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Preparation, Reactivity and Tautomeric Preferences of Novel (1*H*-Quinolin-2-ylidene)propan-2-ones

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1,1-Difluoro-3-(1*H*-quinolin-2-ylidene)propan-2-one **1a**, 1,1,1-trifluoro-3-(1*H*-quinolin-2-ylidene)propan-2-one **1b**, 1,1,1-trifluoro-3-(4-chloro-1*H*-quinolin-2-ylidene)propan-2-one **1c** and 1,3-dibromo-1,1-difluoro-3-(2-quinolyl)propan-2-one **2** are prepared and characterized by various spectroscopic techniques. The crystal structure of **1a** is determined by X-ray diffraction. Furthermore, a series of previously known non-halogenated (1*H*-quinolin-2-ylidene)propan-2-ones **1d-1h** are oxidized with $AgBrO_3$ in the presence of $AlCl_3$. In all cases, 2-(1-bromo-1-chloromethyl)quinoline **3** is obtained in high yield. The bromination order and sites of **1a** are analyzed based on *ab initio* MP2 and DFT calculations for the molecule and its anions.

Keywords: 2-Ketomethylquinolines, Enaminones, Oxidation, Crystallography, GIAO calculations

INTRODUCTION

Enaminones are important organic intermediates and biologically active substances [1-3]. 2-Ketomethylquinolines are a class of enaminones [4]. Tautomerism has been observed for this class of compounds [5-7]. Some 2-ketomethylquinolines have been monobrominated with elemental bromine in the presence of anhydrous potassium acetate in glacial acetic acid [5,7] or in dichloromethane [8]. The resulting bromoketones were spontaneously oxidized by air in a dimethyl sulfoxide solution [5,10]. The bromate anion, BrO_3^-, is also a potential candidate for the oxidation of organic compounds and has been used in different media [11].

As a continuation of our previous work [5], we report here the syntheses and spectroscopic characterization of a new series of halogenated (1*H*-quinolyl-2-ylidene)propan-2- ones **1a-1c** and, for one congener **1a**, a single-crystal X-ray structural analysis. Furthermore, in order to clarify the reactivity of (1*H*-quinolyl-2-ylidene)propan-2-ones, some oxidation reactions have been performed.

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EXPERIMENTAL

Materials and Methods

Chemicals were purchased from Aldrich Chemical Company, and were used without further purification. Diethyl ether was distilled over $CaCl_2$/Na before use. Petroleum ether (pet. ether) was a distillate (40 and 60 °C). TLC was carried out using aluminium plates pre-coated with silica gel (Kieselgel 60 F256, 0.2 mm, Merck) and visualized using UV light. Silica gel (flash Kiesegel 60) was used for column chromatography. ^{1}H and ^{13}C NMR spectra were recorded at

the frequencies stated, using deuterated solvents as internal standards. Spectra were recorded at 300 MHz on a Bruker Avance BVT3200 spectrometer and at 500 MHz on a Bruker Avance DRX 500 or a Jeol spectrometer. Mass spectra were recorded on a Kratos MS80 RF spectrometer. Infrared spectra were recorded on a Nicolet 20-PC Fourier transform IR spectrometer and Shimatzu IR-435.

X-Ray Crystallographic Study

Crystal data: $C_{12}H_9F_2NO$, M = 221.2, monoclinic, space group $P2_1/c$, a = 4.3753 (9), b = 19.402 (3), c = 11.5506 (19) Å, β = 95.02 (2)°, V = 976.8 (3) Å^3, Z = 4, D_c = 1.504 g cm^{-3}, μ = 0.12 mm^{-1} (MoKα, λ = 0.71073 Å), T = 150 K. Of 16866 reflections measured on a Bruker-Nonius KappaCCD diffractometer, 1710 were unique (θ < 25°, R_{int} = 0.0337). The structure was solved by direct methods and refined on F^2 values. Hydrogen atoms were constrained with a riding model. R = 0.0358 (1403 F values, $F^2 > 2\delta$), R_w = 0.1098 (F^2 values, all data), final difference map within ±0.24 e Å^{-3}.

Software: standard Bruker-Nonius COLLECT, EvalCCD and SHELXTL.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary. Publication number CCDC 238108. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: 144-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Procedures

1,1-Difluoro-3-(1*H*-quinolin-2-ylidene)propan-2-one (1a). To a solution of 2-methylquinoline (10.0 mmol, 1.43 g) in dry diethyl ether (30 ml), *n*-butyllithium in hexane 2.5 M (12 mmol, 4.8 ml) was added. Ethyl difluoroacetate (12 mmol, 1.50 g) in dry ether (20 ml) was added drop wise to the dark red solution. The mixture was stirred at 35 °C for 22 h under an argon atmosphere. Water (50 ml) was added after cooling and the organic layer separated and dried ($MgSO_4$). Evaporation of the solvent gave a yellow oil. The resulting crude product was purified by flash chromatography, eluting with 50% ether/pet. ether. The yields of reactions were reported after purification. Yield: 0.8 g, 65%. Yellow crystals, m.p.: 95-97 °C (from ether); Anal. Calcd. for $C_{12}H_9F_2NO$: C, 65.16; H, 4.10; N, 6.33. Found: C, 65.68; H, 3.75; N, 6.50; GC-MS (EI) 222 found M^++1 (10%), 221, M^+ (75%), 170 (100%); IR (KBr): 1640.79 (C=O), 1615.00, 1594.65 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 15.43 (s, 1H, NH), 7.85(d 1H, J = 9.1 Hz, C_4H), 7.65-7.28 (m, 4H, aryl-H), 6.93 (d, 1H, J = 9.1 Hz, C_3H), 6.04 (d, 1H, J = 55.9 Hz, CHF_2), 5.76 (s, 1H, =CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 180.78 (C=O), 155.00 (C), 138.36 (CH), 136.00 (C), 132.12 (CH), 128.28 (CH), 125.24 (CH), 122.04 (C), 118.50 (CH), 111.46 (CH). 92.00 (CHF_2), 87.39 (=CH); ^{19}F NMR (500 MHz, $CDCl_3$): δ (ppm) 76.51, 55.61.

1,1,1-Trifluoro-3-(1*H*-quinolin-2-ylidene)propan-2-one (1b). This compound was prepared by following the method previously published by Kawase *et al* [12]. Yield: 0.5 g, 70%, m.p.: 120-122 °C (from ether). Orange crystals. GC-MS (EI) 240 found M^++1 (10%), 239, M^+ (90%), 170 (100%); IR (KBr): 1640.87 (C=O), 1613.35, 1591.54 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 15.35 (s, 1H, NH), 7.92 (d, 1H, J = 9.0 Hz, C_4H), 7.69-7.28 (m, 4H, aryl-H), 6.92 (d, 1H, J = 9.0 Hz, C_3H), 5.80 (s, 1H, =CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 178.34 (C=O), 155.54 (C), 139.03 (CH), 136.65 (C), 132.47 (CH), 128.41 (CH), 124.17 (CH), 121.86 (C), 118.50 (CH), 114.72 (CH). 92.00 (CF_3), 87.23 (=CH); ^{19}F NMR (500 MHz, $CDCl_3$): δ (ppm) 76.34, 76.52, 76.56.

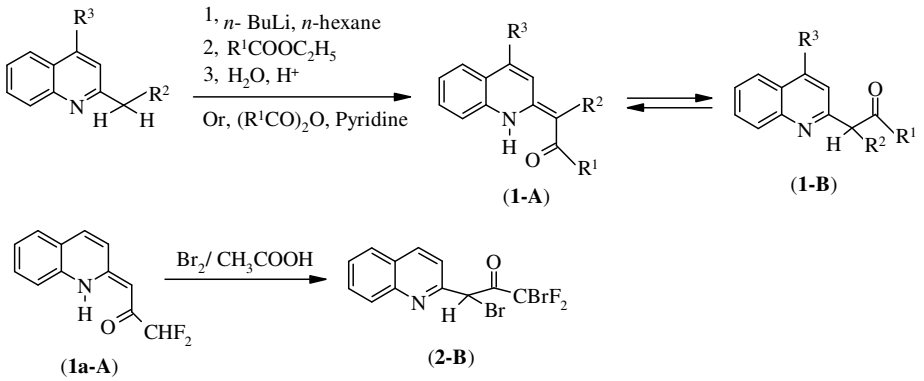
1,1,1-Trifluoro-3-(4-chloro-1*H*-quinolin-2-ylidene) propan-2-one (1c). This compound was prepared by following the Kawase method [12], using 4-chloro-2-methylquinoline (3 mmol, 0.533 g), TFA (9 mmol, 1.3 ml), pyridine (15 mmol, 1.2 ml) and benzene (8 ml). Yield: 0.6 g, 59%, m.p.: 122-124 °C (from ether). Orange crystals. GC-MS (EI) M^+ (68%), 204, M^+-CF_3 (100%). Anal. Calcd. For $C_{12}H_7ClF_3NO$: C, 52.67; H, 2.58; N, 5.12. Found: C, 52.21; H, 3.07; N, 5.35; IR (KBr): 1631.09 (C=O), 1590.04 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 15.21 (s, 1H, NH), 8.07-7.28 (m, 4H, aryl-H), 7.08 (s, 1H, C_3H), 5.75 (s, 1H, =CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 175.00 (C=O), 154.81 (C), 144.85 (C), 137.52 (C), 133.44 (CH), 126.24 (CH), 125.54 (CH), 121.19 (C), 118.82 (CH), 87.10 (=CH).

1,3-Dibromo-1,1-difluoro-3-(2-quinolyl)propan-2-one (2). Difluoro compound (**1a**) (0.5 mmol, 0111 g) was suspended in glacial acetic acid (3 ml) in a 10 ml flask. The mixture was then cooled as much as possible while avoiding the formation of crystals. Bromine (0.55 mmol, 0.09 g) was

added to this solution, which was kept at a temperature below 45 °C. The brominated product separated from the solution after about three-quarters of the bromine had been added. Excess bromine and acetic acid were removed by rotary evaporation after about 2 h of stirring. The crude product was washed with water and aqueous sodium hydrogen carbonate. The product was then purified *via* flash chromatography on a silica column, eluting with 20% ether/pet. ether and crystallization from 20% ethyl acetate/pet. ether. Yield: 85%, m.p.: 85 °C. White crystals. GC-MS (EI) 377, 379, 381, 383 found M^+ (5%), 300, M^+-Br (100%); IR (KBr): 1717 (C=O), 1684.53, 1615.46, 1587.20 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 5.96 (s, 1H, CHBr), 6.74 (s, 1H, C_3H), 7.18-8.11 (m, 4H, aryl-H), 8.47 (s, 1H, C_4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 180.17 (C=O), 158.96 (C), 145.47 (C), 138.62 (C), 134.65 (CH), 130.93 (CH), 129.15 (CH), 127.97 (C), 118.08 (CH), 41.83 (CHBr).

Typical procedure for 2-(1-Bromo-1-chloromethyl) quinoline (3). 1-(Quinolyliden-2-yl)-propan-2-one (0.4 mmol, 74 mg) was dissolved in dry acetonitrile (5 ml), to which $AgBrO_3$ (0.8 mmol, 190 mg) and $AlCl_3$ (0.4 mmol, 54 mg) were added. The mixture was refluxed for 3 h. The progress of the reaction was followed by TLC. After the reaction was complete, the mixture was filtered and the solvent was evaporated. The crude product was purified *via* flash chromatography on a silica column, eluting with 30% chloroform/carbon tetrachloride. Yield: 90%, m.p.: 70 °C. White crystals. GC-MS (EI) 257 M^+ (5%), 211, M^+-Cl (10%). UV λ_{max} (nm): 210 (216 000), 230 (524000); IR (KBr): 3000, 1600 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$): δ (ppm) 7.1 (s, 1H, CHBrCl), 7.5-8.4 (m, 6H, C_9H_6N). Anal. Calcd. For C_1H_7BrClN: C, 46.78; H, 2.72; N, 5.45. Found: C, 46.21; H, 3.07; N, 5.55.

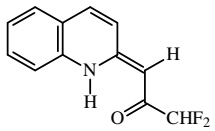
Gaussian 03 software [14] was used for all calculations. Diffuse functions were added to hydrogens and heavy atoms in all calculations. All five forms were calculated at B3LYP/6-31++G(d,p) and B3LYP/6-31++G(2df,2p) levels for geometry optimization. No geometry constraints were used for the optimization step. The chemical shifts for compound **1a** were calculated with the use of the GIAO (gauge-independent atomic orbitals) method for the tested molecule and for the reference-TMS [15].



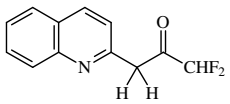
Scheme 1

Table 1. Substitutions on 2-ketomethylquinolines

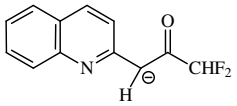
Compound	R^1	R^2	R^3	Ratio A:B
1a	CHF_2	H	H	100:00
1b	CF_3	H	H	100:00
1c	CF_3	H	Cl	100:00
2	$CBrF_2$	Br	H	00:100



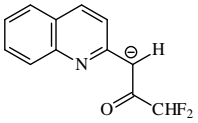
Enaminone form



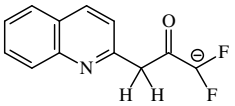
Ketoimino form



A-1



A-2



A-3

Scheme 2. Tautomers of **1a** and its anions formed by deprotonation

Table 2. The Relative Energies Calculated with the Use of B3LYP and *ab initio* MP2 Methods [kJ mol^{-1}]

Form	B3LYP/6-31++G(d,p)	B3LYP/6-31++G(2df,2p)	MP2/6-31++G(2df,2p)//B3LYP/6-31++G(2df,2p)
Enaminone	0	0	0
Ketoimine	43.86	45.61	22.25
A-1	1434.16	1439.60	1421.39
A-2	1465.57	1469.34	1453.98
A-3	1561.36	1565.80	1549.29
A	-792.4186435	-792.4587777	-790.6312239

A – the last row represents the lowest absolute energy of investigated forms [a.u.]

Table 3. Relative Energies of Anions Calculated with the Use of B3LYP and *ab initio* MP2 Methods [kJ mol^{-1}]

Form	B3LYP/6-31++G(d,p)	B3LYP/6-31++G(2df,2p)	MP2/6-31++G(2df,2p)//B3LYP/6-31++G(2df,2p)
A-1	0	0	0
A-2	31.40	29.74	32.59
A-3	127.19	126.21	127.90

RESULTS AND DISCUSSION

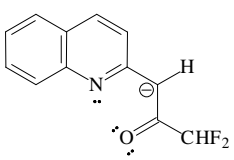
Compounds **1a-1c** (Scheme 1 and Table 1) were prepared as previously published: **1a** [5], **1b, 1c** [12] and compound **2** was prepared from the bromination of compound **1a** [5]. Substitutions (R^1, R^2, R^3) on 2-ketomeethylquinolines are presented in Table 1. Compound **1a**, which is a mixture of enaminone and ketoimino forms, is an appropriate derivative for the comparison of the acidities of the two α-hydrogens adjacent to the carbonyl group. The corresponding anion, after removal of a proton from the methylene group adjacent to the aromatic ring (in the ketoimino form) is stabilized by

resonance with the quiniline ring and the carbonyl group. The anion resulting from the deprotonation of the CHF_2-moiety is stabilized by two adjacent fluorine atoms. We calculated the relative energies of the two tautomeric forms of **1a** and the corresponding anions (Scheme 2). Results of these calculations are shown in Tables 2 and 3.

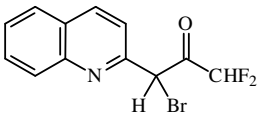
Table 2 shows that the enaminone is the predominant form in the enaminone-ketoimine tautomeric equilibrium. This result is in agreement with the experiment. However, the results suggest that the ketoimino form is the substrate for the deprotonation reaction, although the amount of this form may be less than 0.5% in $CHCl_3$ solution. The fact that the bromination at the benzylic position takes place in acetic acid solution is good evidence that the ketoimino form serves as the substrate. This can shift the tautomeric equilibrium to the ketoimino form, which is stabilized by salt formation with the quinoline nitrogen.

Deprotonation of the ketoimino form should produce A-1 or A-3 anions. The higher energy of the A-3 form compared to the A-1 form suggests that the A-1 form is the main deprotonation product and the $-CH_2-$ proton is more acidic than $-CHF_2$. The difference in energy between the A-1 and A-3 anions is due to the fact that the A-1 negative charge is delocalized over the 2-quinolyl and carbonyl parts, while the A-3 negative charge may be delocalized only on the carbonyl and fluorine atoms. This is the main reason for the lower energy of the A-1 anion. On the other hand, the A-2 anion resembles a deprotonated enamine form. The energy for deprotonation of the ketoimino form, giving the A-1 anion, is 1393.98 kJ mol^{-1} (B3LYP/6-31++G(2df,2p)) and the respective energy for obtaining the A-2 anion from the enaminone form is 1423.73 kJ mol^{-1}. These results show that it is much easier to remove a proton from the ketoimino methylene group than the NH proton of the enaminone form.

The A-1 and A-2 anions are rotamers of the same structure. The difference in energy between these structures is 29.74 kJ mol^{-1}. The higher energy of the A-2 form may be explained by electron repulsion in this anion.



We performed ^{13}C GIAO chemical shift calculations to verify our reasoning, as presented previously for a series of 2-phenacylpyridines [13]. The higher energy of the A-3 anion (127.19 kJ mol^{-1} higher than that of the A-1 anion) means that the first step of bromination should proceed *via* the formation of the monobromo compound shown below.



The next step is the substitution at the CHF_2 group. The energy of deprotonation of the CHF_2 group is 1482.03 kJ mol^{-1} if the above ketoimino form is taken as a reference. This is 35.47 kJ mol^{-1} lower than the deprotonation of the same group in compound **1a** (ketoimino form). These results suggest that the formation of **2** is a two-step reaction as described below:

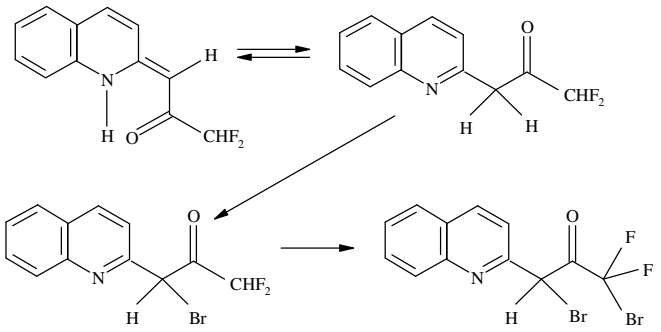


Table 4 shows the DFT/GIAO calculated and experimental ^{13}C NMR chemical shifts in ppm, referenced to TMS, for compound **1a** (enaminone form) according to the following numbering scheme:

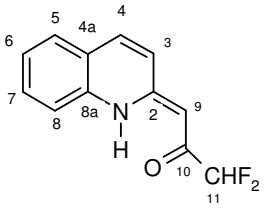
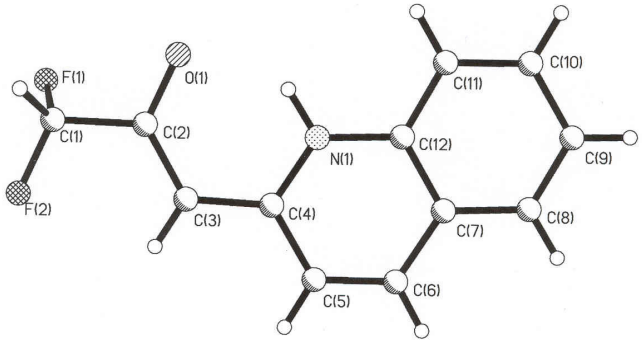


Table 4. Calculated (B3LYP/6-311G//HF/3-21G) and Experimental ^{13}C NMR Chemical Shifts for Compound **1a** (enaminone form) in ppm

Carbon No.	Calculated	Experimental
2	150.02	150.85
3	124.52	124.76
4	136.32	137.84
4a	123.71	123.53
8a	136.34	136.57
5	128.09	127.81
6	124.57	121.49
7	132.11	131.59
8	117.01	117.98
9	89.34	87.31
10	185.03	180.17
11	114.01	111.02

The corresponding correlation coefficient between calculated and experimental chemical shifts for the ketoimino form is 0.996. This provides additional evidence that this compound exists in the enaminone form. The correlation coefficient between experimental data and the ketoimino form calculated with the method given in Table 4 gives the value 0.955. This value is only slightly smaller, but the main criteria for distinguishing individual tautomers are the chemical shifts of C-9, C-10, and C-11. The calculated values for these carbons in the ketoimino form of **1a** are 132.00, 205.93, and 50.66 ppm, respectively.

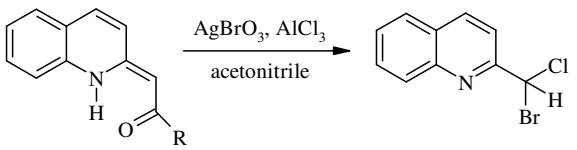
The X-ray crystal structure of **1a** shows that the enaminone form is the predominant one in the crystalline states.



1a

The starting materials **1d-1h** (Scheme 3) for the oxidation reaction with bromine anion have been prepared as previously published [4]. They were purified *via* silica column and recrystallized until a constant melting point was achieved.Surprisingly, all compounds **1d-1h**, (1 mmol) in the presence of silver bromate (1 mmol) and aluminum chloride (0.5 mmol) in acetonitrile were quantitatively oxidized to 2-(1-bromo-1-chloromethyl)quinoline **3** in an appropriate length of time, as shown in Table 5.

The ^1H NMR spectrum of 2-(1-bromo-1-chloromethyl)quinoline **3** shows a singlet at 7 ppm for a methine proton, while the singlet for =CH of the starting materials **1d-1h**, is observed in the range of 5.3-6.4 ppm. MS peaks related to molecular ions M (m/z = 255), M+2 and M+4 appeared in an intensity ratio of 1:1.3:0.3. The peaks at m/z = 176 and 178 (3:1) arise from the cleavage of the carbon-bromine bond and the peak at m/z = 140 from the cleavage of



1d-1h **3**

Scheme 3. R = CN **1d**, Me **1e**, Et **1f**, Pyridyl **1g** and Ph **1h**

Table 5. Reaction Times for Compounds **1d-1h**

Substituent	**1d**	**1e**	**1f**	**1g**	**1h**
R	CN	Me	Et	Py	Ph
Time (min)	45	180	30	120	30

the carbon-chlorine bond.

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