-ENYNES BY THE CROSS-COUPLING OF MAGNESIUM ACETYLIDES WITH ALLYL COMPOUNDS

U. M. Dzhemilev, A. G. Ibragimov,
R. A. Saraev, and D. L. Minsker

UDC 542.91:547.316.4

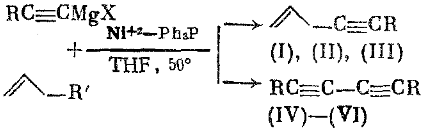
Alkynylmagnesium halides react with either allyl halides or haloacetylenes in the presence of catalytic amounts of CuCl to respectively give 1,4-enynes and diacetylenes [1, 2]. Alkynylzinc halides when reacted with aryl halides in the presence of Pd complexes are converted by an analogous scheme to disubstituted acetylenes in quite high yields [3, 4]. Information is practically lacking on whether these reactions can be run using functional allyl compounds and dialkynylmagnesium derivatives.

In order to develop original and perspective methods for obtaining 1,4-enynes of a given structure from readily available monomers, and also to ascertain the possibility of involving compounds of type $(R{-}C{\equiv}C)_2Mg$ in the cross-coupling reaction, we first investigated the reaction of dialkynylmagnesium derivatives, obtained from hexyne, octyne, and phenylacetylene as described in [5], with allyl acetate, phenyl allyl sulfone, and diallyl sulfide, catalyzed by transition metal complexes.

Of the transition metal (Cu, Fe, Co, Ni, Pd) complexes, tested as catalysts of the mentioned reaction, the Ni^{+2} compounds exhibit the greatest catalytic activity in the coupling with Ph$_3$P. The cross-coupling of dihexynyl-, dioctynyl-, and bisphenylethynylmagnesium with diallyl ether in the presence of Ni(acac)$_2$—Ph$_3$P (1:4) in THF solution (50°C, 4 h) leads to obtaining 1,4-enynes (I)-(III) in yields of 62, 69, and 74% respectively. Besides (I)-(III), the formation of diacetylenes (IV)-(VI) is observed in each experiment, the amount of which is the mixture of hydrocarbons, independent of the reaction conditions, is ~3% in each experiment

The structure of the starting allyl intermediate has practically no effect on the yield of the cross-coupling products. Thus, dihexynylmagnesium reacts with allyl acetate, phenyl allyl sulfone, or diallyl sulfide to give 1-nonen-4-yne (I) in yields of ~62-65%. The reaction of the hexynyl- and octynylmagnesium bromides with allyl acetate and phenyl allyl sulfone in the presence of Ni(acac)$_2$—Ph$_3$P gave 1,4-enynes (I) and (II) in yields of 55 and 64% respectively.

As a result, the cross-coupling reaction of dialkynylmagnesium derivatives and alkynylmagnesium halides with functional allyl compounds, catalyzed by a two-component catalytic system, can serve as a convenient and perspective method for obtaining 1,4-enynes of variable structure.



R = C$_4$H$_9$ (I), (IV); C$_6$H$_{13}$ (II), (V); Ph (III), (VI); X = Br, C≡CR; R′=SO$_2$Ph, OAc, OCH$_2$CH=CH$_2$; SCH$_2$CH=CH$_2$.

EXPERIMENTAL

The purity of the employed allyl acetate, diallyl ether, phenyl allyl sulfone, and diallyl sulfide was at least 99%. The reaction products were identified by comparing with authentic compounds obtained as described in [1]. The GLC was run on a Chrom-41 instrument, equipped with a flame-ionization detector and a 3.7 m × 3 mm column, packed with 15% Carbowax-6000 deposited on Chromaton N-AW, and using helium as the carrier gas at a flow rate of 60 ml/min.

Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 907-908, April, 1984. Original article submitted May 4, 1983.

0568-5230/84/3304-0835$08.50

With vigorous stirring, to a solution of 0.257 g (1 mmole) of Ni(acac)$_2$, 1.048 g (4 mmoles) of Ph$_3$P, and 25 mmoles of the appropriate allyl compound in 15 ml of THF, cooled to −5°C, was added in an argon stream 30 mmoles of magnesium diacetylide and the mixture was kept at this temperature for 15 min. The solution was transferred to a thermostatted glass reactor and heated for 4 h at 50°C. The catalyzate was decomposed with 50% HCl solution and repeatedly extracted with ether. The ether extracts were washed with water until neutral and dried over MgSO$_4$. After removal of the solvent the residue was vacuum-distilled. The obtained 1,4-enynes has the following constants: 1-nonen-4-yne, bp 52°C (12 mm), n_D^{20} 1.4442, M^+ 122 (bp 58° (22 mm), n_D^{25} 1.4413 [1]); 1-undecen-4-yne, bp 51-52° (2 mm), n_D^{20} 1.4485, M^+ 150 (cf. [6]); 5-phenyl-1-penten-4-yne, bp 85-86° (6 mm), n_D^{20} 1.5586, M^+ 142 (bp 107-108° (22 mm), n_D^{25} 1.5574 [1]).

CONCLUSIONS

A method was developed for the synthesis of 1,4-enynes by the cross-coupling of compounds of type (RC≡C)$_2$Mg and RC≡CMgBr with allyl alcohol derivatives using Ni(acac)$_2$–Ph$_3$P as the catalyst.

LITERATURE CITED

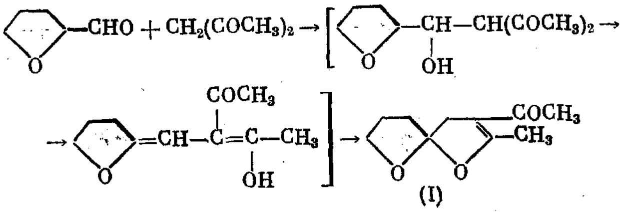
1. J. P. Danehy, D. B. Killian, and J. A. Nieuwland, J. Am. Chem. Soc., 58, 611 (1936).
2. V. Grignard, Compt. Rend., 188, 357 (1929).
3. A. O. King and E. Negishi, J. Org. Chem., 43, 358 (1978).
4. A. O. King, N. Okukado, and E. Negishi, Chem. Communs., 683 (1977).
5. J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, J. Am. Chem. Soc., 78, 1221 (1956).
6. J. Klein and S. Brenner, Tetrahedron., 26, 5807 (1970).

SYNTHESIS AND TRANSFORMATION OF 2-METHYL-3-ACETYL-1,6-DIOXASPIRO[4,4]-2-NONENE

R. A. Karakhanov, M. M. Vartanyan,
T. Yu. Solov'eva, and A. V. Ignatenko

UDC 542.97:547.724.1:547.442.3

2-Methyl-3-acetyl-1,6-dioxaspiro[4,4]-2-nonene (I) is the first member of a new type of 1,6-dioxaspirononenes, which we obtained by the pyrolysis of 2-(1-acetoxy-2-butynyl)tetrahydrofuran [1]. Continuing the study, we developed a new method for the synthesis of 2,3-disubstituted 1,6-dioxaspirononenes by the condensation of tetrahydrofurfurole with 1,3-dicarbonyl compounds. A similar condensation was accomplished with acetoacetic ester [2]. In the present paper it was shown that the reaction of tetrahydrofurfurole with acetylacetone in the presence of catalytic amounts of β-alanine and AcOH gives a 65% yield of 2-methyl-3-acetyl-1,6-dioxaspiro[4,4]-2-nonene (I), whose physicochemical characteristics coincide completely with those for the thermoisomerization product of 2-(1-acetoxy-2-butynyl)tetrahydrofuran [1].



When the chemical transformation of the obtained spirononе were studied we found that the mild alkaline hydrolysis of (I) leads to the formation of 2-(2-hydroxyethyl)-3-methyl-2-cyclopenten-1-one (II) in quantitative yield. 2-Methyl-3-acetyl-5-(3-hydroxypropyl)furan (III) was obtained in good yield when (I) is refluxed in DMSO in an N$_2$ stream. The reaction

---

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 908-910, April, 1984. Original article submitted May 11, 1983.

0568-5230/84/3304-0836$08.50