# NOVEL REACTIONS OF CYCLIC SULFUR YLIDE, 1-CYANO-2-METHYL-3,4-DIHYDRO-2-THIANAPHTHALENE

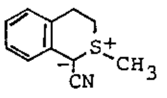
Mikio Hori, Tadashi Kataoka, Hiroshi Shimizu, Masahiro Kataoka,
and Megumi Ikemori
Gifu Pharmaceutical University, 5-6-1 Mitahora-higashi, Gifu 502, Japan

Thermal reactions of 1-cyano-2-methyl-3,4-dihydro-2-thianaphthalene (1) gave 1-cyano-1-methylisothiochroman (2)(39.0%) together with dimers (3a, 10.8%, 3b, 4.6%) in benzene, and 2(8.6%), 3a (31.6%) and 3b (22.6%) in acetonitrile. Geometry of the dimers (3) was determined by the IR and Raman spectroscopy. The dimers (3) were easily formed by the reaction of 1 with 1/15 eq. tetracyanoethylene in benzene at room temperature. Charge transfer interaction would participate in dimerization of 1.

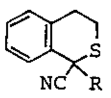
Refluxing the ylide (1) with acetic acid in dichloromethane gave 1-cyanoisothiochroman (4)(37.6%) and a ring-opened product (5)(34.7%), whereas the thermal reaction in benzene afforded 5 (50.0%) and a spiro-compound (6)(33.2%). Interestingly, thermal reaction of 1 with p-toluenesulfonic acid gave 4 (39.6%), methyl p-toluenesulfonate (21.4%), 3a (5.5%) and a ring-opened tosylate (7)(20.7%).

Benzenesulfonic acid and methanesulfonic acid reacted similarly. The tosylate (7) was reduced with sodium cyanoborohydride to ethylbenzene derivative (8).

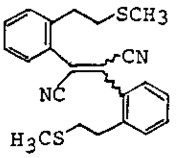
Thermal reactions of 1 with phenol or succinimide in benzene afforded the spiro-compound (6)(69.9% or 85.2%), whereas the reaction with thiophenol gave a ring-opened product (9)(68.0%).



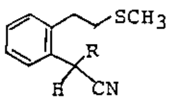
1



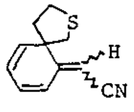
2:R=CH$_3$
4:R=H



3a=E; 3b=Z



5:R=OAc
9:R=SPh



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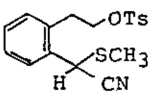

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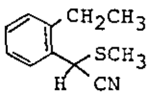

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