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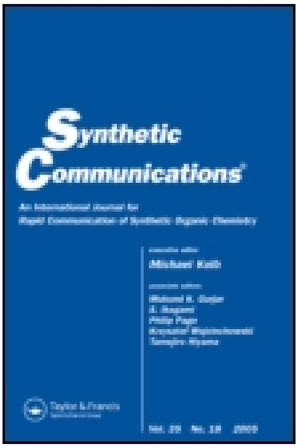

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Photo-Ritter Reaction of Arylmethyl Bromides in Acetonitrile

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PHOTO-RITTER REACTION OF ARYLMETHYL BROMIDES IN ACETONITRILE

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The photo-Ritter reaction of five arylmethyl bromides can occur in acetonitrile to give acetamides. The intermediates, carbocations, which are formed from subsequent electron transfer between the radical pairs generated from initial homolytic cleavage of the C–Br bond, are trapped by acetonitrile, and subsequent hydrolysis generates the corresponding acetamides.

Keywords: Acetamides; arylmethyl bromides; photolysis; Ritter reaction

INTRODUCTION

The Ritter reaction is a chemical reaction that transforms a nitrile into an N-alkyl amide using various alkylating reagents, for example, strong acids and alkenes[1] or alcohols.[2] In recent years, several alternative methodologies have been developed for the Ritter reaction using various catalysts that can generate carbocation intermediates. The main disadvantages of these methods are the use of toxic catalysts or corrosive acids, and these catalysts cannot be reused. Recently, some researchers have been making efforts to find recyclable catalysts.[3] The photo-Ritter reaction is one alternative method that overcomes the disadvantages, and the formation of intermediary carbocation undergoes either a photosensitized electron transfer[4] or a direct photolysis.[5–7] The latter pathway is a more "green" synthetic method. However, for halohydrocarbon as a substrate in the photo-Ritter reaction, only a few examples were found, including alkyl halides,[5] aromatic alkenyl bromides,[6] and an aryl halide.[7]

The photo-Ritter reaction of alkyl halides in acetonitrile was thought to undergo the processes as follows. The substrate in the excited state, after absorbing a photon, has an initial homolytic cleavage of the carbon–halogen bond to afford a radical pair, which undergoes electron transfer to form an ion pair, including a carbocation. The carbocation is trapped by acetonitrile, and subsequent hydrolysis gives a Ritter product.[5]

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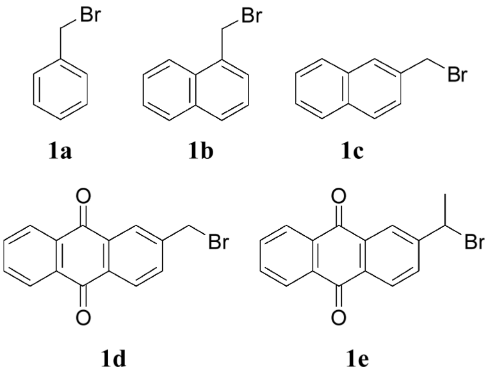
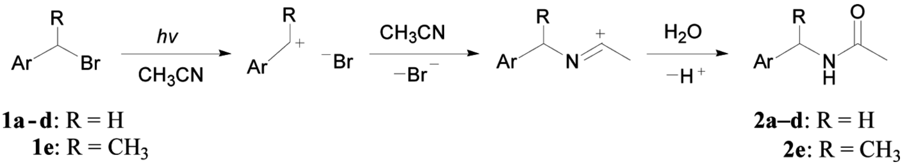


Chart 1. Structures of arylmethyl bromides, **1a**–**e**, in this work.

Herein, we report the photo-Ritter reaction of five arylmethyl bromides including benzyl bromide (**1a**), 1-(bromomethyl)naphthalene (**1b**), 2-(bromomethyl) naphthalene (**1c**), 2-(bromomethyl)anthraquinone (**1d**), and 2-(1-bromoethyl) anthraquinone (**1e**) in acetonitrile (Chart 1). Photolysis of the five compounds in acetonitrile can efficiently generate N-arylmethyl amides.

RESULTS AND DISCUSSION

To investigate photolysis of arylmethyl bromides, acetonitrile solutions of **1a**–**e** were prepared in a quartz tube for **1a**, a Pyrex tube for **1b** and **1c**, and a Pyrex flask for **1d** and **1e**. Under a 300-W high-pressure mercury lamp, acetonitrile solutions of **1a**–**c** were irradiated, and benzylacetamide (**2a**), 1-acetamidomethylnaphthalene (**2b**), and 2-acetamidomethylnaphthalene (**2c**) were obtained in the yields of 42%, 42%, and 63%, respectively. Compounds **1d** and **1e** in acetonitrile were irradiated with a 500-W Xe lamp, giving 2-acetamidomethylanthraquinone (**2d**) and 2-(1-acetamidoethyl) anthraquinone (**2e**) in yields of 72% and 40%, respectively. The selection of the excitation light source and a reactor depends on absorption spectra of arylmethyl bromides, that is, the absorption band of **1a** in the far-ultraviolet region and a longer-band region for **1d** and **1e** as compared with **1b** and **1c**. Based on these photoproducts, the photochemical reactions can be inferred to be a photoinduced Ritter reaction. In the photochemical reaction, the formed carbocation intermediates are trapped by acetonitrile and subsequent hydrolysis by a trace of water in acetonitrile or during the separation process, generating the corresponding amides (**2**) (Scheme 1).

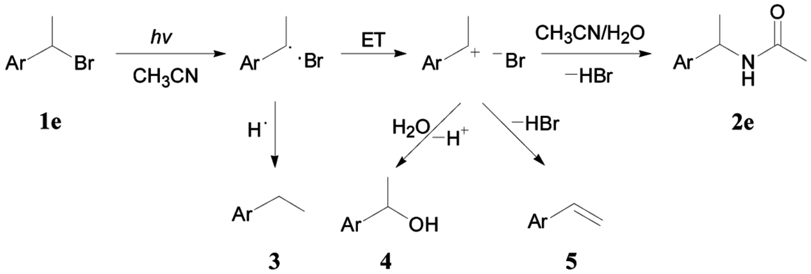


Scheme 1. Photoinduced Ritter reaction of arylmethyl bromides (**1a**–**e**) in acetonitrile.

Competing ionic and radical photobehavior has been observed for a number of alkyl halides.[5] Irradiation of alkyl halides in a variety of media afforded predominantly the nucleophilic substitution product, accompanied by the reduction product norbornane. The results have been explained in terms of initial homolytic cleavage of the carbon–halogen bond to afford a radical pair, which undergoes competing (a) diffusion and hydrogen abstraction to give reduction products and (b) electron transfer (ET) to afford an ion pair. The ion pair, in turn, gives rise ultimately to the substitution and elimination products.[5] The competition between ionic and radical pathways was further demonstrated through investigating photolysis of 1-fluoro-2-halo-1,2-diphenylethanes solutions of tetrahydrofuran (THF), acetonitrile, and cyclohexane.[8] In the hydrolysis system of **1e**, besides the Ritter product (**2e**), a lesser amount of reduction product 2-ethylanthraquinone (**3**, 5%), nucleophilic substitution product 2-(1-hydroxyethyl)anthraquinone (**4**, 6%), and the elimination product 2-vinylanthraquinone (**5**, 30%) in excellent yield were also obtained (Scheme 2). Furthermore, the radical product **3** decreases with increasing solvent polarity. These results can be well explained with this mechanism.

In general, acetonitrile as a solvent does not undergo nucleophilic addition to radical cation species formed from photoinduced ET reactions.[8,9] However, we observed that the photolysis of the arylmethyl bromides gave the corresponding Ritter products in good yields. When the photo-Ritter reactions were preformed in wet acetonitrile, the yields and conversion rates of amides become lower because of the nucleophilic addition of water and gave corresponding hydrolysis products (Table 1). This confirms the formation of carbocaion in photolysis of the arylmethyl bromides.

To measure the quantum yields, acetonitrile solutions (1 mM) of **1a**–**e** were prepared in quartz cuvettes with a Teflon stopper, sealed after bubbling with high pure nitrogen for 15 min, and then irradiated with the monochromatic light at their maximum absorption wavelength from a fluorescence spectrometer with a 20-nm slit. After a certain time of irradiation, the irradiated solution was taken out for HPLC analysis. The irradiation time was selected in terms of their photochemical efficiencies from the synthesis. The products were identified by co-injection with known samples. The concentrations of products in the irradiated solution were analyzed, and conversion rates were obtained, as listed in Table 1. Data show that **2d** and **2a** have good values and that **2e** formed in a poor conversion rate. The poor conversion rate of **2e** results from the elimination reaction, and there is no



Scheme 2. Proposed mechanism for photochemical reactions of arylmethyl bromides in acetonitrile.

Table 1. Conversion rates of products acetamides in phoyolysis of arylmethy bromides in dry acetonitrile[a]

Substrates	λ^b (nm)	Time[c] (min)	Ritter product	Conv. (%, Φ_{rel})
1a	250	60	**2a**	78 (5)
1b	290	30	**2b**	53 (1)
1c	275	30	**2c**	42 (1)
1d	326	20	**2d**	92 (25)
1e	350	10	**2e**	25 (3)

[a] [Substrate] = 1 mM, determined by high-performance liquid chromatography (HPLC) directly on the crude product mixture.

[b] Irradiation wavelengths, which are maxima absorption peaks of arylmethyl bromides.

[c] Irradiation time.

competition for the other four arymethyl bromides because there is no β-hydrogen. Furthermore, the intensity of irradiation light was measured using potassium ferrioxalate actinometry.[10] Based on the yields and the light intensity, the relative quantum yields (Φ_{rel}) were calculated shown in Table 1. The value of **1d** is the highest, 25 times higher than those of **1b** and **1c**.

In general, a photo-Ritter reaction gives a relatively low yield. In this work, photolysis of the arylmethyl bromides in dry acetonitrile was observed to give relative good yields and good conversion rates except for **1e**. Because of the competition of the elimination, the photochemical reaction of **1e** gives a poor conversion rate of Ritter product **2e**. In addition, the conversion rate would be decreased in the presence of a stronger nucleophile, such as water.

EXPERIMENTAL

General Methods

Melting points were uncorrected. ^{1}H and ^{13}C NMR spectra were determined with a Bruker AV300 spectrometer. ^{1}H NMR were run at 300 MHz, and ^{13}C NMR spectra were recorded at 75 MHz, under full proton decoupling. Chemical shifts are given in parts per million from tetramethylsilane (TMS) as the internal reference. Fourier transform–infrared (FT-IR) spectra were carried out on a Bruker Vector22 IR spectrometer. Ultraviolet–visible (UV-vis) absorption spectra were recorded with a Shimadzu UV-2401PC UV–vis spectrometer. Mass spectra were obtained with a Micromass GCF TOF mass spectrometer. HPLC analysis was performed on an HP Agilent (1100 series) HPLC system with C-18 reverse-phase columns (250 mm × 4.6 mm × 5 μm).

Synthesis of Arylmethyl Bromides 1a–e

Methyl aromatic compounds (toluene, 1-methylnaphthalene, 2-methylnaphthalene, 2-methylanthraquinone, and 2-ethylanthraquinone) (20 mmol), NBS (20 mmol), and azobisisobutyronitrile (AIBN) (3 mmol) were dissolved in CCl_4 (30 mL) and refluxed for 7 h. The crude product was obtained by filtration and purified by recrystallizing it in ethanol to give the corresponding arylmethyl bromides.

Synthetic Procedure of 2a–c

Arylmethyl bromides **1a–c** was dissolved in dry acetonitrile, ~30 mM, and placed in a Pyrex tube. The solution was bubbled with very pure nitrogen for 15 min and then was irradiated with a 300-W high-pressure lamp. The reaction followed by thin-layer chromatography (TLC). When TLC showed a maximum concentration of the Ritter product, the irradiation was stopped. The solvent in the reaction mixture was concentrated by rotary evaporation. The residue was subjected to TLC to get the crude product and further purified by recrystallization with petroleum ether to give **2a–c**.

Synthetic Procedure of 2d–e

Compounds **1d** (60 mg, 0.2 mmol) and **1e** (126 mg, 0.4 mmol) were dissolved in dry acetonitrile (20 mL) and placed in a flask. Under a nitrogen atmosphere, the solution was irradiated with a 500-W Xe lamp, and the reaction was followed by TLC. When TLC showed a maximum concentration of the Ritter product, the irradiation was stopped. The irradiated solution was concentrated. The residue was dissolved in dichloromethane (DCM) and subjected to column chromatography to give **2d** and **2e**.

Selected Data

N-Benzylacetamide (2a).[11] Irradiation for 3.5 h, yield 42%; $R_f = 0.31$ (petroleum ether/ethyl acetate 1:1); mp 60–62 °C; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 2.02$ (s, 3H, CH_3), 4.43 (d, $J = 5.4$ Hz, 2H, NHCH_2), 5.79 (b, 1H, NH), 7.26–7.36 (m, 5H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 170.1$ (C=O), 138.4, 128.8, 128.0, 127.6, 43.9 (CH_2), 23.3 (CH_3); IR (KBr): ν (cm^{-1}) = 3297s, 1644s, 1552s, 743m, 696m. TOFMS (EI) calcd. for (M^+) $C_9H_{11}NO$: 149.0841; found 149.0847.

1-(Acetamidomethyl)naphthalene (2b).[11b,12] Irradiation for 3 h, yield 42%; $R_f = 0.48$ (ethyl acetate); mp 124–126 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.00$ (s, 3H, CH_3), 4.88 (d, $J = 5.4$ Hz, 2H, NHCH_2), 5.70 (b, 1H, NH), 7.42–7.56 (m, 4H, H_{Ar}), 7.80–8.02 (m, 3H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 169.9$ (C=O), 134.0, 133.6, 131.5, 128.9, 128.7, 126.8, 126.7, 126.1, 125.5, 123.6, 41.9 (CH_2), 23.2 (CH_3); IR (KBr): ν (cm^{-1}) = 3278s, 1640s, 1558s, 1428m, 1371m 1294s, 1035m, 797s. TOFM (EI) calcd. for (M^+) $C_{13}H_{13}NO$: 199.0997; found 199.0996.

2-(Acetamidomethyl)naphthalene (2c).[11b] Irradiation for 2.5 h, yield 63%; $R_f = 0.43$ (ethyl acetate); mp 121–123 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.06$ (s, 3H, CH_3), 4.59 (d, $J = 4.5$ Hz, 2H, NHCH_2), 5.86 (b, 1H, NH), 7.38–7.51 (m, 3H, H_{Ar}), 7.71–7.83 (m, 4H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 170.2$ (C=O), 135.8, 133.5, 132.9, 128.7, 127.8, 126.5, 126.4, 126.1, 44.0 (CH_2), 23.4 (CH_3); IR (KBr): ν (cm^{-1}) = 3264s, 1640s, 1558s, 1434m, 1371m, 1291s, 1029m, 817s, 797s. TOFM (EI) calcd. for (M^+) $C_{13}H_{13}NO$: 199.0997; found 199.0991.

2-(Acetamidomethyl)anthraquinone (2d). Irradiation for 1 h, yield 72%; $R_f = 0.35$ (ethyl acetate); mp 226–228 °C; ^{1}H NMR (300 MHz, DMSO-d_6) $\delta = 1.93$ (s, 3H, CH_3), 4.45 (d, $J = 5.4$ Hz, 2H, NHCH_2), 7.78–8.23 (m, 7H, H_{Ar}), 8.59 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) $\delta = 182.5$(C=O), 182.2 (C=O), 169.6

(C=O), 147.0, 134.5(2C), 133.1, 133.0, 131.7, 127.0, 126.7(2C), 125.0, 42.0 (CH_2), 22.6 (CH_3); IR (KBr): ν (cm^{-1}) = 3437s, 1673s, 1592s, 1534s, 1332s, 1236m, 846m, 706s. TOFMS (EI) calcd. for (M^+) $C_{17}H_{13}NO_3$: 279.0895; found 279.0887.

2-(1-Acetamidoethyl)anthraquinone (2e). Irradiation for 3.5 h, yield 40%; $R_f = 0.4$ (ethyl acetate); mp 193–195 °C; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 1.56$ (d, $J = 6.9$ Hz, 3H, CH*CH$_3$*), 2.05 (s, 3H, $COCH_3$), 5.24 (quart, $J = 6.9$ Hz, 1H, NH*CH*CH_3), 5.87 (d, $J = 6.9$ Hz, 1H, *NH*CH), 7.73–7.82 (m, 3H, H_{Ar}), 8.23–8.31 (m, 4H, H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 182.6$ (C=O), 182.2 (C=O), 168.7 (C=O), 152.1, 134.6, 134.5, 133.2, 133.0, 132.3, 131.7, 127.2, 126.8, 126.7, 123.9, 48.0 (NH*CH*CH_3), 22.6 (CH_3), 22.0 (CH_3); IR (KBr): ν (cm^{-1}) = 1675s, 1591s, 1324s, 1284s, 931m, 711s. TOFMS (EI) calcd. for (M^+) $C_{18}H_{15}NO_3$: 293.1052; found 293.1059.

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