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Association of Fluorous "Phase-Vanishing" Method with Visible-Light Activation in Benzylic Bromination by Bromine

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In this study the "phase-vanishing" method for diffusion-controlled addition of a reagent (Br_2) to a reaction phase via a fluorous membrane (C_8F_{18}) is combined with an additional mode of activation (visible-light) to achieve the benzyl bromination of various alkyl-substituted aromatic compounds in a concentrated solution. Benzyl bromination of *p*-*tert*-butyltoluene proceeded in various solvents including hexane and methanol, while the reaction of the neat substrate showed a similar selectivity as in carbon tetrachloride. The effect of the substituent on the *para* position of toluene on the course of bromination revealed three processes: benzyl bromination with H, Me, *t*Bu and CO_2Et substituents, aromatic bromination with OMe and NHAc substituents and the reaction of the 4-acetyl derivative at the substituent to form an α-bromo ketone.

Introduction

Fluorous chemistry has become an increasingly important field in organic synthesis[1] and within the spectrum of subjects covered in this topic we find particularly interesting the "phase-vanishing" (PV) method developed by Curran and Ryu.[2] The method was employed for reagents that are denser (Br_2, d = 3.12 and BBr_3, d = 2.65) than the fluorous media (C_6F_{14}, d = 1.67), that is denser than the organic or aqueous medium. Here the fluorous solvent acts as a phase screen or bulk membrane preventing the mixing of the bottom reagent with the upper organic solution (Figure 1). Diffusion is the driving force for the transport of reagent through this bulk membrane – a process facilitated by the depletion of the reagent at the fluorous/organic interface. This makes the PV method ideal for highly reactive reagents and exothermic reactions since diffusion through the phase border is slow and uniform. The transfer of the reagent across the bulk membrane also prevents high-localised concentrations and overheating and avoids the need for low temperatures and/or controlled dropwise addition. Examples from the literature that have taken advantage of the PV method include bromination with Br,[2,3] chlorination with chlorine gas,[4] bromination and chlorination of alcohols by $SOBr_2$ or PBr_3 and $SOCl_2$ or PCl_3, respectively.[2,3,5] The method was also applied to the demethylation of anisoles by BBr_3,[2] Friedel–Crafts acylation by $SnCl_4$,[6] methylation of phenol by dimethyl sulfate and epoxidation/oxidation by *m*-CPBA,[3] although in the latter it was defined as an extractive PV reaction due to the reagents being in solution with 1,2-dibromoethane.[7]

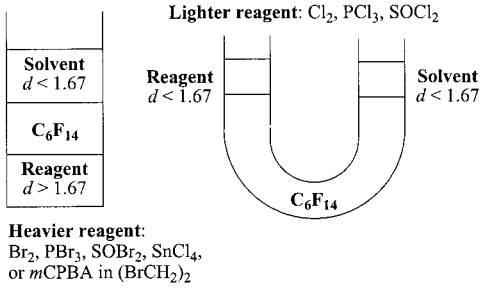

Figure 1. Strategy for fluorous PV functionalization.

The PV method is also applicable for solid reagents, when it is possible to dissolve them in an appropriate solvent. However, little is known about the use of the PV method for the slow diffusion of a reagent and its activation to generate an active species like a bromine radical. In this report, we introduce the idea of using visible light for the activation of molecular bromine at the phase border for the radical bromination of methyl-substituted arenes. This reaction (known as Wohl–Ziegler bromination), which leads to the synthesis of valuable benzyl bromides, is classically conducted using *N*-bromosuccinimide (NBS) in CCl_4 with azobis(isobutyronitrile) (AIBN) as a radical initiator.[8] However, in recent years, there has been a growing interest to develop an environmentally more friendly method for benzyl bromination. So far research has focused on using more benign solvents (e. g., ionic liquids, water, ethyl or methyl acetate),[9–11] the brominating reagent (e. g., Br_2, H_2O_2/HBr, $NaBrO_3$/$NaHSO_3$, polymer-supported reagents)[10,12–16]

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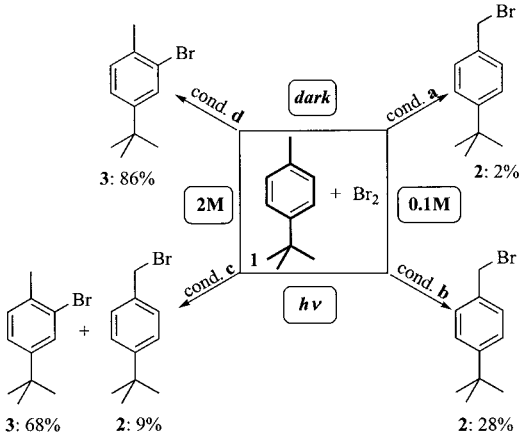
and the mode of activation (e. g., light, microwaves, zeolites, grinding).[11,17–19]

In our study, we investigate the PV method for diffusion-controlled transfer of molecular bromine into the reaction phase and its activation by visible light. We also attempt to elucidate the effects that the slow generation of radicals at the phase border have on the bromination of substituted alkylbenzenes in concentrated solutions.

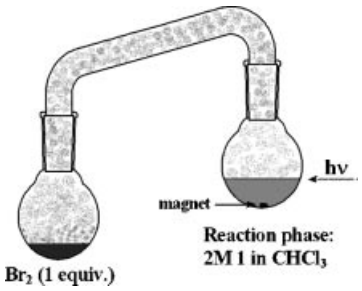
Results

Initially, we performed a series of classical experiments to determine what effects the concentration of bromine (bromine radical) has on the type of bromination of 4-*tert*-butyltoluene (**1**) – the model substrate. We found that the reaction of **1** and Br_2 (0.1 M in $CHCl_3$) in the dark produced only a trace amount 4-*tert*-butylbenzyl bromide (**2**) at room temperature after 24 h (Scheme 1, conditions a). However, when we irradiated the reaction mixture with an incandescent light-bulb (40 W) under the same reaction conditions, conversion was 28% (Scheme 1, conditions b). Next, we reduced the amount of solvent by a factor of 20. With a more concentrated solution (2 M), the reaction (in the dark) proceeded only at the aromatic ring producing the 2-bromo derivative **3** (Scheme 1, conditions d; 86% yield). We also found that irradiation did not alter the course of the reaction to the benzyl position, and benzyl bromide **2** was only a minor product (Scheme 1, conditions c).



Scheme 1.

In our view, if we could keep the concentration of bromine low, then the reaction in the highly concentrated substrate solution should favour the benzyl position. To test this, we assembled the apparatus shown in Scheme 2. We then irradiated the reaction phase with a 40 W light bulb and stirred the solution until all of the bromine had diffused into the reaction solution (22 h). After the reaction was complete, we found that benzyl bromide **2** was the only reaction product (45% yield). The slow addition of bromine into a 2 M solution of **1** altered the course of the reaction from the aromatic substitution in the classical reaction (Scheme 1, path c) to the benzyl bromination in the diffusion process (Scheme 2).



Scheme 2.

This reaction opens the door for an experiment under "phase-vanishing" reaction conditions in which bromine is eliminated from the gaseous phase, while diffusion of Br_2 into the reaction phase is uniform and slow. To facilitate the transport of Br_2, we simultaneously stirred both the bromine phase and the organic phase (in order to stir the upper phase, we prepared a hollow glass bubble with a piece of iron wire inside. It floated in the organic phase and stirred simultaneously with the magnet in the bottom phase) while taking care not to mix the phases (Figure 2). Again, we used a 40 W incandescent light-bulb to irradiate the fluorous/organic phase border [the temperature of the reaction mixture was slightly elevated (26 °C) due to the illumination by 40 W incandescent bulb]. Figure 2 shows how the bromine diffuses through the fluorous membrane to the upper organic phase where it does not accumulate but reacts as soon as it encounters the irradiated phase boundary, i. e., the organic phase remains colourless. At the end of the reaction, the bromine phase literally disappears to leave a biphasic system. After isolating the upper organic phase, we found benzyl bromide **2** to be the major reaction product accompanied by the α,α-dibromo product **4** (**2**/**4** = 3.9:1). The lower fluorous phase was recovered and reused.

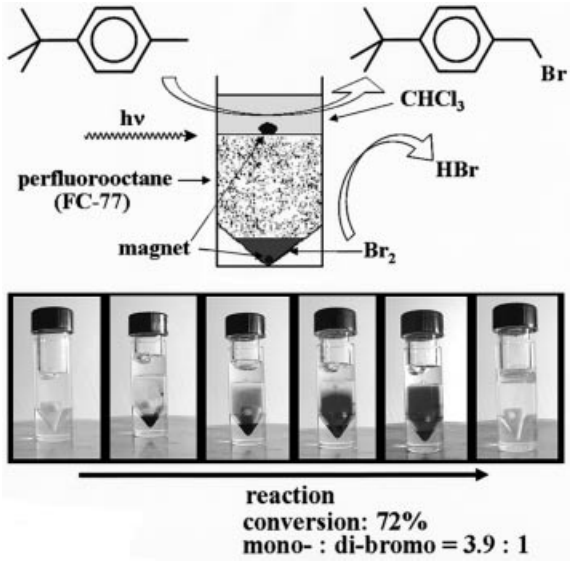


Figure 2. Fluorous "phase-vanishing" visible-light-induced radical bromination.

It is well known that the selectivity of radical bromination and chlorination at the primary/secondary/tertiary carbon atoms is dependent on the type of solvent. A general rule is that the selectivity increases with a decrease in the number of halogen atoms in the solvent molecule.[20] Therefore, we set out to study what effect the solvent has on both the transfer of bromine through the fluorous/organic phase border and the bromination process by performing PV reactions in various solvents with **1** (2 M). Table 1 shows that for non-polar solvents the benzyl bromination proceeds with a high yield and besides benzyl bromide **2** benzyl dibromide **4** also forms. The selectivity of the mono- vs. dibromination in halogenated solvents follows the above-mentioned rule. Surprisingly, in polar solvents like acetonitrile and methanol the reaction is slower, taking 24 h to reach completion; the reaction occurs at the benzyl position and we find only a trace amount of product brominated at the aromatic ring. Finally, we repeated the experiment using the neat substrate. Our results reveal a similarity in terms of yield and selectivity to reactions performed in carbon tetrachloride and hexane. It is clear that the solvent affects the rate of disappearance of the bromine, indicating that the transfer of the reagent through the fluorous/organic phase border plays an important role in the reaction process.

Table 1. Effect of the solvent on the mono- (→ **2**) vs. dibenzyl (→ **4**) bromination of 4-*tert*-butyltoluene (**1**) in the PV method.

Solvent	Time [h]	Conversion (%)[a]	Ratio **2/4**[a]
CCl_4	3.5	77	2.4
$CHCl_3$	6	72	3.9
CH_2Cl_2	4.5	85	4.6
EtBr	4	83	4.2
Hexane	3.5	77	2.4
CH_3CN	24	22	1.0
CH_3OH	23	51	1.5
Neat	4	71	2.7

[a] Conversion and relative ratio of products were determined by ^{1}H NMR spectroscopy.

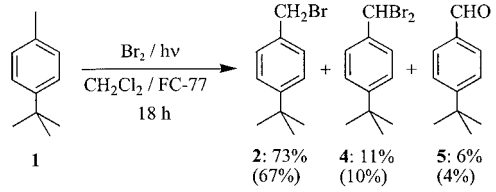
The proposed mechanism of radical bromination suggests that abstraction of the benzyl hydrogen atom by the bromine radical leading to a benzyl radical and HBr is a reversible step (1)[13] indicating that the presence of hydrogen bromide interferes with the benzyl bromination process.

$$ArCH_3 + Br^{\cdot} \rightleftharpoons ArCH_2^{\cdot} + HBr \quad (1)$$

$$ArCH_2Br + Br^{\cdot} \rightleftharpoons ArC^{\cdot}HBr + HBr \quad (2)$$

The PV method enables the use of a highly concentrated reaction mixture and consequently the reaction phase contains a high concentration of hydrogen bromide. To investigate what effect this has on the transformation process, we added an equivalent amount of HBr to the organic solvent. Our experiment reveals that the presence of HBr reduces the selectivity of the benzyl bromination and a 1.2:1 mixture of **2/4** forms with a 62% yield. Next, we eliminated the HBr generated during the reaction by adding water to transfer the HBr into the aqueous phase. In this case, both conversion and selectivity were improved (76% yield, **2/4** = 5.1).

We then took various substituted alkylbenzenes to determine the effect different substituents on the aromatic ring have on the diffusion-controlled bromination. The alkylbenzenes included toluene, *p*-xylene, mesitylene and 4-substituted toluenes (*t*Bu, $COCH_3$, CO_2Et, NHCOMe, OMe). In a typical experiment the transport phase was FC-77 (C_8F_{18}) and the reaction phase was a solution of **1** in CH_2Cl_2 (1 M). We carried out the reaction in an open reactor while gently stirring both bottom and upper phases. We judged the reaction complete when the bromine phase had disappeared and the fluorous phase had become colourless. Our analysis of the reaction products after a workup procedure revealed that only a reaction at the benzyl position had taken place (Scheme 3, numbers in parentheses refer to isolated yields).

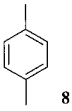
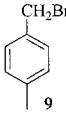
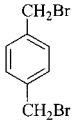
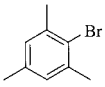
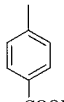
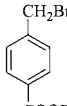
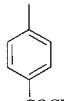
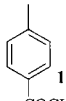
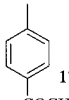
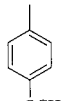
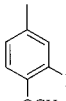
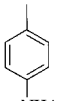
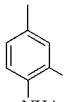


Scheme 3.

In the case of toluene (**6**) we found that the reaction occurs at the benzyl position with benzyl bromide (**7**) being the main product. (Dibromomethyl)benzene was detected only in trace amounts (Table 2). Although a second methyl group attached to the toluene ring in *para* position increases the electron density of the ring, we found that the reaction still favours the benzyl position. Conversion of *p*-xylene (**8**) by PV bromination occurred in 70% and besides benzyl bromide **9**, α,α′-dibromo-*p*-xylene (**10**) also formed. Mesitylene (**11**) was transformed into a mixture of products although only bromomesitylene (**12**) was isolated by column chromatography (37% yield). In a similar experiment we varied the substituent in *para* position of the toluene ring. The first substituent we tested was the electron-withdrawing ethoxycarbonyl group [ethyl 4-methylbenzoate (**13**)]. The only reaction product formed was **14** – a benzyl-brominated one in only 36% yield. The PV bromination of 4-methylacetophenone (**15**) occurred at the α-position to the carbonyl group and only α-bromomethyl (**16**) and α,α-dibromomethyl (**17**) ketones were formed. Alternatively, electron-donor substituents in *para* position of the toluene ring [methoxy (**18**) and acetamido (**20**)] altered the reactivity of the substrate to favour the aromatic ring. We observed no benzyl-brominated products.

When water was added to the organic phase to extract the evolved HBr, bromination of **1** was more selective. Therefore, we performed this experiment with other substrates and the beneficial effect of eliminating HBr from the reaction phase was revealed again for both the radical and polar reaction (Table 2).[33]

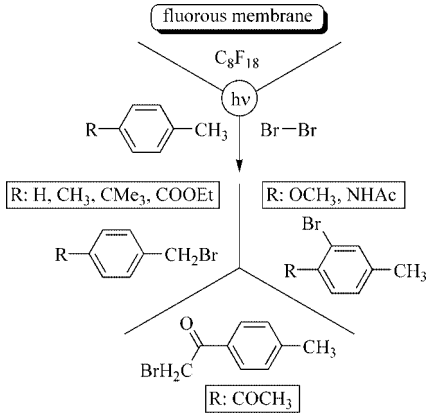
Table 2. PV visible-light-induced bromination of alkylbenzenes.

Substrate		Time [h]	Conv. [%]	Products[a]		Yield[b]
 6	A[c]	2.5	100	 7		63%
	B[c]	3.5	100			72%
					9/10	
 8	A	5.5	70	 9  10	1.7:1	37%, 20%
	B	4	87		1.4:1	45%, 25%
 11	A	4.5	65	 12		37%
	B	6	86			71%
 13	A	8	36	 14		30%
	B	10	86			74%
					16/17	
 15	A	7.5	98	 16  17	4.9:1	70%, 10%
	B	6.5	82		3.5:1	60%, 15%
 18	A	7	71	 19		63%
	B	6	100			92%
 20	A	7	70	 21		70%
	B	6.5	95			90%

[a] Ratio of products determined by NMR spectroscopy of the crude reaction mixture. [b] Yields of isolated products by column chromatography. [c] Method A: typical reaction procedure (Exp. Sect.), Method B: 0.125 mL of H_2O (7 equiv.) was added to the CH_2Cl_2 phase.

Conclusions

The "phase-vanishing" method offers a simple but effective alternative to dropwise addition and furthermore it can be coupled with another mode of activation. The PV methodology enables a selective visible-light-induced benzyl bromination with molecular bromine in a highly concentrated solution, which in turn means a lower amount of solvent is required. Because of the slow addition of bromine through the fluorous/organic interface, a localised high concentration of bromine is avoided and the reaction can proceed at ambient temperature without additional cooling. Our study shows that the organic solvent has a pronounced effect on the course of the reaction and dichloromethane was the solvent of choice. Also important is the possibility to avoid chlorinated solvents by using hexane or the neat substrate. Surprisingly, benzyl bromination of 4-*tert*-butyltoluene (**1**) was possible even in polar solvents like methanol and acetonitrile. Finally, the course of bromination is clearly dependent on the type of substituent in 4-position of the toluene ring and three different reaction sites were observed: benzyl position, aromatic ring and at the substituent (Scheme 4). Extraction of HBr form the reaction phase into the added water had a beneficial effect on the yield of bromination product in free-radical and electrophilic reactions.



Scheme 4.

Experimental Section

General Remarks: Commercial chemicals were used without purification. Ethyl 4-methylbenzoate was prepared as reported in the literature.[21] Column and thin layer chromatography were carried out using silica gel 60 (0.063–0.200 mm) and silica 60F-254 plates, respectively. Reactions were initiated by an incandescent light bulb (40 W). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a Varian Inova 300 MHz spectrometer. The chemical shifts (δ) are reported in ppm units relative to TMS as an internal standard for ^1H NMR and $CDCl_3$ for ^{13}C NMR spectra. Melting points were determined with a Büchi 535 melting point apparatus. Mass spectra were obtained using an Autospec Q mass spectrometer with electron impact ionization (EI, 70 eV).

Bromination of 4-*tert*-Butyltoluene (1) in $CHCl_3$ with Bromine in the Dark: 4-*tert*-Butyltoluene (**1**) (297 mg, 2.00 mmol) was dissolved in $CHCl_3$ (1 mL or 20 mL) and the flask covered with an aluminium foil to shield the reaction mixture from light. Into the stirred solution, bromine (104 μL, 2.02 mmol) was added and the mixture stirred at room temperature for 24 h. Then CH_2Cl_2 (10 mL) was added, the organic phase was washed with an aqueous solution of $NaHSO_3$ (0.1 M), a saturated aqueous solution of $NaHCO_3$ (10 mL) and dried with anhydrous Na_2SO_4. Finally, the solvent was evaporated under reduced pressure and the crude reaction mixture was analyzed by ^1H NMR spectroscopy. Products were determined after isolation by column chromatography (SiO_2, petroleum ether) and by comparison with the literature data.[22] Results are presented in Scheme 1.

Visible-Light-Induced Bromination of 4-*tert*-Butyltoluene (1) in $CHCl_3$: 4-*tert*-Butyltoluene (**1**) (297 mg, 2.00 mmol) was dissolved in $CHCl_3$ (1 mL or 20 mL) and bromine (104 μL, 2.02 mmol) was added. The reaction mixture was irradiated by a 40 W incandescent light bulb and stirred for 24 h. The reaction mixture was isolated and analyzed as above and results are presented in Scheme 1.

Bromination of 4-*tert*-Butyltoluene (1) in $CHCl_3$ by Addition of Bromine through the Gas Phase: A solution of 4-*tert*-butyltoluene (**1**) (297 mg, 2.00 mmol) in $CHCl_3$ (1 mL) was placed in a 10-mL flask. It was connected by a glass tube with another flask containing Br_2 (104 μL, 2.02 mmol) (Scheme 2). The solution of **1** was irradiated by a 40 W incandescent light bulb and stirred for 22 h. The reaction mixture was isolated as above and the analysis of the ^1H NMR

spectrum revealed the presence of 45% of product **2** as determined by comparison with literature data.[23]

The Effect of Solvent on the Bromination of 1 by the PV Method: See Table 1. Bromine (104 μL, 2.02 mmol) was slowly added to octadecafluorooctane (FC-77) (3 mL) in a glass reactor (19 mm diameter 60 mm length) using a glass syringe. Then a solution of **1** (297 mg, 2.00 mmol) in various solvents (1 mL) or neat was added carefully to form three distinct phases. Gentle stirring of the bromine and upper organic phase were performed, taking care not to mix the phases. The fluorous/organic phase border was irradiated by a 40 W incandescent light bulb. The reaction was run at room temperature until all the bromine had disappeared and the fluorous phase had become colourless. The contents of the reactor were then transferred into a separating funnel, into which 10 mL of CH_2Cl_2 and 10 mL of 0.01 M $NaHSO_3$ were added and the phases separated. The lower fluorous phase was recovered and reused without any observable losses. The organic phase was washed with a satd. solution of $NaHCO_3$, dried with Na_2SO_4 and the solvent was evaporated. The crude reaction mixture was then analyzed by ^1H NMR spectroscopy and results are presented in Table 1.

General Procedure for Phase-Vanishing Bromination of Alkylbenzenes: In a typical experiment, bromine (160 mg, 1.00 mmol) was slowly added to octadecafluorooctane (FC-77) (3 mL) in a glass reactor (19 mm diameter, 60 mm length) using a glass syringe. To this was added a solution of alkyl benzene (1.00 mmol) in CH_2Cl_2 (1 mL) to form three distinct phases. Gentle stirring of the bromine and upper organic phase were performed, taking care not to mix the phases. The fluorous/organic phase border was then irradiated (40 W) and the reaction allowed to proceed at room temperature until the bromine had disappeared and the fluorous phase had become colourless. After the aforementioned workup procedure, the crude reaction mixture was analyzed by ^1H NMR spectroscopy, the products separated using chromatography and the pure compounds identified on the basis of comparison with literature data.

Bromination of 4-*tert*-Butyltoluene (1): The reaction products were separated by column chromatography (SiO_2, petroleum ether/CH_2Cl_2, 9:1) and identified as 1-(bromomethyl)-4-*tert*-butylbenzene (**2**) (152 mg, 67%),[23] 1-*tert*-butyl-4-(dibromomethyl)benzene (**4**) (31 mg, 10%),[24] and 4-*tert*-butylbenzaldehyde (**5**) (6 mg, 4%).[24]

Bromination of Toluene (6): The product was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2, 9:1). The product was identified as 1-(bromomethyl)benzene (**7**) (108 mg, 63%).[25]

Bromination of *p*-Xylene (8): The products were separated by column chromatography (SiO_2, petroleum ether/CH_2Cl_2, 1.6:1). The products were identified as 1-(bromomethyl)-4-methylbenzene (**9**) (68 mg, 37%)[26] and 1,4-bis(bromomethyl)benzene (**10**) (53 mg, 20%).[27]

Bromination of Mesitylene (11): The product was purified by column chromatography (SiO_2, petroleum ether/CH_2Cl_2, 4:1) and identified as 2-bromo-1,3,5-trimethylbenzene (**12**) (74 mg, 37%).[25]

Bromination of Ethyl 4-Methylbenzoate (13): The product was purified by column chromatography (SiO_2, CH_2Cl_2/*n*-hexane, 9:1) and identified as ethyl 4-(bromomethyl)benzoate (**14**) (72 mg, 30%).[28]

Bromination of 1-(*p*-Tolyl)ethanone (15): The products were separated by column chromatography (SiO_2, CH_2Cl_2/petroleum ether, 3:1). The products were identified as 2-bromo-1-(4-methylphenyl) ethanone (**16**) (149 mg, 70%)[29] and 2,2-dibromo-1-(4-methylphenyl)ethanone (**17**) (29 mg, 10%).[30]

Bromination of 1-Methoxy-4-methylbenzene (18): The product was purified by column chromatography (SiO_2, CH_2Cl_2/petroleum ether, 4:1) and found to be 2-bromo-1-methoxy-4-methylbenzene (**19**) (127 mg, 63%).[31]

Bromination of *N*-(*p*-Tolyl)acetamide (20): The product was purified by preparative thin layer chromatography (SiO_2, CH_2Cl_2/EtOAc, 2:3) and identified as *N*-(2-bromo-4-methylphenyl)acetamide (**21**) (160 mg, 70%).[32]

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