

THE CHEMISTRY OF CUMMULATED DOUBLE BOND COMPOUNDS IX
THE REACTION OF SULFURDIIMIDES WITH DIPHENYLKETENE

T. Minami, O. Aoki, H. Miki, Y. Ohshiro and T. Agawa

Faculty of Engineering, Osaka University, Yamada-kami, Suita, Japan.

(Received in Japan 2 December 1968; received in UK for publication 27 December 1968)

Although the reactions of hetrocummulenes such as isocyanate, carbodiimide, thionylamine, etc. with ketene are well known(1), the reaction of sulfurdiimide with ketene has not been reported. In this paper we wish to report some of the information obtained from the reaction of sulfurdiimide with diphenylketene.

When diarylsulfurdiimides (I) (2) were mixed with equimolar amounts of diphenylketene in benzene or without solvent, the reaction proceeded exothermically and then the mixture was further heated at temperatures in the range of 80° to 100° for one hour. The reaction proceeded quantitatively. The sticky products (II) obtained could not be purified. The IR bands of II_a in a Nujol mull were at 1700(s)(>C=O), 1600 and 1500(aromatic), 1310(s), 1170(m), 1090(m), 1035(m), 1000(w), 940(w), 920(w), 870(w), 830(w), 800(w), 755(s), 730(m) and 690(s) cm⁻¹.

II_b and II_c gave the IR spectra, respectively, similar to II_a. The mass spectrum of II_a showed peaks at 289(M⁺ - C₆H₅NCO), 285(M⁺ - C₆H₅NS) and 214(M⁺ - (C₆H₅)₂C=C=O).

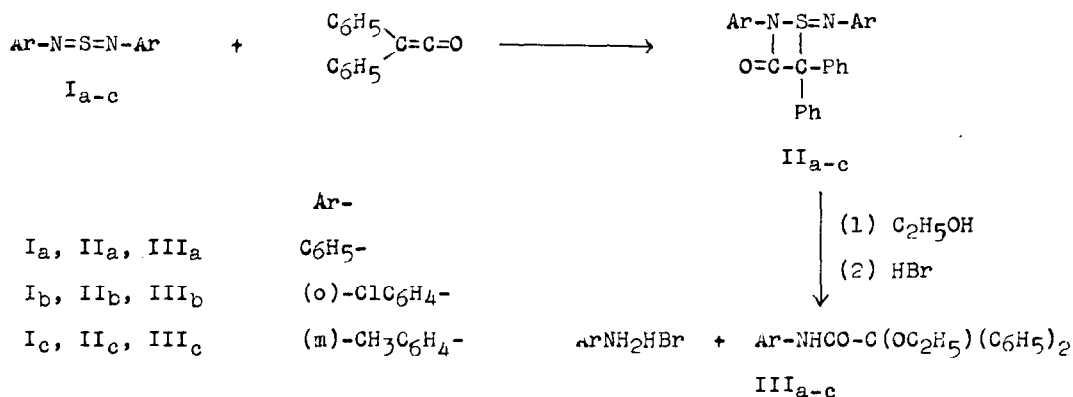
The solution of II_a (25 mmole) in 30 ml of 99% ethanol was refluxed for 16 hrs. in the presence of aqueous hydrobromic acid. After removal of ethanol, the residue was extracted with water and benzene. Aniline hydrobromide was isolated from the water solution.

The benzene-soluble substance was chromatographed over an activated alumina column. Benzene slution gave III_a (5.0g). Recrystallization of III_a from ethanol afforded white needles, m.p. 134°.

The mass spectrum of III_a showed the molecular peak M⁺ at 331 and peaks at

286(M⁺-C₂H₅O), 254(M⁺-C₆H₅), 211(M⁺-C₆H₅NHCO).

Scheme I



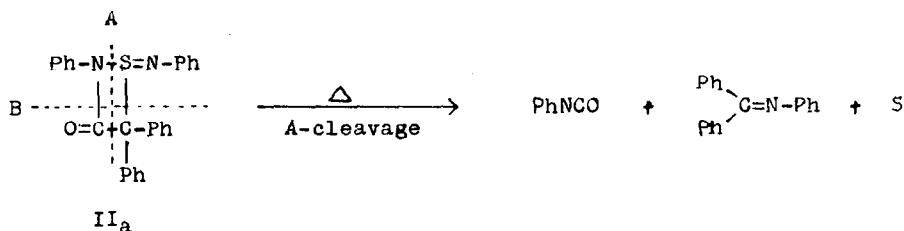
Further, IR and NMR spectra of III_a are shown in Table 2. On the basis of the elemental analyses and the spectroscopic data, the structure of 1-ethoxy-1,1-diphenylacetanilide was assigned to the compound III_a.

Similar treatment of II_b and II_c with aqueous hydrobromic acid in ethanol gave 1-ethoxy-1,1-diphenyl-(o)-chloro-acetanilide(III_b, 67%) and the corresponding anilide(III_c, 55.4%), respectively. The structural assignments for these compounds are based on elemental analyses, IR and NMR spectra (Table 2).

From these results, the structure of II is supported to be 1-imino-4,4-diphenyl-1,2-thiazetidine-3-one formed by 1,2-cycloaddition reaction of diaryl-sulfurdiimide with diphenylketene (Scheme I).

When II_a was pyrolyzed at 190° for 2hrs. in the reduced pressure, phenyl isocyanate was obtained in 39.6% yield.

Scheme II



The residue was chromatographed on an activated alumina column.

Benzophenoneanil, diphenyl acetanilide, azobenzene, benzophenone, sulfur, etc. were isolated.

These results are presented in Table 3.

The formation of phenyl isocyanate and benzophenoneanil seems to be rationalized in scheme II. However, the probable explanation for the formations of diphenylacetanilide, azobenzene and benzophenone is not apparent at present.

Further studies on the sulfurdiiimide-ketene cycloadducts will be published elsewhere.

TABLE 1

The ethanolysis reaction of diarylsulfurdiiimide-diphenylketene cycloadducts^a (II)

Starting materials	Conditions ^b time (hr.)	Products ^c (III)	
		m.p. (°C),	yields (%)
II _a	16	133.5-134.5	60.4
II _b	24	142.5-143.8	67.0
II _c	24	123.5-124.5	55.4

a) The ethanolysis reaction was carried out at the boiling point of ethanol.

b) 25 mmole of II / 30 ml of 99% ethanol / 3 ml of 47% aqueous hydrobromic acid.

c) The elemental analysis data of III are as follows.

III_a ; Calcd for C₂₂H₂₁O₂N : C, 79.73 ; H, 6.39 ; N, 4.23

Found : C, 79.53 ; H, 6.22 ; N, 4.32

III_b ; Calcd for C₂₂H₂₀O₂NCl : C, 72.22 ; H, 5.50 ; N, 3.82

Found : C, 72.16 ; H, 5.15 ; N, 3.79

III_c ; Calcd for C₂₃H₂₃O₂N : C, 79.97 ; H, 6.71 ; N, 4.06

Found : C, 79.31 ; H, 6.58 ; N, 4.02

TABLE 2
Spectroscopic data of ethanolysis products (III)

Compound	I.R.	NMR (CCl ₄)
III	ν nujol (cm ⁻¹)	Chemical Shift (p.p.m)
C ₆ H ₅ NHCOC(OC ₂ H ₅)(C ₆ H ₅) ₂ III _a	N-H (3320)	N-H 1.25 (broad) (1H)
	C=O (1675)	phenylring proton 2.4-3.1 (multiplet) (15H)
	C-O-C ₂ H ₅ (1075)	O- <u>CH₂-CH₃</u> <u>6.84</u> (quartet) (2H) <u>8.72</u> (triplet) (3H)
o-ClC ₆ H ₄ NHCOC(OC ₂ H ₅)(C ₆ H ₅) ₂ III _b	N-H (3360)	N-H 0.4 (broad) (1H)
	C=O (1700)	phenylring proton 2.5-3.2 (multiplet) (14H)
	C-O-C ₂ H ₅ (1065)	O- <u>CH₂-CH₃</u> <u>6.85</u> (quartet) (2H) <u>8.74</u> (triplet) (3H)
m-CH ₃ C ₆ H ₄ NHCOC(OC ₂ H ₅)(C ₆ H ₅) ₂ III _c	N-H (3360)	N-H 1.35 (broad) (1H)
	C=O (1685)	phenylring proton 2.5-3.4 (multiplet) (14H)
	C-O-C ₂ H ₅ (1075)	O- <u>CH₂-CH₃</u> <u>6.92</u> (quartet) (2H) <u>8.81</u> (triplet) (3H) (m)-CH ₃ 7.80 (singlet) (3H)

TABLE 3

The pyrolysis reaction of diphenylsulfurdiimide-diphenylketene cycloadduct (II_a)

Products ^a (%)					
C ₆ H ₅ NCO	C ₆ H ₅ N=C(C ₆ H ₅) ₂	C ₆ H ₅ N=NC ₆ H ₅	C ₆ H ₅ NHCOCH(C ₆ H ₅) ₂	(C ₆ H ₅) ₂ CO	S
39.6	1.8	23.8	4.7	9.6	5.4

a) Yields based on the mole ratio of product to starting material.

REFERENCES

- 1) H. Ulrich, Cycloaddition Reactions of Heterocumulenes, p. 18. Academic Press, New York (1967).
- 2) T. Minami, Y. Ohshiro, T. Agawa, et al, Tetrahedron Letters, 3049 (1968).