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REACTION OF 2-PHENYL-1-AZIRINE WITH COPPER BROMIDES. SELECTIVE FORMATION OF TWO TYPES OF BROMO-DIMERIC COMPOUNDS DEPENDING ON THE SOLVENTS

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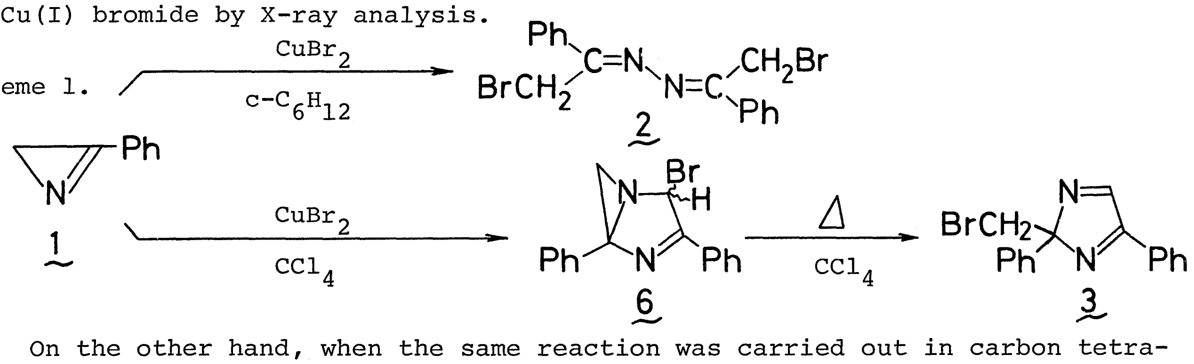
Treatment of 2-phenyl-1-azirine in cyclohexane with Cu(II) bromide afforded ω-bromoacetophenone azine, but in carbon tetrachloride gave 2-bromomethyl-2,4-diphenyl-2H-imidazole via 2-bromo-3,5-diphenyl-1,4-diazabicyclo[3.1.0]hex-3-ene.

Although many investigations were performed on 1-azirines since these highly strained compounds became accessible recently, little is known about the reactions with transition metal compounds. During the course of our investigation on the chemistry of 1-azirines, it was found that 2-phenyl-1-azirine 1 reacted with Cu(II) bromide under mild conditions affording two types of bromo-dimeric compounds depending on the solvents as shown in scheme 1. We wish to report these new reactions of 1-azirine promoted by Cu(II) bromide.

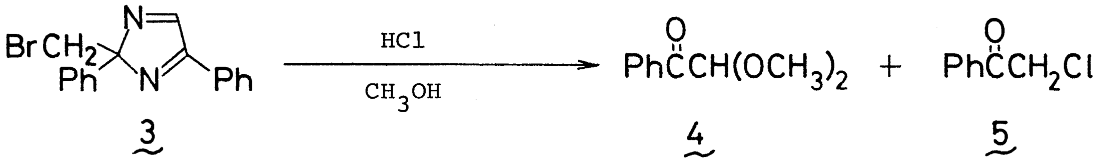
A cyclohexane solution of 1 (0.6g, 5.1mmol) was added to anhydrous $CuBr_2$ (1.26g, 5.6mmol). After the mixture was stirred for 1 day at room temperature, precipitates were filtered off and the cyclohexane solution was washed with 2N-ammonia water and water successively. Evaporation of the solvent in vacuo gave orange needles ($C_{16}H_{14}Br_2N_2$), mp 151∿152°C, in 74% yield. On the basis of the spectral results and mixed melting point with authentic specimen, this compound was identified as ω-bromoacetophenone azine 2[1]. The precipitates were ascertained to be Cu(I) bromide by X-ray analysis.

Scheme 1.



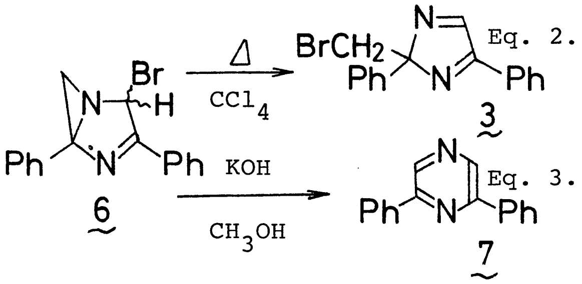
On the other hand, when the same reaction was carried out in carbon tetrachloride at room temperature, a different compound was formed mainly, accompanied by small ammounts of 2 (below 3%) which was determined by nmr spectrum. Recrystallization from benzene-hexane (1:4) gave colorless needles, mp 158∿159.5°C, in 52% yield. The structure of this compound was assigned as 2-bromomethyl-2,4-diphenyl-2H-imidazole 3 by elemental analysis [Found: C, 61.25; H, 4.11; N, 9.02%. Calcd for $C_{16}H_{13}BrN_2$: C, 61.40; H, 4.18; N, 8.95%] and spectral data [MS m/e 312 and 314

(M^+); ir (nujol) 1620cm^{-1}(C=N); nmr (δ in CCl_4) 4.05 s (2H, $BrCH_2$-), 8.33 s (1H, -CH=N-) and 7.10∿8.03 m (10H, arom.)]. Treatment of 3 in methanolic HCl gave ω,ω-dimethoxyacetophenone 4 and ω-chloroacetophenone 5 in 1 : 1 ratio (eq. 1). This transformation strongly substantiated the assigned structure of 3.



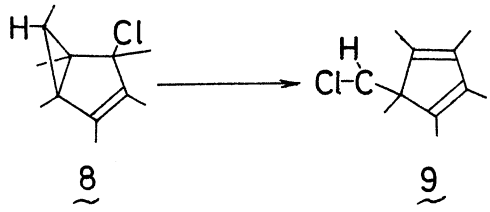
Eq. 1.

The reaction in CCl_4, when carried out by cooling in an ice-salt bath, gave still another isomeric product. Recrystallization from hexane gave colorless needles 6, mp 123°C(dec.). Nmr spectrum of 6 showed AB quartet at δ3.9 and 4.4 with a coupling constant of 15Hz, which indicated the presence of a methylene group having unequivalent protons. The structure of 6 was assigned as 2-bromo-3,5-diphenyl-1,4-diazabicyclo[3.1.0]hex-3-ene by the above nmr spectrum and the following chemical transformations (eq. 2 and 3). Standing of the CCl_4 solution of 6 at room temperature for 1 day afforded 3 (eq. 2). Similar transformation, which was reported for carbocyclic homolog 8 as shown in eq. 4[2], strongly supported the structural assignment of 6. Treatment of 6 in methanolic KOH gave 2,6-diphenylpyrazine 7 (eq. 3).



Eq. 2.

Eq. 3.



Eq. 4.

When Cu(I) bromide was used for the above reaction in cyclohexane, 1 remained after 2 days treatment. On the other hand, 2 and 3 were obtained in 16 and 3% yield respectively, when 1 was treated with Cu(I) bromide in CCl_4. Preferred formation of 2 in CCl_4 in this case would imply some important role of CuBr in the formation of 2. Formation of Cu(II) halide from Cu(I) halide in CCl_4 by redox reaction is well known[3], so that the occurrence of the reaction of 1 by Cu(I) in CCl_4 may be ascribed to the reaction with Cu(II) which is produced in the course of the reaction. Alternatively, formation of 2, when 1 was allowed to react with $CuBr_2$ in cyclohexane, might be attributed to CuBr which was produced as the reaction proceeded.

Further investigations on the scope and the mechanistic aspect of these reactions are in progress in our laboratory.

References.

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