Tetrahedron Letters No. 26, pp. 2421-2424, 1971. Pergamon Press. Printed in Great Britain.

PHOTOCYCLOADDITION OF THIOCARBONYL COMPOUNDS TO MULTIPLE BONDS. VIII. THE REACTION OF THIOBENZOPHENONE WITH IMINES

A. Ohno, N. Kito, and T. Koizumi

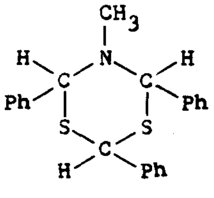
Sagami Chemical Research Center
3100 Ohnuma, Sagamihara-shi, Kanagawa, 229, Japan

(Received in Japan 17 May 1971; received in UK for publication 25 May 1971)

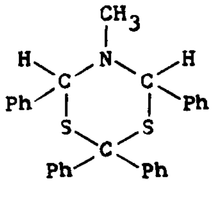
In previous papers of the series, we have reported that photocycloaddition takes place when thiobenzophenone is irradiated with light in the presence of an olefin or acetylene (1). In order to extend the scope of the reaction, it will be interesting to study whether thiobenzophenone reacts with carbon-heteroatom multiple bonds.

In this communication, we wish to report photocycloaddition of thiobenzophenone to carbon-nitrogen double bond of imines. So far we know, no claim has been reported on analogous reactions with ketones (2).

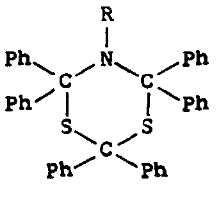
A mixture of thiobenzophenone in benzaldehyde N-methylimine was irradiated under an atmosphere of argon with light of 3150 Å from a 450W high-pressure mercury lamp. After decolorization of thiobenzophenone, the mixture was fractionated with column chromatography on silica gel affording colorless crystals of I, II, and benzophenone in 48, 19, and 31 % yield, respectively, along with



I



II



$(R = H, CH_3)$

IV

sulfur-containing red oil, the structure of which is not yet known. The same reaction proceeds when the mixture is irradiated with light of 5890 Å from eight 60W sodium lamps that are arranged in merry-go-round style. It has been confirmed that benzophenone comes from benzophenone N-methylimine, III, by catalytic hydrolysis on silica gel: an nmr spectrum of the reaction mixture shows an intence signal at δ ($CDCl_3$, TMS) 3.23 due to methyl protons in III; III can be isolated by direct distillation of the reaction mixture; quantitative amount of benzophenone is eluted when III is subjected to column chromatography on silica gel; there is no carbonyl signal in the ir spectrum of the reaction mixture.

Structures of I and II have been elucidated by the following evidence (3):

I. mp 178 - 9° (decomp changing color to red): nmr δ ($CDCl_3$, TMS) 2.04 (s, 3H), 5.48 (s, 1H), 5.95 (s, 2H), and 7.20 - 8.20 (m, 15H): mass (m/e) 363 (M^+), 241, 209, 194, 180, and 121.

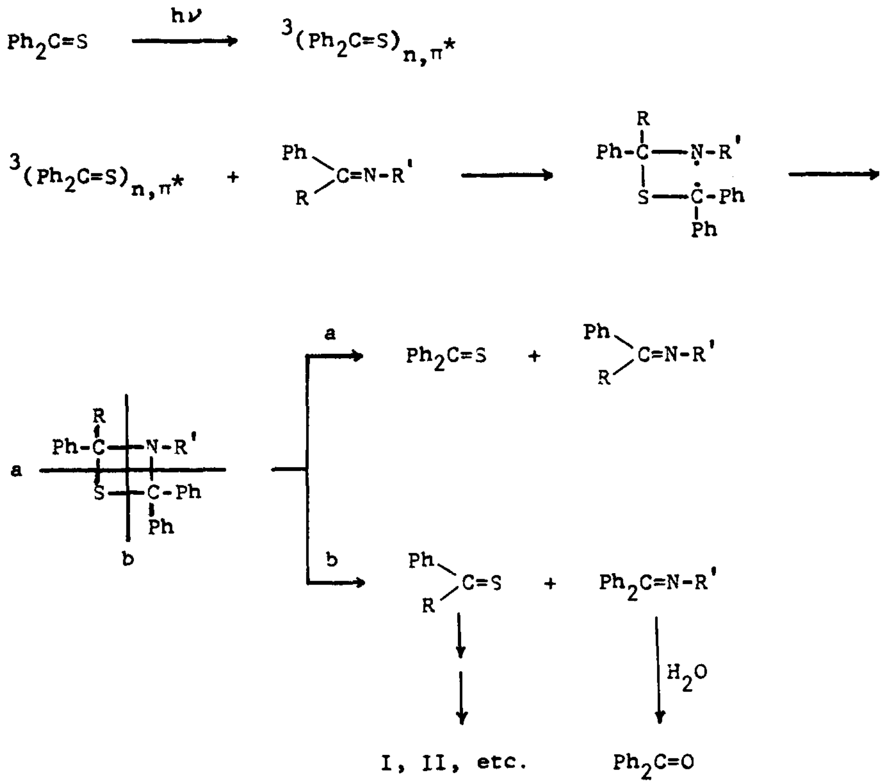
Reductive desulfurization of I with Raney Ni (W-2) resulted in the formation of toluene (18 %), stilbene (18 %), dibenzyl sulfide (6 %), dibenzyl methylamine (6 %), and benzaldehyde N-methylimine (6 %).

II. mp 158 - 60° (decomp changing color to blue): nmr δ ($CDCl_3$, TMS) 2.09 (s, 3H), 5.66 (s, 2H), and 7.20 - 8.19 (m, 20H): mass (m/e) 320 (M^+ - $PhCH{=}NCH_3$), 288, 276, 241, 198, and 121.

Treatment of II with Raney Ni afforded diphenylmethane (4 %), stilbene (19 %), 1,2-diphenylethane (3 %), 1,1,2,2-tetraphenylethane (13 %), and benzaldehyde N-methylimine (28 %).

Thiobenzophenone also undergo photocycloaddition with benzophenone imine or benzophenone N-methylimine on irradiation with light of 3150 Å yielding IV in 7 or 10 % yield, respectively. However, light of 5890 Å is not practically effective to this reaction probably because of low quantum efficiency (4) and low intensity of the light.

Since light of 5890 Å is effective to the photocycloaddition, it is obvious that thiobenzophenone of n,π^* state (probably in triplet) is involved in the reaction (1a, 5). Then, the following mechanism seems to be most plausible.



When R is a phenyl group, both decomposition processes result in the formation of starting materials. Then, high steady-state concentration of the intermediate might be required in order to produce the product IV. On the other hand, since thioaldehyde is a quite reactive compound, it undergoes further reactions spontaneously producing I, II, and polymerized compounds. In this connection, it will be noteworthy that a 1 : 1 mixture of thiobenzophenone and benzaldehyde N-methylimine in tetrahydrofuran (1 mol/l) affords only III as an isolable product. This supports the above mechanism, since it is reasonably expected that thioaldehyde can find its counterpart with difficulty in such a diluted solution.

The research is in progress toward the end to isolate the four-membered ring intermediate and to prove the formation of thioaldehyde.

REFERENCES

(1) (a) A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *J. Amer. Chem. Soc.*, **91**, 5038 (1969); (b) A. Ohno, T. Koizumi, and Y. Ohnishi, Bull. Chem. Soc. Jap., in press; (c) A. Ohno, T. Koizumi, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron* Lett., 2025 (1970).

(2) Ketones abstract a hydrogen either from solvent or imine itself affording a dihydro dimer of the imine or corresponding nitrile, respectively. See (a) A. Padwa, W. Bergmark, and D. Pashayan, *J. Amer. Chem. Soc.*, **91**, 2653 (1969); (b) H. Ohta and K. Tokumaru, Abstracts, 24th National Meeting of the Chemical Society of Japan, Suita, Osaka, Aprile 1971, p 1367 (in Japanese).

(3) Elemental analyses gave satisfactory results.

(4) Absorption coefficients of thiobenzophenone at λ_{max} of 316.5 and 599 nm are 15,800 and 181, respectively: O. Korver, J. U. Veenland, and Th. J. de Boer, *Rec. Trav. Chim. Pays-Bas*, **84**, 289 (1965).

(5) A. Ohno, Y. Ohnishi, M. Fukuyama, and G. Tsuchihashi, *J. Amer. Chem. Soc.*, **90**, 7038 (1968).