Communications to the Editor

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A CONVENIENT METHOD FOR THE PREPARATION OF CARBOXYLIC ESTERS

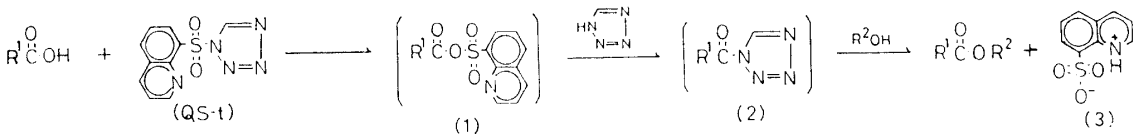
Hiroshi Takaku,* Naohiko Sasaki, and Kazuhiro Morita
Laboratory of Organic Chemistry, Chiba Institute of Technology, Narashino-shi, Chiba 275, Japan

8-Quinolinesulfonyl tetrazolide (QS-t) was found to be a useful coupling agent for the preparation of carboxylic esters.

KEYWORDS——esterification; carboxylic esters; coupling agent; coupling reaction; base; alcohols; carboxylic acids

Carboxylic esters were synthesized from free alcohols and carboxylic acids by using p-toluenesulfonyl chloride,[1] N,N'-dicyclohexylcarbodiimide,[2] dipyridyl disulfide and triphenylphosphine,[3] trifuloroacetic anhydride,[4] diethyl phosphorocyanide,[5] 2-haropyridinium salt,[6] 2,4,6-trichlorobenzoyl chloride.[7] The esterification of alcohol is an important reaction for the synthesis of macrolides. Recently, we found that 8-quinolinesulfonyl tetrazolide (QS-t) was effectively used as a coupling agent for the synthesis of internucleotidic bonds by the phosphotriester approach.[8] In this communication, we wish to report a convenient and practical method for the preparation of carboxylic esters from alcohols and carboxylic acids by using QS-t as a coupling agent.

The reaction is carried out with equivalent amounts of carboxylic acid and alcohol, and coupling agent[9] (QS-t). A typical procedure is as follows: QS-t (420 mg, 1.7 mmol) was added to a mixture of benzoic acid (210 mg, 1.7 mmol), benzyl alcohol (0.17 ml, 1.7 mmol), and triethylamine (0.24 ml, 1.7 mmol) in dry methylene chloride at 0°C. The reaction mixture was gradually warmed to room temperature and stirred for 1 h. The 8-quinolinesulfonic acid was removed by filtration. The filtrate was quenched with ice-water and then methylene chloride was added. The methylene chloride layer was washed with 5% sodium bicarbonate solution and water, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness under reduced pressure. The residue was separated by silica gel column chromatography, and benzyl benzonate was isolated in 310 mg (89%). Similary, various esters were prepared in good yields as summarized in Table I.



The procedure is very effective in the esterification of sterically hindered

Table I. Preparation of Carboxylic Esters from Carboxylic Acids and Alcohols with 8-Quinolinesulfonyl tetrazolide (QS-t)

Run	Acid R^1	Alcohol R^2	Isolated yield[10] (%)	Run	Acid R^1	Alcohol R^2	Isolated yield[10] (%)
1	C_6H_5	$C_6H_5CH_2$	85[a]	7	C_6H_5	$(CH_3)_3C$	82
2	C_6H_5	$C_6H_5CH_2$	89	8	$(CH_3)_2CH$	$C_6H_5CH_2$	84
3	C_6H_5	$C_6H_5CH_2$	0[b]	9	$(CH_3)_3C$	$C_6H_5CH_2$	79
4	C_6H_5	$C_6H_5CH_2$	93[c]	10	C_6H_5	C_6H_5	90
5	C_6H_5	$(CH_3)_2CHCH_2$	74	11	CH_3	$C_6H_5CH_2$	86
6	$C_6H_5CH=CH$	$C_6H_5CH_2$	87				

a) Collidine was used in place of triethylamine.
b) In this case, tertiary amine was absent.
c) 1.5 Molar equiv. of QS-t was used.

alcohols or carboxylic acids as can be seen in runs 5, 7, and 9. Furthermore 8-quinolinesulfonic acid produced in the process of the reaction forms a neutral inner salt and separated as precipitates from the reaction mixture.

The mechamism is illustrated in scheme. The mixed anhydride (1) is produced very rapidly by a nucleophilic attack of the carboxylate on QS-t. This intermediate further reacts with tetrazole to afford an acyltetrazole (2), which in turn converted into the corresponding carboxylic ester and the acid (3).

REFERENCES AND NOTES

1) J.H. Brewster and C.J. Ciotti,Jr., J.Amer.Chem.Soc., 77,6214(1955).
2) S. Neelakuntan, R. Padmasani, and T.R. Seshadri, Tetrahedron, 21,3531(1965).
3) T. Mukaiyama, R. Mastueda, and M. Suzuki, Tetrahedron Lett., 1970,1901; E.J. Corey and K.C. Nicolaou, J.Amer.Chem.Soc., 96,5614(1974).
4) R.C. Parish and L.M. Stock, Tetrahedron Lett., 1964,1285; idem, J.Org.Chem., 30,927(1965).
5) T. Shioiri, Y. Yokoyama, Y. Kasai, and S. Yamada, Tetrahedron, 32,2211,2854 (1976).
6) T. Mukaiyama, T. Usui, E. Shimada, and K. Saigo, Chemistry Lett., 1975,1045.
7) R.C. Fuson, J.W. Bertetti, and W.E. Ross, J.Amer.Chem.Soc., 54, 4380(1932); J. Inanaga, K. Hirata, H. Saeki, T.Katsuki, and M.Yamaguchi, Bull.Chem.Soc. Jpn., 52,1989(1979).
8) H. Takaku, M. Yoshida, and T. Hata, Nucleic Acids Res.Spec.Publ., No.6,s181 (1979); H. Takaku, and M. Yoshida, J.Org.Chem., 45,3347(1981); 8-Quinolinesulfonyl tetrazolide (QS-t) was decomposed on storage within 4 days.
9) When 8-quinolinesulfonyl chloride (QS) (of H. Takaku, M. Kato, and S. Ishikawa, J.Org.Chem., 46,4062(1981) and referendes cited therein) was used in place of QS-t, carboxylic esters was obtained in 17-77% yields along with acid anhydrides as a by-product. From these results, QS is unsuitable as a coupling agent for the preparation of carboxylic esters.
10) All compounds exhibited IR and NMR spectra in agreement with the assigned structure.

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