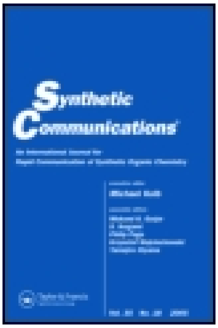

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Perfluorohexane As a Novel Reaction Medium For Bromination Reactions

Suzanne M. Pereira [a], G. Paul Savage [a] & Gregory W. Simpson [a]
[a] CSIRO Division of Chemicals & Polymers, Private Bag 10, Rosebank MDC, Vic., 3169, Australia

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PERFLUOROHEXANE AS A NOVEL REACTION MEDIUM FOR BROMINATION REACTIONS

Suzanne M. Pereira, G. Paul Savage, and Gregory W. Simpson*

CSIRO Division of Chemicals & Polymers,
Private Bag 10, Rosebank MDC, Vic. 3169, Australia

ABSTRACT: Perfluorohexane is shown to be a good alternative to carbon tetrachloride as a non-toxic, non-ozone-depleting, inert reaction medium for bromination reactions. Yields of brominated products were nearly quantitative and the reaction work-up was easier.

Carbon tetrachloride is often the solvent of choice for bromination reactions. However, in response to the threat of global ozone depletion, the production of carbon tetrachloride will be phased out, for all but a very limited number of essential uses, by January 1996.[1] We were therefore interested in investigating alternative media for the bromination of alkenes.

Perfluorohydrocarbons have been used as reaction media for various reactions including esterifications and transesterifications,[2] polymerisations,[3] and flash photolysis reactions.[4] Perfluorohydrocarbons

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* To whom correspondence should be addressed

have unusual properties such as high density and stability, and low miscibility with water and organic compounds. We herein report the use of perfluorohexane (d_4^{25} 1.68 g/ml, b.p. 57°C) as a reaction medium for alkene bromination.

Neither bromine nor most organic alkenes are miscible with perfluorohexane. Bromine is more dense (d_4^{20} 3.12 g/ml) than perfluorohexane whereas most organic alkenes are of lower density. Thus, equimolar amounts of bromine and the alkene can be added to perfluorohexane and they do not come into contact until the mixture is rapidly stirred. The perfluorohexane acts as an inert diluent and heat sink for the reaction.

After the reaction is complete the brominated product is usually immiscible with perfluorohexane and can be conveniently filtered off in the case of solids, or phase separated in the case of liquids. Alternatively, the perfluorohexane can be evaporated under reduced pressure or extracted with an organic solvent. The separated perfluorohexane is usually free of reaction residues and in most cases can be used for subsequent reactions without further purification.

Thus, for example, bromine and ethyl cinnamate (see Table, Entry 3) were stirred rapidly at room temperature in perfluorohexane for one hour. The crystalline dibromo product formed in quantitative yield, and was filtered off. The recovered perfluorohexane was not coloured and could be reused without purification.

In conclusion, perfluorohexane can be used as an inert reaction medium, as a non-toxic, non-ozone-depleting alternative to carbon tetrachloride, for bromination reactions.

TABLE

Entry	Reactant	Product*	b.p./mmHg or m.p., °C (lit.)
1	1-hexene	$C_4H_9CHBrCH_2Br$	29.5/0.04 (103-5/36)[5]
2	$CH_3CH{=}CHCO_2Et$	$CH_3CHBrCHBrCO_2Et$	29/0.04 (100-10/20)[6]
3	ethyl cinnamate	$PhCHBrCHBrCO_2Et$	74.5-76.5 (74-5)[7]
4	styrene	$PhCHBrCH_2Br$	73.5-74 (73.5-74)[8]
5	α-methyl styrene	$PhC(CH_3)BrCH_2Br$	150/2 (95-97/0.07)[9]
6	allyl bromide	$CH_2BrCHBrCH_2Br$	150/75 (220/760)[10]

* Yields were near quantitative in all cases. All products gave ^1H n.m.r., ^{13}C n.m.r., and mass spectra consistent with expected structures.

EXPERIMENTAL SECTION

Boiling points refer to the temperature for bulb to bulb distillation, melting points were taken in open capillary tubes and are uncorrected. ^1H and ^{13}C n.m.r. spectra were recorded at 250 MHz and 62.9 MHz, respectively. Mass spectra were obtained on a Hewlett-Packard MSD 5970 GC-MS instrument. Commercially available solvents and reagents were used without further purification. Perfluorohexane was purchased from BNFL Fluorochemicals Ltd. (kilogram quantities).

General procedure for bromination reactions. – Bromine (10 mmol) was added dropwise to a rapidly stirred mixture of the alkene (10 mmol) in perfluorohexane (50 ml) at room temperature. The heterogeneous mixture was stirred for one hour then filtered (solid products) or phase separated (liquid products) to give the crude brominated compounds which were purified by recrystallisation or distillation under reduced pressure, according to literature procedures. Products were examined by ^{1}H and ^{13}C n.m.r., and by GC/MS to confirm their structure and assess purity.

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