

A HIGHLY EFFICIENT REACTION OF THIOBENZOPHENONE FOR 1-DIAZOALKENE

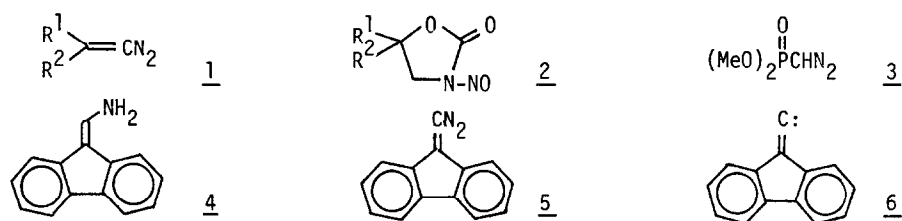
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Summary: 9-(Diazomethylene)fluorene formed in situ in the reaction of 9-(aminomethylidene)fluorene with n-butyl nitrite, was successfully trapped by thiobenzophenone to afford 1,3,4-thiadiazoline derivative which was confirmed by spectroscopic and analytical data.

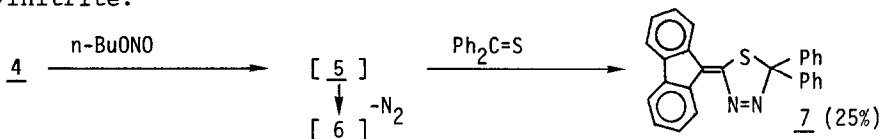
In contrast to diazoalkane, 1-diazoalkene is an extremely unstable chemical species and is neither directly observed nor trapped, only being considered to be a reaction intermediate.¹⁾ Hitherto reported are reactions of alkylidene carbene derived from the corresponding 1-diazoalkene. Treatment of ethylenic diazonium salt with Lewis acid did not yield 1-diazoethylene.²⁾ Newman reported the possible formation of 1 in the decomposition of 5,5-disubstituted N-nitrosooxazolidones 2 with lithium alkoxide, but only obtained carbene-induced products.³⁾ Treatment of 9-(aminomethylidene)fluorene 4 with n-butyl nitrite in the presence of olefines afforded fluorenylidene cyclopropanes, in which Curtin⁴⁾ suggested the intermediacy of 9-(diazomethylidene)fluorene 5 which is quickly decomposed to carbene 6. Recently, Berson was reported that base-promoted reaction of dimethyl(diazomethyl)phosphonate 3 with acetone in the presence of 3,3-dimethylcyclopropene affords allenes and tricyclic nitrogenous compound, which is believed to result from diazopropene (1:R¹=R²=Me),⁵⁾ is only described in supplementary material. Similarly, the diazomethyl phosphonate-acetone-olefin reaction was carried out and the intervention of 1 was postulated from failure to detect it.⁶⁾ In order to confirm 1-diazoalkene, thioketone was selected as a potent trapping agent since it reacts well with diazoalkane to give thiadiazoline but scarcely with carbene and carbenoid.⁷⁾ We now present a highly efficient reaction of thiobenzophenone for 1-diazoalkene.

To a gently refluxing solution of 4 (0.375g, 1.94mmol) and thiobenzophenone (3.84g, 19.4mmol) in dry ether (7.5mL) was added dropwise n-butyl nitrite (280μL) under nitrogen atmosphere. The resulting mixture was refluxed for 18 h until 4 completely disappeared as observed by TLC. The mixture concentrated was subjected to alumina column chromatography (eluent; hexane:ether=10:1). Orange



colored product was recrystallized from hexane and orange-red crystals (7) were obtained (203mg, 25%); mp 120–121°C (decomp.); $^1\text{H-NMR}$ (CCl_4) δ 8.10–7.23 (m, 17H), 9.08–8.90 (m, 1H); $^{13}\text{C-NMR}$ (CDCl_3) δ 156.0, 141.9, 140.7, 139.3, 137.2, 136.7, 132.7, 129.7, 129.0, 128.7, 128.1, 127.9, 127.7, 127.3, 125.2, 120.0, 119.6, 117.4, 115.3; Mass m/e 374 [$\text{M}^+ - \text{N}_2$]; Anal. Calcd for $\text{C}_{27}\text{H}_{18}\text{N}_2\text{S}$. C: 80.56; H: 4.51; N: 6.96. Found: C: 80.14; H: 4.55; N: 6.96. The product structure, 1,3,4-thiadiazoline derivative 7, was supported by above spectroscopic and analytical data. Low field shifted proton signal at region from 9.08 to 8.90 in $^1\text{H-NMR}$ is assigned to that at peri-position of benzene ring near to nitrogen. $^{13}\text{C-NMR}$ indicates that two resonance at 156.0 and 115.3 ppm are those of two carbon of thia-diazoline ring. In mass spectrum of 7, no molecular ion peak was observed but denitrogenated ion peak appeared at m/e 374, as expected from the structure 7.

Formation of 7 is clearly explained by 1,3-dipole addition of 9-(diazo-methylidene)fluorene 5 to thiobenzophenone, like that of diazoalkane.⁸⁾ Much less stability of 5 in contrast to diazoalkane is consistent with lower yield of the addition product 7 (25%) than that of diazoalkane ($\sim 90\%$)⁸⁾ even in the presence of ten-fold amount of the thioketone. The diazoalkene 5 once formed is swiftly converted to carbene 6 which eventually gives decomposition products because of very low reactivity toward thioketone. Thus, formation of 7 represents clear evidence of the intervention of diazoalkene 5 in the reaction of 4 with *n*-butylnitrite.



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