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Synthesis of Novel 4,6-Diazaspiro[2.3]hex-1-en-5-ones by the Reaction of Diphenylcyclopropenone Oxime with Isocyanates [#]

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Diphenylcyclopropenone oxime hydrochloride (3) was prepared in an 83% yield from diphenylcyclopropenone and hydroxylamine hydrochloride in methanol. The salt 3 reacted with alkyl and aryl isocyanates in the presence of triethylamine to yield 1:2 addition products diazaspiro[2.3]hexenones in good yields.

Physical and chemical properties of cyclopropenones, cyclopropenium ions, and triafulvenes have been highly interested and currently investigated1) as microcyclic aromatics. In the continuation of our studies on the chemistry of cyclopropenium salts posessing heteroatom substituents we have found an easy route for the preparation of diphenylcyclopropenone oxime (4),2) the chemical nature of which has not been explored. Below we describe the preparation and reaction of 4 with isocyanates to yield novel 4,6-diazaspiro[2.3]hexenes.

A solution of diphenylcyclopropenone (1)[20 mmol] and hydroxylamine hydrochloride (2)[60 mmol] in methanol(25 cm^3) was allowed standing at room temperature for a day. The precipitated salt 1-hydroxyamino-2,3-diphenylcyclopropenium chloride (3) was obtained in an 83% yield by filtration. The salt 3 gave satisfactry spectroscopic data3) and yielded yellow needles of free 4 4) on treating with aqueous sodium hydrogencarbonate or triethylamine in benzene.

An equimolar reaction of 3 with methyl isocyanate (5a) in the presence of triehtylamine gave 4-methyl-6-methylcarbamoyloxy-1,2-diphenyl-4,6-diazaspiro[2.3]-hex-1-en-5-one (6a) in a 40% yield. The use of twice excess moles of 5a at room temperature for a day gave 6a in a 70% yield. The structure of 6a was assigned from its ^{1}H- and ^{13}C-NMR, and mass spectroscopic studies.5) Similar treatment of 3 with two moles of isocyanates such as propyl, t-butyl, phenyl, 3-methylphenyl, and 4-chlorophenyl isocyanates (5b-f) yielded in 63, 69, 71, 67, and 48% yield respectively. No 1:1 addition product was isolated in our hands. To our knowledge no spiro derivatives like these have been reported, though it has been shown that some C=N derivatives react with isocyanates to afford the 1:1 cycloaddition products, 1,3-diazetidines.6)

It is well known that aldoximes and ketoximes react with isocyanates to afford carbamates.6b) Although the isolation of (carbamoyloxy)iminocyclopropene

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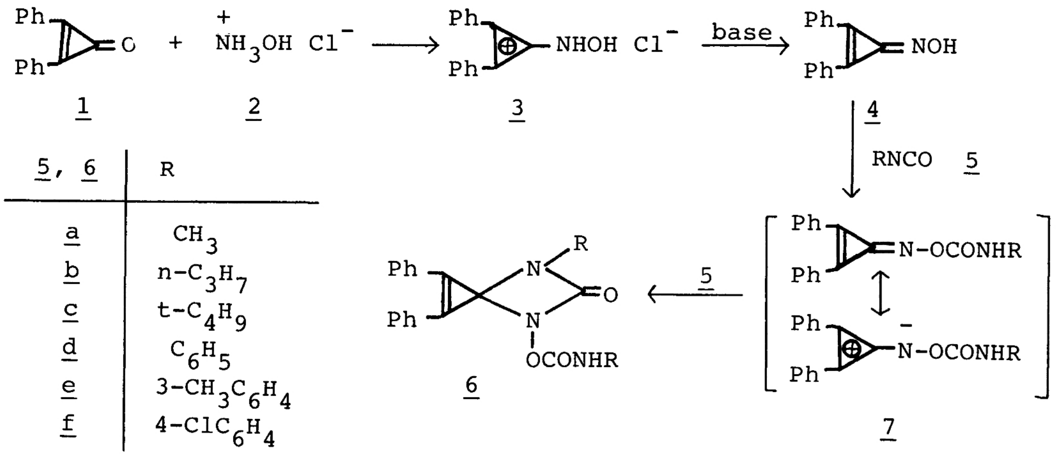
[#] This paper is dedicated to the late Professor Ryozo Goto, Kyoto University.



5, 6	R
a	CH_3
b	n-C_3H_7
c	t-C_4H_9
d	C_6H_5
e	3-$CH_3C_6H_4$
f	4-ClC_6H_4

(7), a 1:1 addition product, failed, the intermediacy of 7 was clear from the final product 6. The reaction of highly polarized 7 with 5 would be faster than that of 4 with 5.

References

1) Recent examples:R. A. Moss, S. Shen, K. Krogh-Jespessen, J. A. Potenza, H. J. Schugar, and R. C. Munjal, J. Am. Chem. Soc., 108, 134(1986). F. J. Kaiser, G. Offermann, and G. Seitz, Chem. Ber., 119, 2141(1986). T. Sugimoto, M. Shibata, S. Yoneda, Z. Yoshida, Y. Kai, K. Miki, N. Kasai, and T. Kobayashi, J. Am. Chem. Soc., 108, 7032(1986). K. Takahashi, K. Ohnishi, and K. Takase, Chem. Lett., 1985, 1447.

2) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner[J. Am. Chem. Soc., 87, 1320(1965)] have reported the reaction of 1 with 2 in aqueous ethanol to yield deoxybenzoin oxime and diphenylisoxazolone. Y. Kitahara and M. Funamizu[Bull. Chem. Soc. Jpn., 37, 1897(1964)] have obtained 4 as colorless needles from 1 and 2 in methanol by treating with aqueous $NaHCO_3$. T. Eicher and G. Frenzel[Z. Naturforsch., B, 20, 274(1965)] have reported 3 (BF_4 salt) from the ethoxy derivative of 1 and 2, however the chemical nature of 3 and 4 have never been explored.

3) 3:mp 198-202 °C;IR(KBr) 2940, 2740, and 1920 cm^{-1};^{13}C-NMR($CDCl_3$+CF_3CO_2H) δ= 119.1(s), 119.2(s), 129.9(d), 130.3(d), 133.6(d), 133.8(d), 136.2(d), and 139.5(s).

4) 4:mp 133-136 °C;IR(KBr) 3150, 1880, and 1850 cm^{-1};MS(m/z) 221(M^+).

5) 6a:mp 135-137 °C;IR(KBr) 3450, 1770, and 1710 cm^{-1};^1H-NMR($CDCl_3$) δ=2.59(s, 3H, CH_3N), 2.85(d, J=6 Hz, 3H, $NHCH_3$), 6.13(q, J=6 Hz, 1H, NaOD/D_2O exchange, NH), and 7.2-7.9(m, 10H, 2Ph);^{13}C-NMR($CDCl_3$) δ=26.5(q), 26.6(q), 65.7(s), 118.4(s), 125.9(s), 128.9(d), 129.9(d), 130.4(d), 155.4(s), and 160.0(s); MS(m/z) 335(M^+).

6) a)H. Ulrich,"Cycloaddition Reaction of Heterocumulenes,"Academic Press, New York(1967);b)R. Richter and H. Ulrich,"The Chemistry of Cyanates and Their Thio Derivatives," ed by S. Patai, John Wiley & Sons, Chichester(1977) Part 2, p. 619;c)J. W. Timberlake and E. S. Elder,"Comprehensive Heterocyclic Chemistry," ed by W. Lwowski, Pergamon Press, Oxford(1984), Vol. 7, p. 449.

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