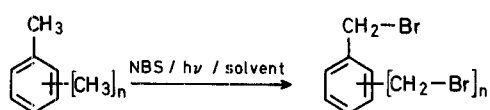


solvents occasionally mentioned in literature did not seem to offer any advantages⁵. We have now found that the *selectivity*⁶ of bromine attack⁷ depends on the solvent employed⁸, a result rarely observed in radical chemistry⁹.



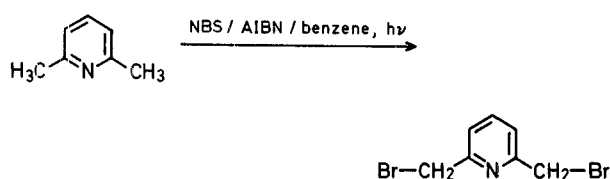
These findings can be exploited synthetically:

(1) Solvents of "high selectivity" (*vide infra*; examples see Table) increase yields in the bromination of polymethylated hydrocarbons (see Table).

(2) Solvents of "low selectivity" (and corresponding "high reactivity") allow the bromination of compounds carrying electron-withdrawing groups, which are well documented to hamper this reaction¹².

Tentatively we ascribe the influence of the solvent to its electron donating/accepting properties, foremostly its polarizability, the latter apparently decreasing the selectivity of bromine attack¹³.

Thus, 2,6-bis[bromomethyl]pyridine, up to now only accessible from 2,6-bis[hydroxymethyl]pyridine¹⁴, which is very expensive or has to be synthesized from 2,6-lutidine following a cumbersome route¹⁵, is now prepared in 20% yield in a one-step *N*-bromosuccinimide bromination in benzene as solvent (former attempts to perform this reaction gave only a 2% yield of impure product¹⁶).



2,6-Bis[bromomethyl]pyridine from 2,6-Dimethylpyridine:

A stirred mixture of 2,6-lutidine¹⁷ (3.0 g, 25 mmol), *N*-bromosuccinimide (10.7 g, 60 mmol), azobis [isobutyronitrile] (~50 mg), and

Side Chain Brominations by *N*-Bromosuccinimide; IV¹. Novel and Improved Preparations by Selective Choice of Solvents

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Tetrachloromethane has been accepted as general solvent in *N*-bromosuccinimide side chain brominations⁴. Other

Table. *N*-Bromosuccinimide Brominations using Individually Selected Solvents^a

Substrate	Product ^b	Amount of substrate	Solvent	Yield ^c [%]	Yield [%] in CCl ₄	m.p. (Lit. m.p.)
		10 mmol	HCOOCH ₃	89 ^d	67 ¹¹	— (—) ¹¹
		100 mmol	HCOOCH ₃	62	31 ¹	75° (75–77°) ¹
		25 mmol	HCOOCH ₃	48	23 ²	93–94° (94°) ²
		50 mmol	H ₃ C—COOCH ₃ / CH ₂ Cl ₂ (3:2)	35	18 ³	206–208° (208–210°) ³

^a Reaction conditions were similar to those reported below¹⁰. ^c Scaling up the experiment may diminish the yield and vice versa.

^b Pure according to the ¹H-N.M.R. spectra.

^d Calculated from the ¹H-N.M.R. spectra.

benzene¹⁸ (100 ml) was refluxed under illumination (200 W incandescent bulb) for 12 h. The resultant red solution was extracted with sodium carbonate solution and water and the benzene removed under reduced pressure. The oily residue was extracted with petroleum ether, from which the colorless, very lachrymatory product crystallized on chilling; yield: 1.4 g (20%); m.p. 83–86° (Lit.¹⁴, m.p. 84–89°).

¹H-N.M.R. (Varian EM 360; CDCl₃/TMS): $\delta = 7.9-7.24$ (m of AB₂ type corresponding to $\delta_A = 7.70$, $\delta_B = 7.37$, $J = 7.9$ Hz¹⁹, rel. int. 3, H_{arom}), 4.54 ppm (s, rel. int. 4, —CH₂Br).

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