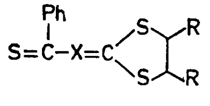
Cycloaddition Reactions of *N*-Thioacyl Dithioimidocarbonates

By RENJI OKAZAKI, MASAHARU O-OKA, and NAOKI INAMOTO*

(*Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo* 113, *Japan*)

Summary *N*-Thioacyl dithioimidocarbonates undergo 1,2- and 1,4-cycloaddition reactions with active olefins, diphenylketen, and diphenyldiazomethane; the products obtained with the latter two reagents differ from those obtained in the reactions with a related conjugated system, thioacylketen thioacetal.

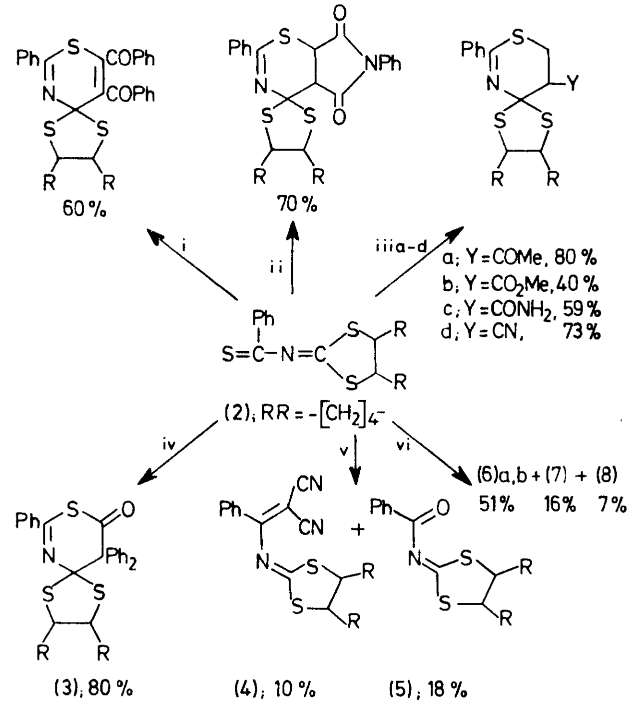
WE have previously reported 1,2- and 1,4-cycloadditions of thioacylketen thioacetals (**1**).[1] Recent articles concerning



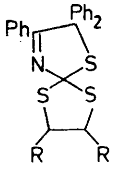
(**1**); X = CH
(**2**); X = N

the reactions of *N*-(perfluoroisopropylidene)thiocarboxamide[2] and *N*-thioaroylformamidine[3] prompted us to report our preliminary results on a similar conjugated system, the *N*-thioacyldithioimidocarbonate (**2**).

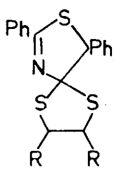
We have found that compound (**2**; RR = $-[CH_2]_4-$)[4] also undergoes 1,2- and 1,4-cycloadditions but that some of the products are of a different type to those formed from (**1**) (Scheme).[5] In reactions (i)—(iii), compound (**2**) gave adducts similar to those obtained with (**1**),[1] although (**2**) requires more severe conditions. Formation of the 1,4-cycloaddition product (**3**) in reaction (iv) is in contrast with the reaction of (**1**) under comparable conditions which leads to a vinylketen thioacetal (**9**)[6] *via* 1,2-cycloaddition to the thiocarbonyl bond followed by elimination of COS. A similar preference of compound (**2**) for 1,4- over 1,2-cycloaddition was also observed in the reaction with diphenyldiazomethane; (**1**) gave the corresponding episulphide (**10**),[1] whereas (**2**) afforded mainly the 1,4-addition product (**6**) together with (**7**) and (**8**) as minor products. The most likely pathways to (**6**)—(**8**) would be rearrangement or fragmentation of (**10**) as indicated [(**6**) *via* path a, (**7**) *via* path b, and (**8**) *via* paths a and c]. It is interesting to note that path a is favoured over path b.



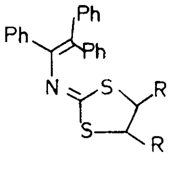
SCHEME. i; Dibenzoylacetylene in C_6H_6, reflux, 9·5 h. ii; *N*-Phenylmaleimide in C_6H_6, reflux, 58 h. iii; (a) Methyl vinyl ketone, (b) methyl acrylate, (c) acrylamide, and (d) acrylonitrile, all in xylene, 140 °C, 24 h. iv; Diphenylketen in dimethylformamide, room temp., 2 days. v; Tetracyanoethylene in MeCN, reflux, 28 h. vi; Diphenyldiazomethane in C_6H_6, room temp., 5 days: compounds (**6a**) (43%) and (**6b**) (8%) are isomers, isolable by t.l.c., in which the cyclohexane ring is directed either towards N-3 or S-1, although it has not been determined which is which.



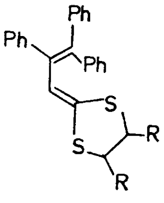
(**6**)



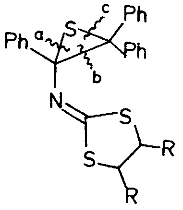
(**7**)



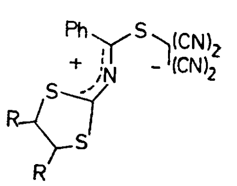
(**8**)



(**9**)



(**10**)



(**11**)

The formation of (**4**) and (**5**) can be explained in terms of the intermediacy of the zwitterion (**11**); 1,2-addition followed by elimination of $(CN)_2C{=}S$[7] would give (**4**) and hydrolysis by adventitious water in the solvent would lead to (**5**).

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