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THE CHEMISTRY OF CUMULATED DOUBLE BOND COMPOUND VI
THE REACTION OF DIPHENYLKETENE WITH THIIRANES

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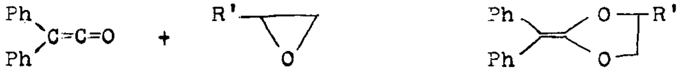
The cycloaddition of epoxide to diphenylketene was studied by K. Gulbins and his co-workers (1). The epoxy group attacked C=O bond, and the acetals were obtained.



In this report, reactions of diphenylketene with thiiranes were studied and the structure of products were discussed.

The mixture of 10 g of diphenylketene, 7 g of stylenesulfide and 0.1 g of LiCl (catalyst) was heated at 160°C for 2 hr. and the reaction mixture was chromatographed over activated alumina with benzene.

Small amount of 2,2,3-triphenyl cyclobutanone-1 was isolated as a byproduct (m.p.: 140.0-140.5°C, IR: 1770 cm^{-1} (C=O), nmr: 2.3-3.3$_\tau$(Ph-), 5.5$_\tau$(CH), 6.6$_\tau$(CH_2)).

Following data were obtained for the main product.

Molecular weight (V.P.O. method) : 33o (calc'd value for equimolar adduct of ketene and thiirane : 330.3)

Elemental analysis : observed value

C 79.98% H 5.44% S 9.46%

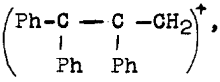
calc'd value for $C_{22}H_{18}OS$

C 79.90% H 5.49% S 9.70%

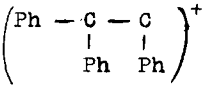
IR : 1720 cm^{-1} (C=O), no absorption in C=C region 1500-1700cm^{-1}

Nmr : 2.7-2.9τ(Ph), 5.4τ(CH), 6.9τ(CH_2)

Mass spectrum : m/e 270



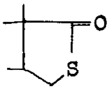
$\left(\mathrm{Ph{-}\underset{Ph}{C}{-}\underset{Ph}{C}{-}CH_2}\right)^+$, m/e 255



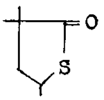
$\left(\mathrm{Ph{-}\underset{Ph}{C}{-}\underset{Ph}{C}}\right)^+$

m.p. : 202-203°C

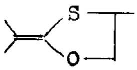
The molecular weight and elemental analysis indicated an equimolar adduct of diphenylketene and stylene sulfide, and four structures were considered.



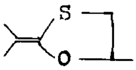
I



II



III

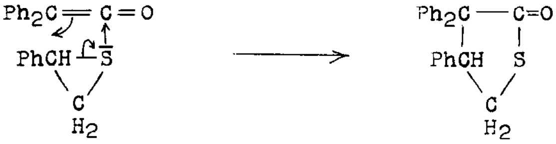


IV

IR spectrum denied III and IV (similar to the reaction of stylene oxide).

For I and II, some differences will be expected in the spectra of nmr and mass spectrometry.

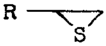
In conclusion, the presented results supported that the main product was α,α,β-triphenyl-γ-thiolactone (I).



The abnormal addition of thiirane to C=C bond of ketene was recognized and some differences for the reaction of epoxide were clarified.

In the case of Et_3N-catalyst in stead of LiCl, γ-thiolactone was not obtained, but ketene dimer and polymeric material were produced.

In the reactions of diphenylketene with 3-chloropropylene-, 3-ethoxypropylene- or ethylene-sulfide, γ-thiolactone was not isolated, but polymeric materials were produced only. It may be due to the unstability of thiiranes during heating. The results were shown in the table.

No.		mole ratio (ketene/sulfide)	reaction temp. °C	reaction time hr	yield of γ-thiolactone	yield of cyclobutanone
1	Ph-	1.0	160	2	20%	2-3%
2a)	Ph-	1.0	160	2	13	2-3
3	$ClCH_2$-	1.0	100	10	0b)	0
4	$EtOCH_2$-	1.0	150	5	0b)	0
5	H-	0.2	160	-	0b)	0

Diphenylketene was prepared from diphenyl acetylchloride and triethylamine.

Thiiranes were prepared from corresponding epoxides and KSCN (2). LiCl was used as a catalyst.

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a) Without catalyst.

b) Large amount of polymeric materials were obtained.

REFERENCES

1) K. Gulbins et al, *Ber.*, **94**, 3287 (1961)

2) C.O. Guss & D.L. Chamberlain, *J. Am. Chem. Soc.*, **74**, 1342 (1952)