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Direct, simple and efficient iodination of some α-aroyl ketene dithioacetal derivatives using iodic acid

Girish Deshmukh, Sarla Kalyankar* and Mohan Kalyankar

P. G. Research Center Department of Chemistry, Yeshwant Mahavidyalaya, Nanded, Maharashtra, India

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ABSTRACT

Direct, Simple and efficient and iodination of some α- aroyl ketene dithioacetals derivatives using iodine and iodic acid in a particular proportion. This combination yields iodinated products of some α- aroyl ketene dithioacetals in very short reaction time.

Keywords: α-aroyl ketene dithioacetals , iodine , iodic acid , Ethanol.

INTRODUCTION

The iodination of aromatic compounds is an important reaction in organic synthesis. Aromatic iodides are generally more reactive than their respective bromides and chlorides. For the synthesis of various iodoaromatic compounds several methods have been described in the literature using different reagent. As iodination is concerned these Ketene dithioacetals can be classified on the basis of their substitution patterns at the α-position of the ketene dithioacetal functionality [1-3]. For instance, α-oxo ketene dithioacetals, which bear a carbonyl group at the α-C atom, are versatile intermediates in organic synthesis and their preparation and diverse applications, especially serving as 1,3-electrophilic three- carbon synthones have been reported [4-7]. Based on the structural features, the α-C of ketene dithioacetals is reactive towards electrophiles and this electrophilic susceptibility makes the functionalization of ketene dithioacetals a convenient tool for the construction of diverse ketene dithioacetal scaffolds and other useful building blocks [8-9]. These arylketones are well known for their use, as a building block for the synthesis of various pharmaceutical and pharmacologically important compounds [10-11]. Iodination of aromatic compounds is an electrophilic substitution reaction with wide range of application in organic synthesis, particularly in the synthesis of pharmaceuticals [12-13].

In recent years, iodoaromatic compounds have assumed increasing importance in organic synthesis because, iodine being more reactive than the respective bromides and chlorides. More over they are able to form a large variety of stable aromatic polyvalent iodine compounds, which have found increasing significance in modern synthesis procedure [14-16].

The Substituted α-Aroylketene Dithioacetals derivatives with iodination possess so many application in pharmaceuticals such as antitumor, anticancer, antibacterials, fungicidal, herbicidal and also plant growth regulators [17-18].

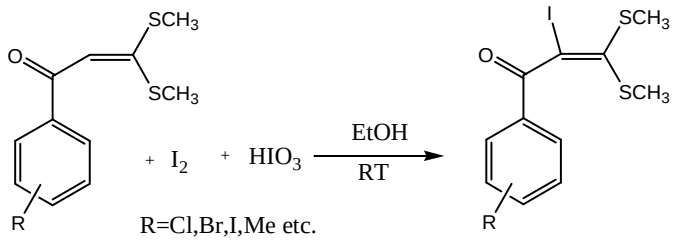
The iodination of organic compounds by using number of reagent like iodine, hypoiodous acid, iodinium ion, hypoiodous aecidium ion, iodine acetate , iodine monochloride and N-iodosuccinimide are more effective [19-21].

The Substituted α-Aroylketene Dithioacetals derivatives we will synthesise by the reported method . We are interested to investigate the kinetics of iodination of Substituted α-Aroylketene Dithioacetals derivatives by using iodine and iodic acid there are number of iodinating reagent but that are toxic, expensive and generates hazardous waste. The iodine and iodic acid is efficient solid iodinating agent which has no hazardous effect and are ecofriendly [22-24].

MATERIALS AND METHODS

IR spectra were recorded on a Shimadzu FTIR using KBr discs. 1H NMR spectra were recorded in DMSO-d6 at 400 MHz using TMS as an internal standard. Mass spectra were recorded on Shimadzu GC-MS using electrospray ionization technique. The elemental analysis was carried out on Flash EA-1112, 50/60 Hz, CHNS analyzer. The progress of the reactions was monitored by TLC.

Substrate (0.05 mol.), iodine (0.02 mol) were dissolved in ethyl alcohol (15 ml) and solution was heated to 35 ^{0}C. To this hot solution, iodic acid (0.01 mol.) in minimum amount of water was added and reaction mixture stirred for one to one and half hour or till solid separate out. Separated solid was treated with saturated sodium thiosulphate to decompose traces of unreacted iodine. Solid obtained was washed with water and crystallized from ethanol.



Scheme: Iodination of α-aroyl ketene dithioacetal

RESULTS AND DISCUSSION

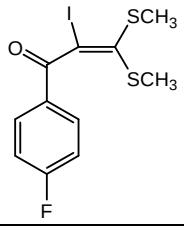
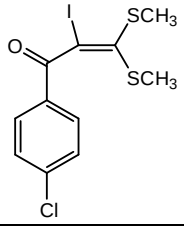
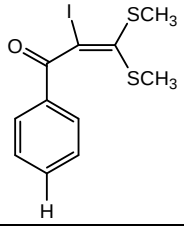
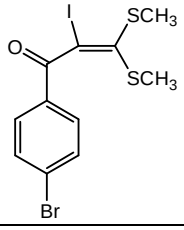
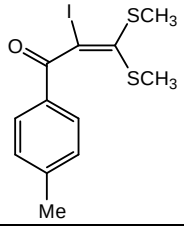
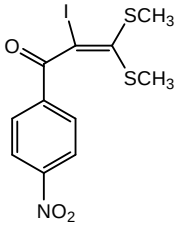
Due to poor electrophilic strength of iodine, direct iodination of aromatic compound with iodine is difficult and requires the presence of an activated agents in order to produce a strongly electrophilic I^+ species .In combination of iodine and iodic acid reagent, the iodic acid was dissolved in to the water to produce H_3O^+ and IO^{-3} to facilitate the oxidation of diiodine by HIO3 and to produce the I+ species. In the table given above formation of some iodinated α-aroyl ketene dithioacetal with reaction time, yield and melting point is given from that we can conclude about it.

1) 1-(4-fluorophenyl)-2-iodo-3,3bis(methylthio) prop-2-en-1-one:
Reddish brown Solid, IR (KBr): 3049, 2925 ,1631, 1222, 1202, 531 cm^{-1}; ^{1}H NMR(DMSO) :7.31(d, 1H), 7.25(d, 1H), 2.50(s, 6H) ; ^{13}C NMR (DMSO) :187.4,166.3,133.1,111.5,107.7,19.5 ; Mass (m/z): 367.4($m^{+\cdot}$), 369.3(m+2); $C_{11}H_{10}FIOS_2$, C-35.87, H-2.75, F-5.18, I-34.42, O-4.36, S- 17.43.

2) 1-(4-chlorophenyl)- 2-iodo-3,3 bis (methylthio) prop-2-en-1-one:
Yellow Solid, IR (KBr): 3031, 2918 ,1688, 1238, 775, 585, 474 cm^{-1}; ^{1}H NMR(DMSO) :7.71(d, 1H), 7.51(d, 1H), 2.34(s, 6H) ; ^{13}C NMR (DMSO) :182.7,168.3,138.2,107.9,16.9 ; Mass (m/z): 383.7($m^{+\cdot}$), 385.8(m+2) ; $C_{11}H_{10}ClIOS_2$,C-34.32, H-2.64, Cl-9.24,I-33.01,O- 4.15, S- 16.67.

3) 2-iodo-3,3 bis(methylthio)-1-phenylprop-2-en-1-one:
Brown Solid, IR (KBr): 3059, 2928 ,1678, 1241, 782, 592 cm^{-1}; ^{1}H NMR(DMSO) :7.76(d, 1H), 7.41(t, 1H) 7.43(t, 1H), 2.21(s, 6H) ; ^{13}C NMR (DMSO) :190.6, 172.2,131.8,123.8,109.5,18.2 ; Mass (m/z): 349.8($m^{+\cdot}$) ; $C_{11}H_{11}IOS_2$,C-37.73, H-3.18, I-36.24,O-4.55, S- 18.31.

Table: 1

Sr. No.	Product	Reaction Time (hr.)	Melting Point (^{0}C)	Yield (%)
1.		1-1.5	89.3	62
2.		1-2	91.6	70
3.		1-2	92.7	63
4.		1-1.5	90.9	74
5.		1-2	92.6	69
6.		2-3	88.5	68

4) 1-(4-bromophenyl)- 2-iodo-3,3 bis(methylthio) prop-2-en-1-one:
Dark Brown Solid, IR (KBr): 3067, 2923 ,1678, 1241, 551, 463 cm^{-1}; ^{1}H NMR(DMSO):7.48(d, 1H), 7.33(d, 1H), 2.42(s, 6H) ; ^{13}C NMR (DMSO) :190.3,169.1,129.8,131.8,18.7 ; Mass (m/z):429.9($m^{+\cdot}$),431.7(m+2) ; $C_{11}H_{10}BrIOS_2$,C-30.79, H-2.38, Br-18.59,I-29.55,O-3.75, S- 14.94.

5) 2-iodo-3,3 bis(methylthio)-1-p-tolylprop-2-en-1-one:
Brown Solid, IR (KBr): 3122, 2869 ,1710, 1301, 768, 589, 457 cm^{-1}; ^{1}H NMR(DMSO) :7.48(d, 1H), 7.22(d, 1H), 2.29(s, 6H), 2.33(s, 3H) ; ^{13}C NMR (DMSO) :191.5, 167.8, 139.4, 133.4, 105.6, 18.1 ; Mass (m/z): 363.5($m^{+\cdot}$) ; $C_{12}H_{13}IOS_2$,C-39.54, H-3.63, I-34.86, O-4.36, S- 17.62.

6) 2-iodo-3,3 bis(methylthio)-1-(4-nitrophenyl) prop-2-en-1-one:
Red Solid, IR (KBr): 3039, 2899 ,1714, 1247, 787, 591, 478 cm^{-1}; ^{1}H NMR(DMSO) :7.67(d, 1H), 7.35(d, 1H), 2.28(s, 6H) ; ^{13}C NMR (DMSO) : 192.2, 168.2, 152.8, 131.9,110.7, 19.4 ; Mass (m/z): 394.4($m^{+\cdot}$) ; $C_{11}H_{10}INO_3S_2$,C-33.41, H-2.57, I-32.12, O-12.15, S- 16.24.

CONCLUSION

In summary, a convenient and very simple method of iodination of substituted α- aroyl ketene dithioacetals is given in details. As this method uses alcohol as a solvent hence non hazardous in nature or environment friendly. Also reaction time is very less for this process without the use of any catalyst.

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