CHEMISTRY LETTERS, pp. 355-356, 1973. Published by the Chemical Society of Japan

ADDITION REACTION OF THIOL TO OLEFIN BY THE USE OF $TiCl_4$

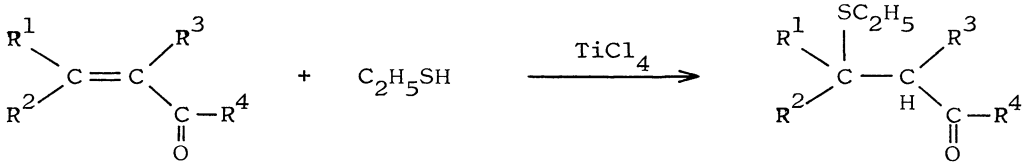
Teruaki MUKAIYAMA, Toshio IZAWA, Kazuhiko SAIGO, and Hisashi TAKEI
Laboratory of Organic Chemistry, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo

It was established that, in the presence of $TiCl_4$, α,β-unsaturated carbonyl compounds react with ethanethiol at room temperature to afford the addition products, 3-ethylthiocarbonyl compounds, in good yields.

As part of our continuing studies[1] on the exploration of useful synthetic reactions by using $TiCl_4$, the addition reaction of active hydrogen compounds with α,β-unsaturated carbonyl compounds in the presence of $TiCl_4$ was investigated. Relatively little work has been reported on the addition of thiols to α,β-unsaturated carbonyl compounds under an acidic condition expect for the case of using HCl.[2]

In a typical experiment, a solution of methyl acrylate (0.861 g, 10 mmol) in 20 ml of dichloromethane was added drop by drop into a stirred solution of ethanethiol (1.24 g, 20 mmol) and $TiCl_4$ (1.90 g, 10 mmol) in 30 ml of dichloromathane at room temperature under an argon atmosphere, and the reaction mixture was stirred for an additional 24 hr. Usual work-up and distillation afforded methyl 3-ethylthiopropionate in 94% yield (1.39 g), bp 98°C/26 mmHg.

In a similar manner, the addition reactions of ethanethiol to α,β-unsaturated carbonyl compounds in the presence of $TiCl_4$ afforded 3-ethylthiocarbonyl compounds in good yields. On the other hand, in the case of the reaction of methyl crotonate or dimethyl fumarate, with ethanethiol, it was found that the yields were very low under the similar condition. This problem was overcome by carrying out the above mentioned reaction in highly concentrated solution, and the addition products were obtained in good yields.

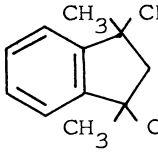


Olefin R^1	R^2	R^3	R^4	Conditions Temp.	Time	Product Yield(%)	Bp(^oC/mmHg)
H	H	H	OCH_3	r.t.	24 hr	94	98/26
H	H	CH_3	OCH_3	r.t.	24	87	103/28
CH_3	H	H	OCH_3	r.t.	22	75[a]	101-103/29
H	CH_3OOC	H	OCH_3	r.t.	24	94	94-95/1.6
CH_3OOC	H	H	OCH_3	r.t.	48	74[a]	125-127/10
CH_3	CH_3	H	CH_3	-50^{o}C-r.t.	2.5	66[b]	97-99/15

a) The total valume of dichloromethane is 15 ml.

b) $[Olefin]/[C_2H_5SH] = 1$

Next, the reactions of olefins, having no electron withdrawing group, with ethanethiol in the presence of $TiCl_4$ were investigated. When α-methylstyrene was allowed to react with ethanethiol at 0^{o}C, 2-phenyl-2-ethylthiopropane resulted only in 18% yield and 1,1,3-trimethyl-3-phenylindane, i.e., dimer of α-methylstyrene, was obtained predominantly. However, the yield of the addition product was increased by the choice of suitable solvents such as cyclohexane or benzene.

Olefin	Solvent	Conditions Temp.	Time	Addition product [Bp(^{o}C/mmHg)]	Yield(%)	Another product [Bp(^{o}C/mmHg)]	Yield(%)
$C_6H_5C(CH_3)=CH_2$	CH_2Cl_2	0^{o}C-r.t.	1 day	$C_6H_5C(CH_3)_2SC_2H_5$	18		78
	CH_2Cl_2	r.t.	1		69		18
	C_6H_{12}	r.t.	1		99		0
	C_6H_6	r.t.	1	[67/1.2]	96		0
$C_6H_5CH=CH_2$	CH_2Cl_2	r.t.	1	$C_6H_5CH(SC_2H_5)CH_3$	65	[117-118/1.4]	–
$C_2H_5OCH=CH_2$	CH_2Cl_2	r.t.	1	$C_2H_5OCH(SC_2H_5)CH_3$	62		–

In conclution, it is noted that $TiCl_4$ is effectively used for the addition reaction of ethanethiol to various olefins under mild condition.

REFERENCES

1) T. Mukaiyama, K. Kamio, S. Kobayashi, and H. Takei, Bull. Chem. Soc. Japan, 45, 3723 (1972); T. Mukaiyama, T. Imamoto, and S. Kobayashi, Chem. Lett., (1972), in press; T. Mukaiyama, M. Hayashi, and K. Narasaka, ibid., (1972), in press; T. Mukaiyama and K. Saigo, J. Amer. Chem. Soc., submitted for publication; T. Mukaiyama, K. Kamio, S. Kobayashi, and H. Takei, Chem. Lett., submitted for publication.

2) T. Posner, Ber., 40, 4788 (1907); C. D. Hurd and L. L. Gershbein, J. Amer. Chem. Soc., 69, 2328 (1947); K. L. Mallik and M. N. Das, Z. Phys. Chem. (Frankfurt), 41, 33 (1964).

(Received February 9, 1973)