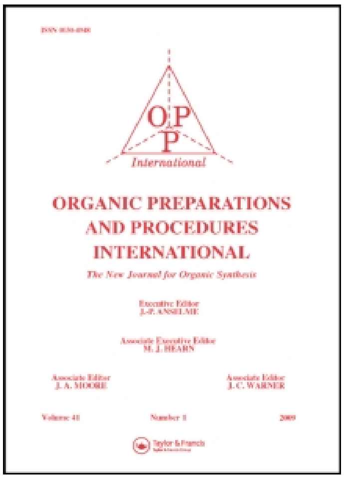

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SYNTHESIS OF PHENACYL ESTERS *via* POLYMER SUPPORTED REAGENTS

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OPPI BRIEFS

SYNTHESIS OF PHENACYL ESTERS *via* POLYMER SUPPORTED REAGENTS

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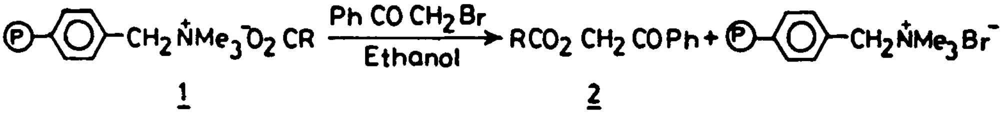
Reagents supported on insoluble polymers have found wide applications in organic synthesis.[1] In view of the importance of phenacyl esters as a protective group,[2] a simple and efficient route is now reported for the preparation of these esters in quantitative yield and purity under mild conditions. This method is inexpensive as the resin may be used repeatedly, because it can be regenerated to its initial activity by treatment with a solution of hydrochloric acid.



Hendrickson and Kandall had reported earlier that phenacyl esters can be synthesized according to traditional methods[3] which can be plagued by slow reaction times,[3] by hydrolysis of the alkylating agents,[4] by low yields of products and by contamination of products with starting alkylating reagents. Durst[5] overcame some of these problems by carrying out the reaction with the potassium salt of the acid in the presence of dicyclohexyl-18-crown-6 under reflux while Clark and Miller[6] utilized potassium fluoride in glacial acetic acid for the preparation of phenacyl esters.

EXPERIMENTAL SECTION

Polymer Supported Carboxylate Anion (1). General Procedure.- Commercial strongly basic anion exchange resin (5 g) in the chloride form [Amberlite IRA-400 (Cl^-)] packed in a column was washed with 0.25 N aqueous sodium salt of carboxylic acid (prepared by dissolving 25 mmoles of carboxylic acid in 100 ml 0.25 N NaOH) until complete removal of chloride ion, confirmed by silver nitrate test. The resin was then successively washed with water and ethanol until the excess of carboxylic acid anion is removed, which is tested by acidification with dilute hydrochloric acid. The excess of carboxylate anion which is not bounded to the resin can be used for the next batch or the acid can be recovered by acidification. The resin was finally dried in *vacuo* at 50° over P_2O_5 for 10 hrs. The exchange capacity is determined by passing aqueous 1 M sodium chloride solution (100 ml) through the resin (0.3 g) in a column. The amount of carboxylate anion in the eluent is titrated with 0.01 N hydrochloric acid using methyl orange as an indicator.

Phenacyl Esters (2) of Carboxylic Acids. General Procedure.- The Amberlite IRA-400 carboxylate resin (5 g; capacity 1 mmole carboxylic acid anion/gm of dry resin) was placed in a flask and phenacyl bromide (5.0 mmoles) in ethanol was added and the mixture was then stirred at room temperature. The progress of the reaction was monitored by the disappearance of phenacyl bromide on tlc plates. After completion of the reaction, the resin was filtered off and the filtrate slowly distilled under reduced pressure to remove the solvent. Distillation of the solvent furnished the essentially pure phenacyl ester in quantitative yield. The products were characterized by NMR, IR and comparison with authentic samples. The used resin in the bromide form can be used as such; however the chloride form of the resin was used in order to obtain standard comparative data.

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TABLE. Phenacyl Esters

Acid	Time (hrs)	Yield (%)	mp. (lit.) (°C)
Benzoic	2	99	118 (119-120)[7]
Salicylic[a]	1	97	109 (106-108)[8]
Benzilic	9	98	123 (121-125)[8]
2-Methoxybenzoic	5	97	62 (62)[6]
Palmitic	12	96	49 (52)[9]
4-*t*-Butylbenzoic	7	99	71 (71)[6]
Acetic	2	98	50 (51-52)[7]
Propionic	2.5	97	26 (26)[6]
Mesitoic	10	98	81 (80-81)[10]

a) The sodium salt was prepared by using sodium bicarbonate solution.

REFERENCES

1. a) C. C. Lenzoff, Chem. Soc. Rev., 3, 65 (1974).
   b) A. McKillop and D. W. Young, Synthesis, 401, 481 (1979).
   c) A. Akelah and D. C. Sherrington, Chem. Rev., 81, 557 (1981).

2. J. B. Hendrickson and C. Kandall, Tetrahedron Lett., 343 (1970).

3. R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 5th Ed., John Wiley and Sons, Inc., New York, NY (1964), p. 235; N. D. Cheronis, J. B. Entrikin and E. M. Hodnett, "Semimicro Qualitative Organic Analysis", 3rd Ed., Interscience, New York, NY (1965).

4. Kubota and Matsuura, J. Inst. Polytech. Osaka, 1, 49 (1950); Chem. Abs., 46, 2011d (1952).

5. H. D. Durst, Tetrahedron Lett., 2421 (1974).

6. J. H. Clark and J. M. Miller, ibid., 599 (1977).
7. P. N. Giraldi, Farmaco (Pavia) Ed. Sci., 14, 90 (1959); Chem. Abs., 54, 3299 (1960).

8. W. T. Moreland, J. Org. Chem., 21, 820 (1956).

9. J. B. Rather and E. Emmet, J. Am. Chem. Soc., 21, 75 (1919).

10. G. Berti, F. Bottari and B. Macchia, Ann. Chim., 52, 1101 (1962); Chem. Abs., 59, 3818e (1963).