

Reaction of Tribromonitromethane with Aldehydes and Ketones in the Presence of Zn Metal in Aqueous Medium

Ali Shaker MAHASNEH

*Chemistry Department, Mu'tah University,
Al-karak-JORDAN*

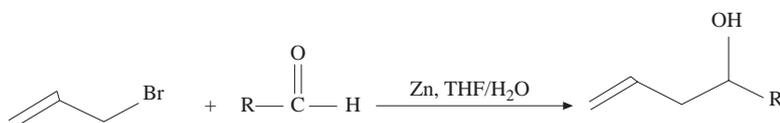
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Aldehydes and ketones react with tribromonitromethane in the presence of zinc metal dust, ammonium chloride and water to give dibromonitroalcohols in good yields.

Introduction

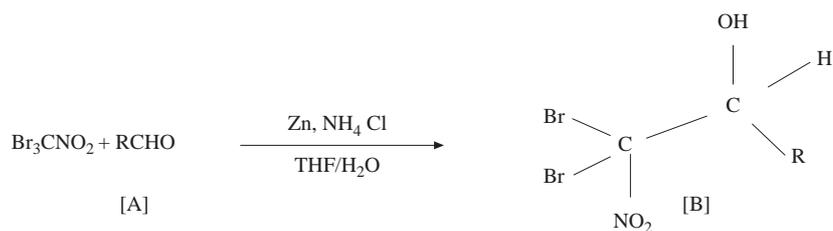
Organic chemists usually prevent the presence of even a trace of water in reactions leading to C-C bond formation. The use of water is postponed until workup step. However, some chemists deliberately use water to increase the rates of some slow reactions. Papers in this field began to appear in the literature¹⁻⁶ in the mid eighties. There are two theories that attempt to explain the increased rates of such reactions in aqueous media (a) the hydrophobic interactions that induce a favourable aggregation of the polar components in water³ and (b) the formation of micelles from organic reactant molecules in water¹.

Of these reactions, quite relevant to the subject of this paper is the reaction of allyl bromide with aldehydes and ketones in the presence of THF/water yielding homoallylic alcohols according to scheme (i).



Scheme (i)

Recently⁷ trichloronitromethane Cl₃CNO₂ (Chloropicrin) was found to add to aldehydes in the presence of tin (II) chloride to yield dichloronitroalcohols in yields ranging between 52 and 92% by Reformatsky-like reaction. Our reaction here describes the preparation of dibromonitroalcohols from tribromonitromethane Br₃CNO₂ and aldehydes or ketones in the presence of Zn metal dust in aqueous media according to scheme(ii).



A,B	R and R ¹	A, B	R and R ¹
a	H	e	n-(C ₄ H ₉)
b	CH ₃	f	n-(C ₆ H ₁₃)
c	C ₂ H ₅	g	C ₆ H ₅
d	n-(C ₃ H ₇)	h	CH ₃ , CH ₃

Scheme (ii)

Experimental

Chemicals and Instruments

All aldehydes and ketones used were purchased from E. Merck. Ethyl acetate and n-hexane used for chromatography were redistilled from commercial quality reagents. Silica gel for preparative T.L.C was Merck 254 GF.

IR spectra were determined on a Unicam Mattson 5000 FTIR spectrometer.

¹H-NMR and ¹³C-NMR spectra were determined on a Bruker 200 MHz/52 MM spectrometer.

Mass spectra were obtained on a V. G. Trio2 Spectrometer at ionization energy 70 eV.

Tribromonitromethane; Preparation Procedure

Into a 1L 2-necked round-bottomed flask fitted with a condenser, separatory funnel and stirred magnetically, 500 ml of water, 265g Na₂CO₃ and 23g of picric acid were introduced. Liquid bromine was added slowly to the stirring mixture for 6h until the yellow color of sodium picrate disappeared. The mixture was then steam distilled yielding 82g, 91% of pure Br₃CNO₂ after having dried over CaCl₂. No further purification was needed.

Dibromonitroalcohols B; General procedure

In a 50ml round-bottomed flask, 5ml THF, 1ml of saturated aqueous solution of NH₄Cl, aldehyde or ketone (5 mmol) and Br₃CNO₂ (1.5g ~ 5 mmol) were stirred in a water bath at 20°C. Zn metal dust (0.33g 5mmol) was added gradually to the stirring mixture for 20 minutes, during which the zinc metal disappeared. The mixture was left stirring at the bath temperature for another 20 minutes. The reaction mixture was then diluted with 50ml of diethylether and washed with 5% HCl, saturated NaHCO₃ solution, brine and dried over MgSO₄. Ether was evaporated leaving an oily product. Samples for spectroscopy were purified using preparative 20x20 cm silica gel plates chromatographed by ethylacetate/hexane mixture Table 1. When water was excluded the reaction failed to give any desired product even when left stirring overnight.

Table 1. Chromatography Solvents, percentage yield and Ms values

Comp.	Recryst. Solvent	% Yield	Ms: M/Z
a	EtoAc/hexane 1:3	95 %	249 M ⁺
b	EtoAc/hexane 1:3	93 %	263 M ⁺
c	EtoAc/hexane 1:4	90 %	277 M ⁺
d	EtoAc/hexane 1:4	95 %	291 M ⁺
e	EtoAc/hexane 1:4	88 %	305 M ⁺
f	EtoAc/hexane 1:4	85 %	333 M ⁺
g	EtoAc/hexane 1:4	53 %	325 M ⁺
h	EtoAc/hexane 1:5	45 %	265 M ⁺

Table 2. Infrared data of the prepared compounds

Compd.	Characteristic IR bands frequency Cm ⁻¹
a	3700-3000 (b), 1574 (s), 1443(w), 1327(m), 1084(m), 845(m), 683(m)
b	3700-3100(b), 2936(m), 1566(s), 1454, 1381, 1138, 949, 794
c	3690-3407(b), 2980(m), 2882(w), 1566(s), 1466(m), 1327(m), 1165(m), 1095(w), 864(w), 841(w), 717(m), 621(m)
d	3700-3100 (b), 2963(s), 2874(m), 1578(s), 1462(w), 1400(m), 1331(s), 1122(s), 1018(w), 956(w), 860(m), 821(m), 617(w)
e	3600-320(b), 2959(m), 2870(m), 1574(s), 1426(w), 1396(w), 1327(m), 1126(m), 1045(w), 929(w), 849(m), 721(m), 621(w)
f	3600-3100(b), 2955(s), 2859(w), 1636(w), 1574(s), 1462(w), 1327(w), 1092(w), 841(w), 725(w).
g	3650-3300(b), 3100(m), 2900(m), 1640(m), 1574(s), 1410(m), 1350(m), 1092(w), 841(w)
h	3689-3300(b), 2986(m), 2882(m), 1566(s), 1327(s), 1165(m), 814(m)

Table 3. ¹H-NMR data of the prepared compounds In(CDCl₃)

Compd.	¹ H-NMR bands δ ppm (multiplicity, no of protons)
a	3.2(t,1H) exchangeable with D ₂ O, 4.5(d,2H)
b	1.5(d,3H), 3.2(b,1H), 4.6(b,1H)
c	1(t, 3H), 1.4(m,2H), 2(m,1H), 4.05(m,1H)
d	1(t,3H), 1.6(m,2H), 2.0(m,2H), 2.5(b,1H), 4.4(m,1H)
e	0.9(,3H), 1.4(m,2H), 1.6(m,2H), 2(m,2H), 2.6(b,1H), 4.4(b,1h)
f	0.9(t,3H), 1.4(m,6H), 1.6(m,2H)
g	3.2(b,1H), 5.3(s,1H), 7.4(s,5H)
h	1.45(two singlets, 6H), 3(s,1H)

Table 4. ¹H decoupled ¹³C-NMR δ (ppm)

Compd.	Bands δ (ppm)
a	72.3, 87
b	20, 76, 96
c	15, 28, 81, 97
d	14, 19.5, 35, 78, 97
e	14, 22, 28, 33, 78, 96
f	14, 22, 27, 30, 32, 35, 78, 96
g	(127-130) six signals, 97, 82
h	25.5, 26, 73, 88

Results and Discussion

Tribromonitromethane, Br₃CNO₂, molecule Contains only one carbon atom and when used as a d¹ synthon is quite relevant to the field of C-1 Chemistry. Bearing three bromine atoms and a nitro group gives the molecule and advantage over other C-1 synthons. In our products, bromonitroalcohols, the nitro group could be reduced to an amino group and amino alcohols which proved to have biological activity⁸. Furthermore the products contain two bromine atoms that could be easily functionalized. Nitroalcohols containing halogens have antimicrobial activity; they inhibit the growth of a broad range of organisms^{9,10}.

As can be clearly seen from the data in table 1, aliphatic aldehydes give good yields while aromatic aldehydes and ketones give poor yields. Tribromonitromethane can be considered a valuable C-1 unit in C-C bond formation reactions. The low cost of the chemicals, relatively short reaction time and the presence of other functionalities give the Br₃CNO₂ compound the advantage over other C-1 synthons.

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