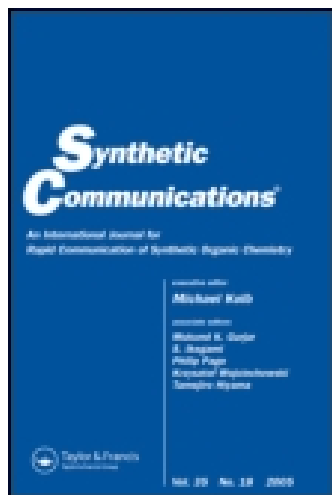


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A Convenient Preparation of Diazo Carbonyl Compounds Under Tri-Phase Phase-Transfer Catalysis Conditions

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A CONVENIENT PREPARATION OF DIAZO CARBONYL COMPOUNDS
UNDER TRI-PHASE PHASE-TRANSFER CATALYSIS CONDITIONS

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ABSTRACT : A simple and convenient one-pot preparation method for pure diazo carbonyl compounds under tri-phase phase-transfer catalysis conditions is described.

The transformation of an active methylene group adjacent to one or more electron withdrawing groups into the corresponding diazo derivative is a well established and widely used synthetic application¹. The most commonly used reagent for base catalysed diazo transfer reactions has been p-toluenesulphonyl (tosyl) azide². However, difficulties have been reported in the separation of the desired product from excess reagent and p-toluenesulphonamide following diazo transfer with tosyl azide³. The other diazo transfer reagents such as 2-azido-3-ethylbenzthiazolium tetrafluoroborate (Ballis reagent)⁴, polymer bound tosyl azide⁵, 4-carboxylbenzenesulphonyl azide⁶, and N,N-dimethylazido

chloromethyleniminium chloride⁷ also have been reported in the literature. These reagents have drawbacks in that undesirable side reactions such as ester amidation⁸, azo coupling⁹, or azide formation¹⁰ can compete with the diazo transfer reaction. Further, the high cost and complicated preparation methods involving less common starting materials make these reagents unattractive. A more recent report¹¹ claims that the acidic methylene compounds can be conveniently converted into diazo compounds in high yields making use of the reagent azidotris (diethylamino) phosphonium bromide.

In addition to the development of various diazo transfer reagents, several alternative preparation methods have been developed to circumvent the separation problems involved in the diazo product separation from the reaction mixture. Leydon¹² has shown that by conducting the reaction in two-phase system under phase transfer catalytic conditions, the isolation procedure is greatly simplified, since the organic layer contains only the diazo compound and traces of the quaternary ammonium salts. Recently Taber et.al¹³ have shown that methanesulphoyl (mesyl) azide is a generally superior reagent for diazo transfer compared to tosyl azide. Easy separation from the desired product and its low cost makes mesyl azide the better choice. However, due to its potentially explosive nature mesyl azide has to be handled with care¹⁴.

In our earlier communication¹⁵, we have reported the convenient preparation of sulphonyl azide under solid-solid-liquid tri-phase catalytic conditions, involving a polymer supported PTC catalyst and sodium azide powder in a relatively non-polar solvent like dichloroethane. The present communication reports the convenient preparation of mesyl azide and its subsequent utilisation in diazo transfer reaction in a single-pot under tri phase phase-transfer catalytic conditions.

The present simplified method eliminates the handling of potentially explosive mesyl azide and facilitates the preparation of pure diazo carbonyl compounds with improved yields. Easy isolation, and purification are the other advantages. In a conventional two-phase phase-transfer system, where in a soluble phase-transfer catalyst like quaternary ammonium salt is used removal of the traces of the catalyst after the reaction is always a problem. In tri-phase catalytic system, the catalyst can be separated by simple filtration and no traces of the catalyst are present in the product. Moreover, the catalyst can be reused in a minimum of five further preparative runs without significant loss in activity.

EXPERIMENTAL

Commercially available samples of active methylene carbonyl compounds (4) and methanesulphonyl chloride (1) (Fluka and

SCHEME A

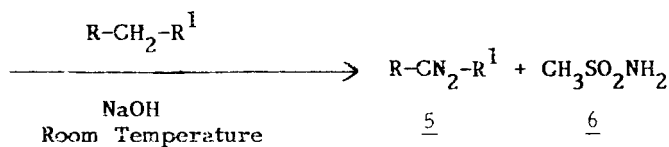
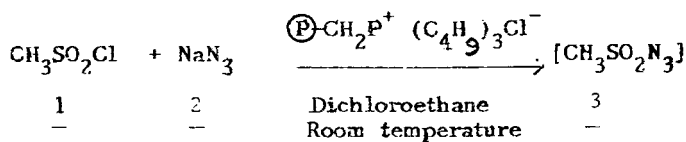


TABLE : Diazo carbonyl compounds (5) prepared

5	R	R ¹	Strength of NaOH	Time (h)	Yield (%)
a.	CH ₃ CO	C ₂ H ₅ O ₂ C	2.5 N	8	92
b.	CH ₃ CO	(CH ₃) ₃ CO ₂ C	3 N	4	94
c.	CH ₃ O ₂ C	CH ₃ O ₂ C	2.5 N	10	90
d.	(CH ₃) ₃ CO ₂ C	(CH ₃) ₃ CO ₂ C	5 N	6	69
e.	C ₂ H ₅ O ₂ C	C ₂ H ₅ O ₂ C	2.5 N	10	88
f.	C ₆ H ₅	CH ₃ CO	5N	12	96
g.	C ₆ H ₅	C ₆ H ₅ CO	5 N	8	94
h.	C ₆ H ₅ CO	C ₆ H ₅ CO	5 N	6	92

a. The yields are for pure distilled products

b. All products show satisfactory elemental analysis and spectral data.

Aldrich) were used as received. The commercial grade sodium azide was used without further purification or activation.

The catalyst, tributylmethyl ammonium chloride immobilised on polystyrene matrix, was prepared by quaternisation of tributyl amine with chloromethyl polystyrene (2% p-divinylbenzene cross linked) as described in the literature¹⁶.

Preparation of diazo carbonyl compounds (5). General procedure:

Methanesulphonyl chloride (1) (0.05 mole), powdered sodium azide (2) (0.075) and the catalyst (1.25 g, 2 m equiv. Cl^- /g) were taken in dichloroethane (200 ml). The reaction mixture was stirred vigorously for 3 h at room temperature. After complete conversion of methanesulphonyl chloride into methanesulphonyl azide (3), carbonyl compound (4) (0.05 mole) was added and stirred for 10 minutes. Then aqueous sodium hydroxide (15 ml) was added and stirring continued at room temperature. The strength of the sodium hydroxide and reaction time is shown in the TABLE. The organic layer was separated, washed with two 100 ml portions of water, and dried with anhydrous magnesium sulphate. After filtration of the drying agent, the solvent was removed on a rotary evaporator using a water bath kept at 30°C. The residual yellow-orange liquid was distilled at high vacuum to give pure diazo carbonyl compounds (5) listed in the TABLE.

All products listed in the TABLE were previously described^{2,3,9}.

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