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**Manganese (II) Catalysed Hunsdiecker Reaction:
A Facile Entry to α -(Dibromomethyl) benzenemethanol**

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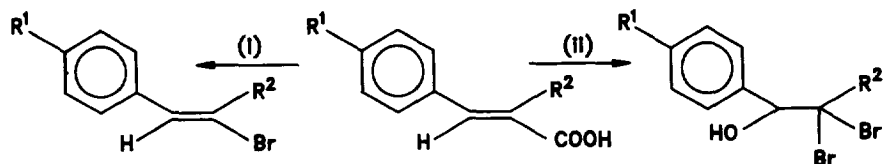
ABSTRACT : *Manganese (II) acetate catalysed reactions of α , β -unsaturated aromatic carboxylic acids **1** with NBS (1 and 2 eq.) in MeCN / water afford haloalkenes **2** and α -(dibromomethyl) benzenemethanols **3** respectively.*

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The bromodecarboxylation of silver carboxylates with molecular bromine, trivially known as Hunsdiecker reaction, is an extremely useful methodology in the armoury of an organic chemist for the synthesis of organic halides.¹ Classical Hunsdiecker reaction and all further modifications thereof relies on a stoichiometric protocol involving metal carboxylates and molecular halogen or halide.² In addition an oxidative decarboxylation protocol using stoichiometric PhIO/NBS is recently reported.³ A conceptually simple strategy to employ a catalytic metal salt pool in mediating an one-pot Hunsdiecker synthesis from in-situ generated metal carboxylate has been envisioned and successfully demonstrated by us for the synthesis of β -halostyrenes **2** from corresponding α , β -unsaturated aromatic carboxylic acids **1** and N-halosuccinimides using Group-1 metal acetates as catalysts.⁴ Encouraged by the results and in keeping with our program⁵ on "naked-metal catalysis", we sought to investigate the above reaction using a catalytic transition metal salt pool. We have identified manganese(II) acetate as the catalyst with the hope of evaluating, vis-a-vis, its potential towards the formation of β -bromostyrene epoxide via an oxidative halodecarboxylation pathway. Serendipitously we have discovered, instead, the remarkable role of water in promoting the halodecarboxylation thereby offering a mild and highyielding synthesis of α -(dibromomethyl)benzenemethanol **3** [Scheme 1].

Initial reaction of **1a** with NBS (1 eq.) and Mn(OAc)₂ (0.1 eq.) in MeCN/H₂O [97:3v/v] led to a complex mixture containing unreacted acid, β -bromostyrene **2a**, α -(dibromomethyl) benzenemethanol **3a** and α -(dibromomethyl)tolylbromide in 44:42:10:4 ratio by NMR. Upon increasing the water concentration by steps, a simultaneous increase in the yield of **2a** was noticed; the optimized condition requiring MeCN/H₂O in 1:1 v/v ratio, the reaction time (TLC inference) and the isolated yield of **2a** being 16h and 83% respectively. Utilizing this methodology, β -bromostyrenes **2b-2e** were synthesized in good to excellent yields from the corresponding acids **1b-1e** [Scheme 1]. Further attempt to reduce the reaction time by increasing the concentration of NBS led to a novel observation wherein α -(dibromomethyl)benzenemethanols **3a-3e** were obtained as exclusive products when 2 eqv. of NBS was used. Uncatalysed reaction of **1a** with 1 and 2 eq. of NBS in MeCN/H₂O (1:1 v/v) affords **3a** in 11% and 39% yields respectively alongwith unreacted acid and minor uncharacterised products. The intermediacy of β -bromostyrene towards the formation of α -(dibromomethyl)benzenemethanol has been confirmed in control experiments with **2a**, NBS (1 eq.) and Mn(OAc)₂ (0.1 eq.).

Scheme 1



Pdt.No.	Yield (%)	R ¹	R ²	Pdt.No.	Yield (%)
2a	83	Me	H	3a	82
2b	73	H	H	3b	78
2c	91	OMe	H	3c	87
2d	95	OMe	Me	3d	98
2e	35	Cl	H	3e	37

(i) NBS (1 eq.) / Mn(OAc)₂ (0.1 eq.) / MeCN-H₂O (1:1) / 16h / rt; (ii) NBS (2 eq.) / Mn(OAc)₂ (0.1 eq.) / MeCN-H₂O (1:1) / 16h / rt. Work-up : ref. 6

While mechanistic investigation is in progress, the success of our stratagem puts forth Hunsdiecker reaction into yet another frontier that comprises of atom economy, mild reaction condition and reduced environmental hazard thereby enhancing its industrial merit. In this context, the present synthesis of α -(dibromomethyl)benzenemethanol must be viewed with respect to earlier procedures which require stringent low temperature Grignard methodologies. For example, α -(dibromomethyl)benzenemethanol **3b** was synthesized⁷ in 20% yield by coupling benzaldehyde with dibromomethanemagnesium bromide, the latter being generated in situ from ethylmagnesium bromide and bromoform at -78°C. Improved yield was obtained⁸ using LDA and dibromomethane at -78°C. In yet another method, **3b** was prepared by hydride reduction of corresponding dibromoketone.⁹

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- Work-up : After removal of MeCN, the residue was saturated with NaCl and extracted with EtOAc. The organic layer was dried over magnesium sulfate and subjected to flash chromatography (silica-gel). Eluent: hexane[for 2], hexane - EtOAc (95: 5) [for 3].
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