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Halogenation of 1,5-Diketones

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Abstract—Published and experimental data of authors on halogenation of 1,5-diketones from acyclic (among them chalcogen-containing), semicyclic and bicyclic series resulting in formation of mono-, di-, tri-, and tertahalosubstituted 1,5-dioxo compounds, pyrylium halides, and their fused analogs or aroylfurans are reviewed.

Much research was dedicated to the chemistry of 1,5-diketones. This type compounds attracted interest already to the end of XIX century as show works of Knoevenagel, Rabe, Kostanetsky and others [1, 2]. At present a number of scientific schools systematically develop the synthetic procedures for 1,5-diketones and investigate their properties in Russia, Japan, France, Italy, and Czechia [1, 2].

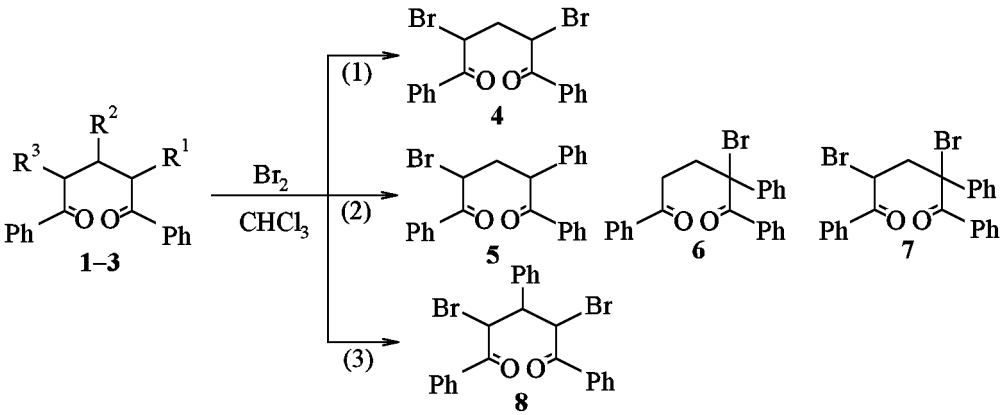
The location of carbonyl groups in 1,5-diketones imparts them valuable properties: ready carbocyclization [3], heterocyclization [2, 4] furnishing five- and six-membered mono- and polycyclic compounds containing heterocycles with oxygen, nitrogen, sulfur, phosphorus, and selenium [2, 4–6] when treated with acids and nucleophilic reagents.

Unlike nucleophilic reactions the electrophilic processes involving 1,5-diketones are less understood and are not summarized in publications. Among electrophilic reactions of 1,5-diketones may be cited, in particular, reactions with halogens and halogenating agents. Introduction of halogens in the structure of 1,5-diketones supplies to the 1,5-dicarbonyl compounds new features and extends their synthetic opportunities.

BROMINATION OF 1,5-DIKETONES

First publications on halogenation reported the bromination of arylaliphatic 1,5-diketones [1–3]. Therewith mono- and dibromo-substituted 1,5-diphenyl, 1,2,5- and 1,3,5-triphenylpentane-1,5-diones were obtained [7–9]. However the structure of bromo-substituted 1,5-diketones was confirmed only by elemental analyses.

Simalty and Caretto [1], and also Katritzky et al [11] showed the possibility of formation from acyclic 1,5-diketones at bromination and iodination in acetic acid of pyrylium bromides and periodides.



1, 4, $R^1 = R^2 = R^3 = H$; **2, 5–7,** $R^1 = Ph$, $R^2 = R^3 = H$; **3, 8**, $R^1 = R^3 = H$, $R^2 = Ph$.

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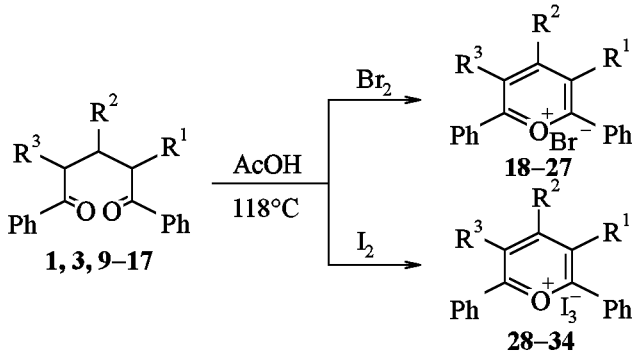
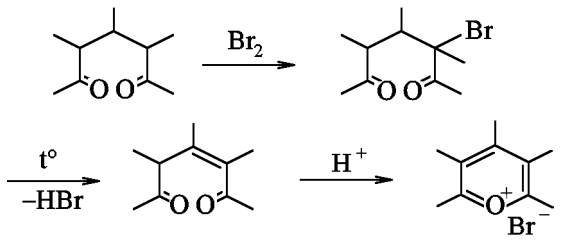


1, 3, 9–17 **18–27** **28–34**

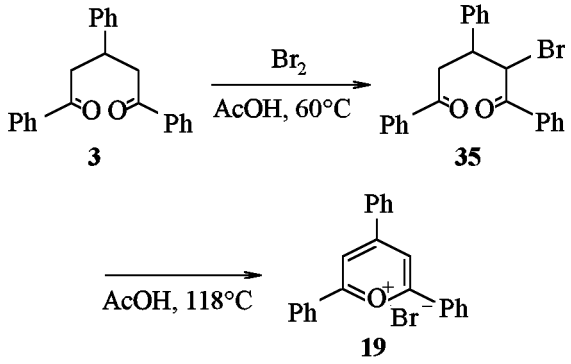
1, 18, 29, $R^1 = R^2 = R^3 =$ H; 3, 19, 30, $R^1 = R^3 =$ H, $R^2 =$ Ph; **9, 20, 31,** $R^1 = R^3 =$ Ph, $R^2 =$ H; **10, 21, 32,** $R^1 = R^2 = R^3 =$ Ph; **11, 28**, $R^1 = R^3 =$ Me, $R^2 =$ H; **12, 22, 33,** $R^1 = R^3 =$ H, $R^2 =$ COOH; **13, 23, 34,** $R^1 = R^3 =$ H, $R^2 =$ COOEt; **14, 24,** $R^1 = R^3 =$ Ph, $R^2 = 4\text{-ClC}_6\text{H}_4$; **15, 25,** $R^1 = R^3 =$ Ph, $R^2 = 4\text{-MeOC}_6\text{H}_4$; 16, 26, $\mathbf{R^1 = R^3 = Ph, R^2 = 2\text{-ClC}_6\text{H}_4}$; **17, 27,** $R^1 = R^3 =$ Ph, $R^2 = 2\text{-MeC}_6\text{H}_4$.

The bromination conditions (temperature, solvent) govern to significant extent the direction of the reaction.

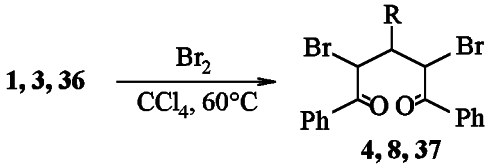
As shown in [10], 1,5-diketones when treated with bromine afford monobrominated derivatives which at heating in acetic acid eliminate hydrogen bromide to furnish unsaturated 1,5-dioxo compounds. The latter readily undergo cyclization into pyrylium bromides. The increasing of steric bulk of substituents does not hamper hydrogen bromide elimination and does not reduce the yield of salts;



The assumed mechanism is confirmed by isolation of 2-bromo-1,3,5-triphenylpentane-1,5-dione (**35**) at bromination of 1,3,5-triphenylpentane-1,5-dione (**3**) at 60°C. The brominated compound **35** heated to 118°C in acetic acid transformed into bromide **19** [12].

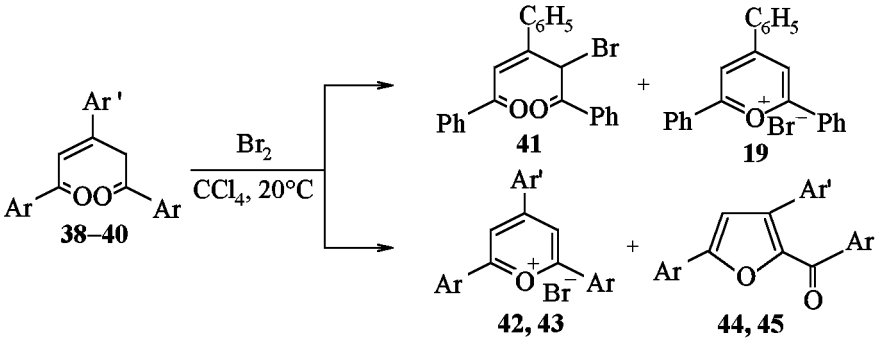


In tetrachloromethane occurred electrophilic substitution of hydrogen atoms in the α,α'-positions with respect to carbonyl function of the dioxo compounds **1, 3, 36** [12].



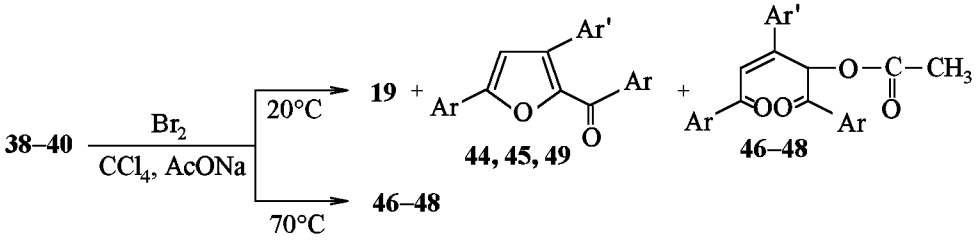
36, 37, R = Me.

In the first publication on bromination of unsaturated diketones only formation of pyrylium bromides was reported [13]. It was shown later that with unsaturated analogs of acyclic dicarbonyl compounds, 1,3,5-triarylpent-2-ene-1,5-diones even under mild conditions (20°C) the bromination takes concurrent routes [14, 15].



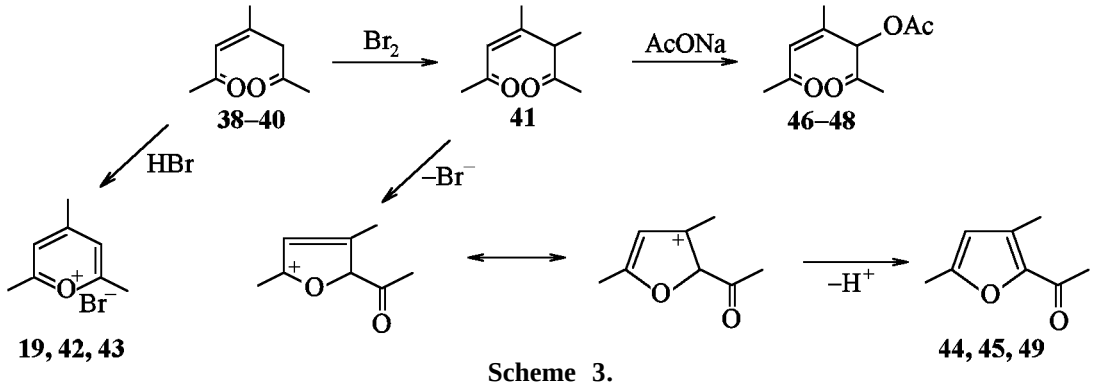
38, Ar = Ar' = Ph; **39, 42, 44**, Ar = Ph, Ar' = $4\text{-ClC}_6\text{H}_4$; 40, 43, 45, Ar = $4\text{-ClC}_6\text{H}_4$, Ar' = Ph.

Scheme 1.

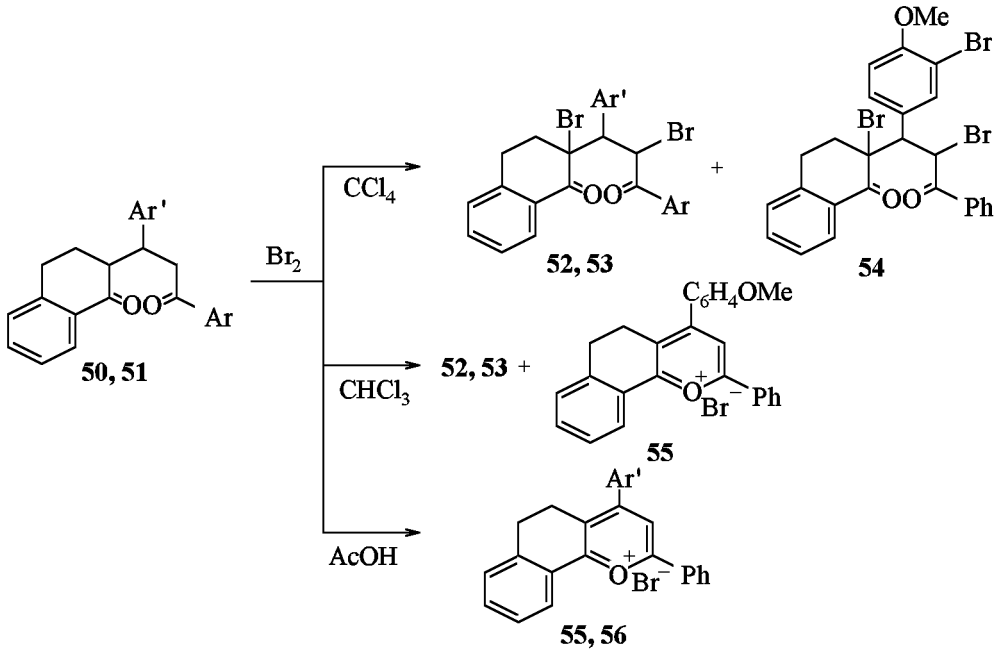


46, 49, Ar = Ar' = Ph; 47, Ar = Ph, Ar' = 4-ClC_6H_4; **48**, Ar = 4-ClC_6H_4, Ar' = Ph.

Scheme 2.



Scheme 3.



Only at bromination of diketone **38** was isolated in 34% yield 4-bromopent-2-ene-1,5-dione (**41**). Alongside this product in 50% yield was obtained pyrylium bromide **19**. In reactions of diketones **39, 40** a new reaction path was observed resulting in aroylfurans **44, 45**. Carrying out bromination in the presence of four-fold molar excess of sodium acetate hampered salts formation or prevented it [14] and favored an exchange process: nucleophilic substitution of bromine at C^4 atom by acetoxy group providing 4-acetoxy-1,3,5-triphenylpent-2-ene-1,5-diones **46–48**. At heating the reaction mixture to 70°C the yield of the latter compounds attained 79% [14] (Scheme 1).

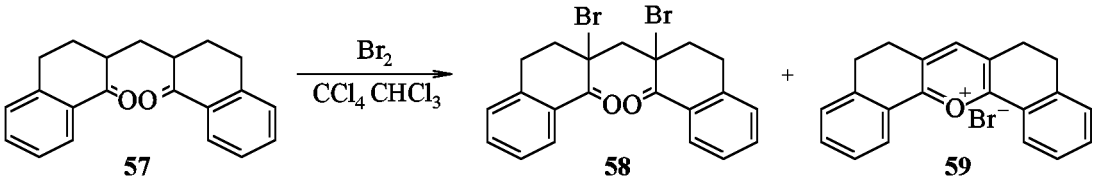
The generation of aroylfurans **44, 45, 49** is caused by intramolecular cyclization of bromine-substituted unsaturated dioxo compounds with participation of a labile bromine and a conjugated carbonyl group (Scheme 2).

The bromination of semicyclic 1.5-diketones was studied by an example of 2-(1,3-diarylpropan-3-on-1-yl)tetrahydronaphthalenones (**50, 51**) which furnished in tetrachloromethane the corresponding α,α'-dibromo-1,5-diketones (**52, 52**) [16] (Scheme 3).

The reaction mechanism is understood as electrophilic addition of bromine to the double bonds of the enol forms of substrate followed by dehydrobromination. When diketone **51** has in the side chain a 4-methoxyphenyl substituent alongside dibromodiketone **53** arises tribromo-substituted diketone **54**. Thus the electron-donor methoxyphenyl group favors electrophilic bromination of the substituent. In chloroform the yields of dibromodiketones **52, 53** increase. and the bromination of the methoxyphenyl substituent does not occur. In the reaction mixture was detected 2-phenyl-4-(4-methoxyphenyl)-7,8-benzo-5,6-dihydrochromylium bromide **55** that was not isolated in pure state [16, 17]. In acetic acid as solvent and at heating to 118°C formed only benzodihydrochromylium bromides **55, 56**. The latter apparently are generated in the acetic acid similarly to the acyclic analogs through heterocyclization of unsaturated diketones arising at dehydrobromination of monobromoderivatives of 1,5-diketones.

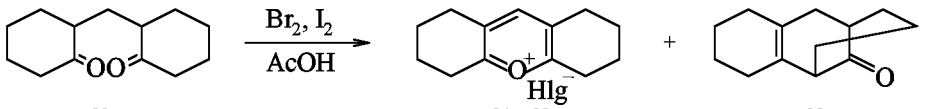
It was found that bromination of methylenebis-2,2'-(1,2,3,4-tetrahydronaphthalen-1-one) (**57**) in tetrachloromethane and chloroform gave rise to α,α'-dibromodiketone **58** (26–52%). In the latter case 1,2,7,8-dibenzo-3,4,5,6-tetrahydroxanthylium bromide (**59**) was isolated in 14% yield (Scheme 4) [16, 17].

Scheme 4.



57 **58** **59**

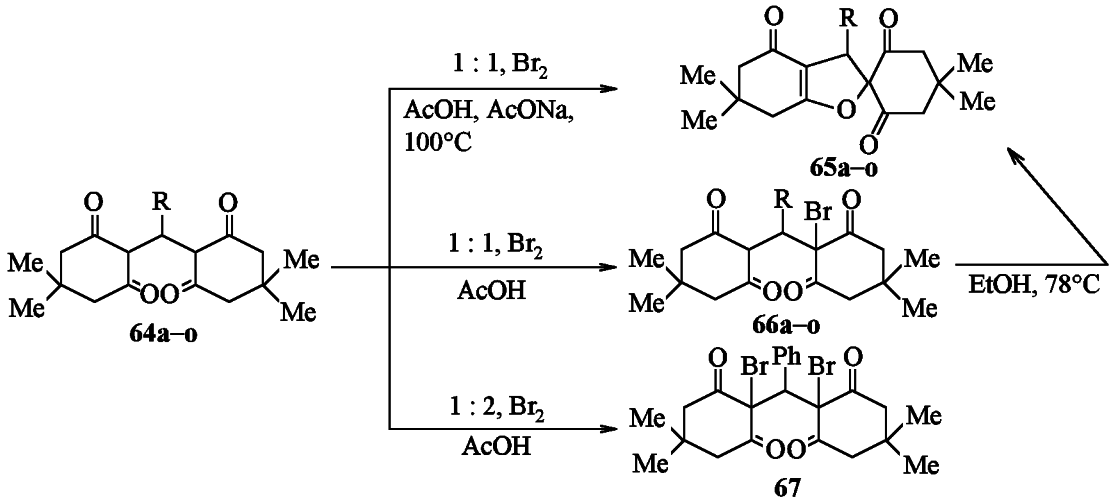
Scheme 5.



60 **61, 62** **63**

Hlg = Br (**61**), I (**62**).

Scheme 6.



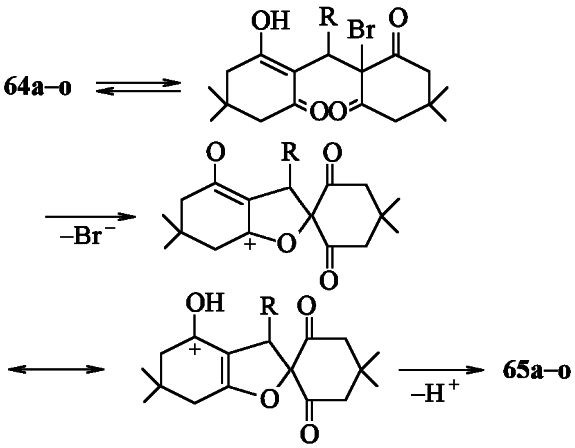
64a–o **65a–o** **66a–o** **67**

64, 65, 66: R = H (**a**), Me (**b**), Et (**c**), *i*-Bu (**d**), Ph (**e**), 2-$NO_2C_6H_4$ (**f**), 3-$NO_2C_6H_4$ (**g**), 4-$NO_2C_6H_4$ (**h**), 4-$MeOC_6H_4$ (**i**), 2-$MeOC_6H_4$ (**j**), 4-$Me_3NC_6H_4^+$ (**k**), 4-$(ClCH_2CH_2)NC_6H_4$ (**l**), 4-$(ClCH_2CH_2)$N-2-MeC_6H_3 (**m**).

The bromination and iodination of methylenebiscyclohexanone (**60**) in acetic acid at 18°C gave rise to symm.-octahydroxanthylium halides **61, 62** alongside tricyclic unsaturated ketone **63** (Scheme 5) [18, 19].

Bicyclic dioxo-1,5-diketones **64a–m** treated with bromine at 1:1 ratio either in acetic acid in the presence of sodium acetate or in benzene with triethylamine transformed in 50–93% yield into spiro derivatives of dihydrofuran **65a–m** [20]. In the absence of sodium acetate the monobromoxo compounds **66a–m** were successfully isolated that on recrystallization provided spiro compounds **65a–m**. At the reagents ratio compound **64e** to bromine equal to 1:2 dibromo derivative **67** was obtained that was more stable than the monobrominated analog (Scheme 6) [20].

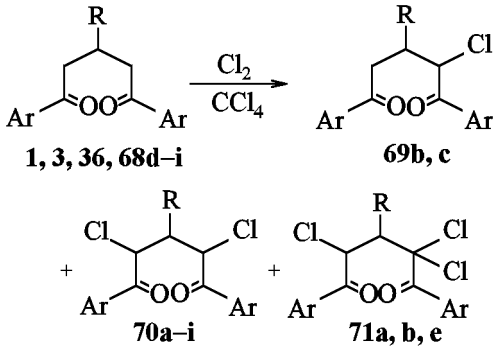
Formation of spiro compounds **65a–m** can be represented as follows:



The cited data on bromination and iodination of acyclic, semicyclic, and bicyclic 1,5-diketones demonstrate the decisive role of the substrate nature and certain influence of reaction conditions on the direction and character of the halogenation process.

CHLORINATION OF 1,5-DIKETONES

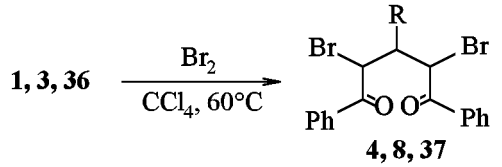
The chlorination of 1,5-diketones is in some respects different from bromination and iodination due to the nature of the reagent. The chlorination proceeds less actively apparently because chlorine is less prone to ionization. The primary reaction products, monochloro derivatives of 1,5-dioxo compounds, are a lot more stable than the monobromo derivatives where the bromine atom is highly labile. The latter fact results in occurrence of number of concurrent processes, in particular of heterocyclization of 1,5-diketones into pyrylium bromides and their fused analogs. Acyclic 1,5-diketones **1, 3, 36, 68d–i**) at chlorination in tetrachloromethane yield mono-, di-, and trichloro-substituted pentane-1,5-diones **69b, 70a–i, 71a, b, e** [12, 21]. Therewith the main chlorination products of 1,5-di- and 1,3,5-trisubstituted diketones **1, 3, 36, 68d–i** are 2,4-dichloropentane-1,5-diones **70a–i**. Sometimes it is possible to isolate mono- (**69b, c**) and trichloro (**71a, b, e**) derivatives of the dioxo compounds.



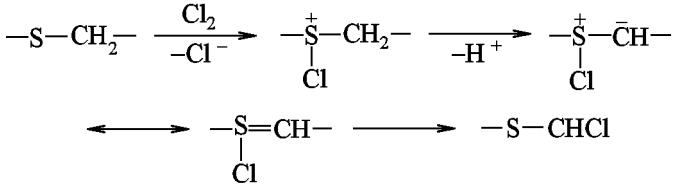
1, 70a, 71a, Ar = Ph, R = H; **3, 69b, 70b, 71b**, Ar = R = Ph; **36, 69c, 70c**, Ar = Ph, R = Me; **68d, 70d**, Ar = Ph, R = 4-$MeOC_6H_4$; **68e, 70e, 71e**, Ar = 4-ClC_6H_4, R = H; **68f, 70f**, Ar = 4-$MeOC_6H_4$, R = H; **68g, 70g**, Ar = 4-$MeOC_6H_4$; **68h, 70h,** Ar = R = 4-$MeOC_6H_4$; **68i, 70i**, Ar = Ph, R = 4-$MeOC_6H_4$.

1,5-Diphenyl- and 3-methyl-1,5-diphenylpentane-1,5-diones (**1, 36**) do not change at several hours of contact with chlorine in tetrachloromethane: This fact suggests that trichloro-substituted diketones (**71a, b, e**) originate from chlorination of gem-dichloropentane-1,5 diones.

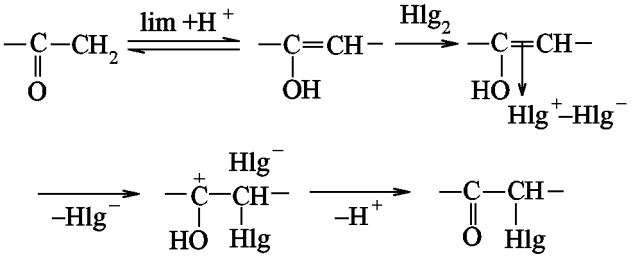
Trichloro-substituted 1,5-diketones **73** are readily obtained at chlorination of 1,5-diphenyl-3-thiapentane-1,5-dione (**72**). The reaction stops only after introduction of three chlorine atoms into the molecule. No salt formation is observed [21].



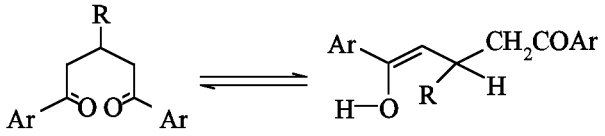
This reaction mode is due to participation of sulfur in chlorine transfer [22, 23].



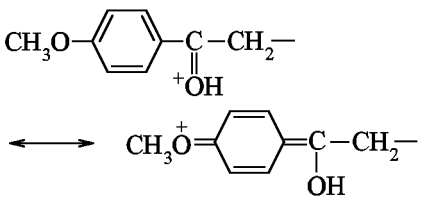
The halogenation of 1,5-diketones is an electrophilic process [12, 21] and analogous to monoketones includes an enolization stage and formation of π and σ-complexes, therefore the number and bulk of substituents in 1,5-diketones affects the duration of their chlorination.



For instance, 1,5-diphenyl- and 3-methyl-1,5-diphenylpentane-1,5-diones (**1, 36**) are more active in reaction with chlorine than 1,3,5-triaryl-substituted 1,5-diketones **3, 68d, f, h** (4–8 and 39 h respectively). Apparently the enolization of each carbonyl group that is the limiting stage of reaction requires approach of enol hydroxy group to the substituent at the third carbon atom of the diketone, and this involves steric hindrances.

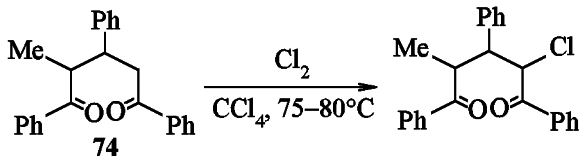


As a result on displacing R = H, Me by R = Ar the energy of 1,3-interaction between the oxygen atoms and the substituent in enol grows, decreasing the enol concentration and the chlorination rate. In diketones **68h, i** operate apparently also electronic factors. The methoxyphenyl substituent favors delocalization of the positive charge in the protonated form of 1,5-diketones **68h, i** thus hampering proton cleavage from the α-position and enol formation [21].



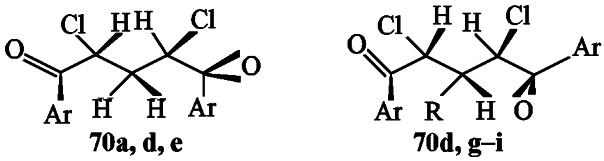
In chlorophenyl substituents attached to C^1 and C^5 of diketone **68e** the chlorine atom due to its negative inductive effect reduces the ability of carbonyl groups to get protonated and then to enolize.

The presence of a methyl group in the α-position to a carbonyl prevents substitution of hydrogen by chlorine at this carbon atom. Therefore diketone (**74**) affords 2-methyl-1,3,5-triphenyl-4-chloropentane-1,5-dione in 93% yield [12, 21].



2,4-Dimethyl-1,5-diphenylpentane-1,5-dione (**11**) does not react with chlorine [12].

It was established that chlorine and carbonyl group in 1,5-disubstituted 2,4-dichloropentane-1,5-diones **70a, e, f** are present in eclipsed conformation characteristic of acyclic α-chloroketones [25].



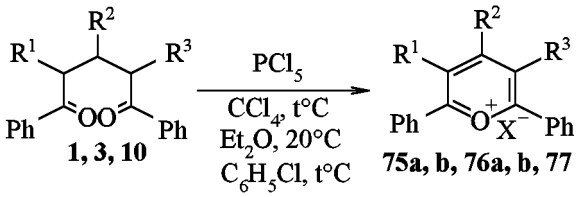
In 1,3,5-substituted 2,4-dichloroketones **70d, g, i** oxygen and chlorine atoms at C^1 and C^2 are mutually eclipsed, the C^5=O bond is in eclipsed conformation with respect to C^4–C^3 bond, but not with C^4–Cl bond as confirmed by the data of ^{1}H NMR [12, 21] and ^{13}C NMR spectroscopy [21], and also by X-ray diffraction study [26]. This structure is due to spatial factors: by the presence or absence of a substituent at the C^3 atom of the aliphatic chain of the 1,5-diketone. This substituent can prevent one carbonyl group to take eclipsed position with respect to chlorine atom. Therewith all dichloropentanediones **70a–i** are threo-isomers with respect to position of chlorine atoms [12, 21].

The diketones can be chlorinated with benzyltrimethylammonium dichloroiodate and iodobenzene dichloride. Therewith the stereoselectivity and direction of the process depend both on the character of the chlorinating agent and the conditions of the reaction (Scheme 7) [27].

Unusual character of reaction with phosphorus pentachloride was observed with pentane-1,5-dione and 3-chalcogen-containing pentane-1,5-diones. The structure and reactivity of phosphorus pentachloride depended on the reaction conditions [28, 29].

Monoketones of aliphatic series with PCl_5 yield gem-dichlorides or vinyl chlorides [29]. 1,5-Diketones **1, 3** in tetrachloromethane [30] and diketone **10** in chlorobenzene [31] were converted respectively in pyrylium chlorides **75a, 76a** and chloride-hydrochlorides **77**.

At the use of anhydrous ethyl ether instead of trichloromethane formed pyrylium chlorophosphates **75b, 78b** [32].



1, 75a, b, $R^1 = R^2 = R^3 = H$, X = Cl (**a**), Cl 0.5 PCl_5 (**b**); **3, 76a, b**, $R^1 = R^3 = H$, $R^2 = Ph$; X = Cl (**a**), Cl 0.5PCl_5 (**b**); **10, 77**, $R^1 = R^2 = R^3 = Ph$, X = Cl–HCl.

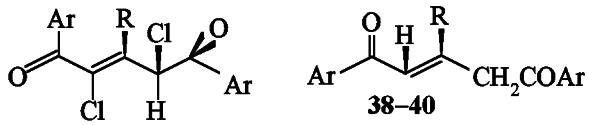
3-Thia(selena)pentane-1,5-diones **72, 78** react with phosphorus pentachloride in dichloromethane at the heteroatom. Therewith the sulfur-containing diketones **72a–c** undergo rearrangement in the course of reaction providing α-chloro derivatives **79a–c, 80**), whereas the selenium-containing analog **78** gives rise to a stable product of attack on the heteroatom [81] that can be isolated. The latter in acetic anhydride undergoes rearrangement into an α-chloro-substituted diketone **82** (Scheme 8) [32].

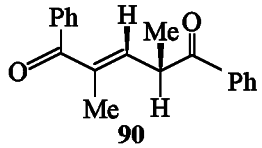
The presumable reaction mechanism is shown on the Scheme 9.

The features of chlorination were studied of unsaturated arylaliphatic 1,5-diketones that exclusively readily underwent heterocyclization into pyrylium salts under mild conditions [33, 34]. For instance, pent-2-ene-1,5-dione **38** in contrast to the saturated analog already at 20°C afforded a mixture of 2,4-dichloropent-2-ene-1,5-dione **83** and pyrylium chloride **84** (Scheme 10).

To suppress salt formation occurring due to hydrogen chloride liberation sodium acetate should be added to the reaction mixture. In this case the chlorination is selective, and dichlorodiketone (**83**) is obtained in 80% yield. Under similar conditions were obtained in hugh yields (72–80%) dichlorodiketones (**85, 86**) [33]. The chlorination of diketones (**38–40**) at 70°C within 2 h gave rise to 2,4,4-trichloropent-2-ene-1,5-diones (**87–89**) in 73–77% yield [15].

The data of IR, ^1H and ^{13}C NMR spectroscopy showed that the aryl-substituted dichloropentenediones (**83, 85, 86**) exist predominantly as *trans-S-trans*-isomers with eclipsed conformation of C=O and C–Cl groups in the saturated fragment of the molecule [34].

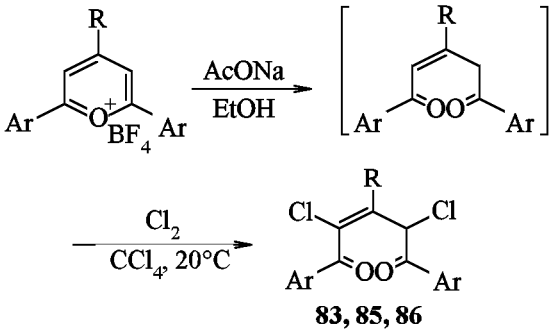




Note that the original pentenediones (38–40) are *cis-S-cis*-isomers. The structure of compounds **83, 85, 86** demonstrates the change in the geometry of the double bond in the course of chlorination.

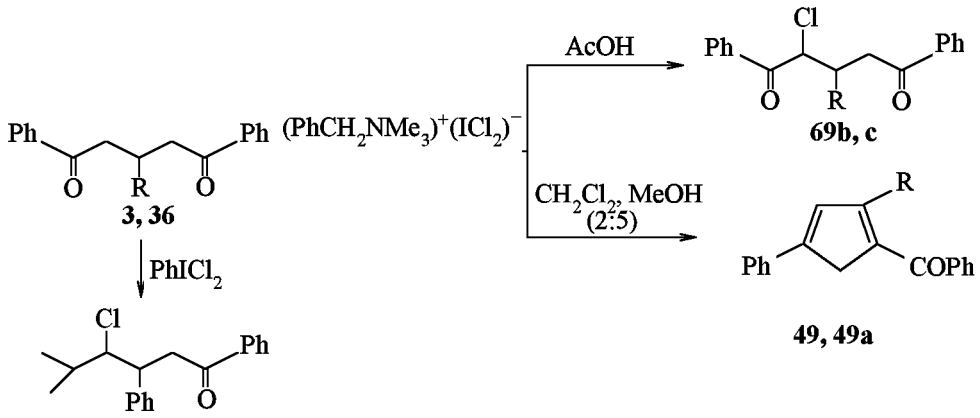
The capability of pent-2-ene-1,5-diones to undergo chlorination is affected by extent of substitution and the reciprocal position of the substituents [15]. For instance, 2,4-dimethyl-1,5-diphenylpent-2-ene-1,5-dione (**90**) remained intact after 4 h at 75°C in contact with chlorine. Its ^1H NMR spectrum evidences the *trans-S-trans*-structure [34]. Apparently the mutual position of methyl and carbonyl groups hampered the electrophilic addition of chlorine to the double bond and the substitution of allyl hydrogen [15].

It should be noted that 2,4-dichloropentene-1,5-diones (**83, 85, 86**) can be obtained from the corresponding pyrylium salts since the latter furnish pent-2-ene-1,5-diones (**38–40**) at alkaline hydrolysis. To this end the pyrylium salts are treated with sodium acetate, and the arising pentendiones are subjected to chlorination without isolation from the reaction mixture [33].



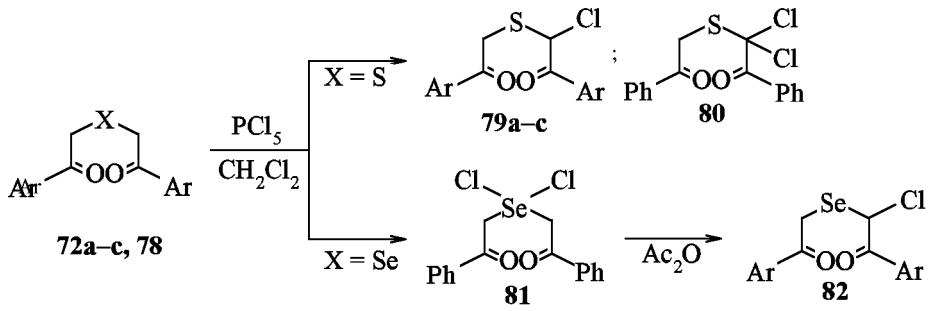
Semicyclic 1,5-ketones react with chlorine under various conditions. The character of conversion depends on the substrate structure. For instance, treating of 2-(1,3-diphenylpropan-3-on-1-yl)cyclohexan-1-one (**91**) with chlorine without heating afforded in 48% yield diketone **92**, the product of hydrogen

Scheme 7.



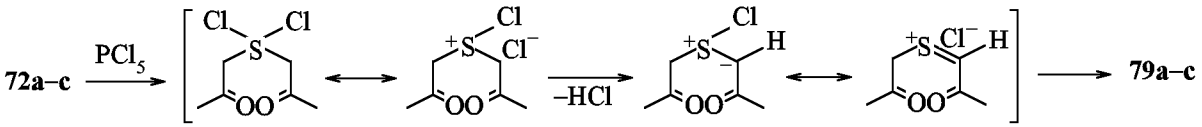
R = CH_3.

Scheme 8.

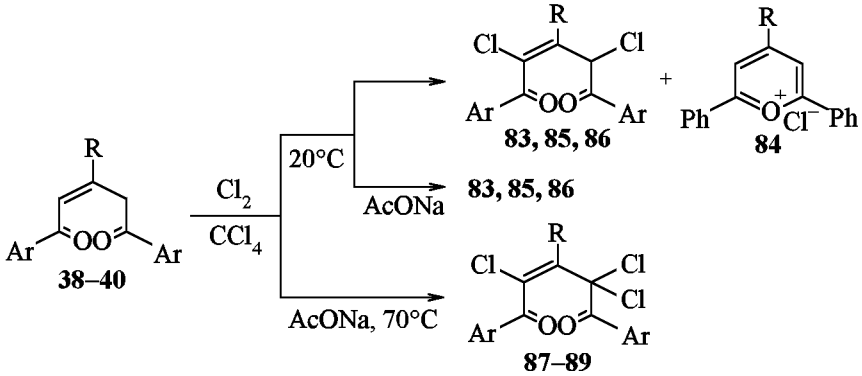


72, 79, X = S, Ar = Ph (**a**), 4-ClC_6H_4 (**b**), 4-$EtOC_6H_4$ (**c**); **78**, X = Se, Ar = Ph.

Scheme 9.

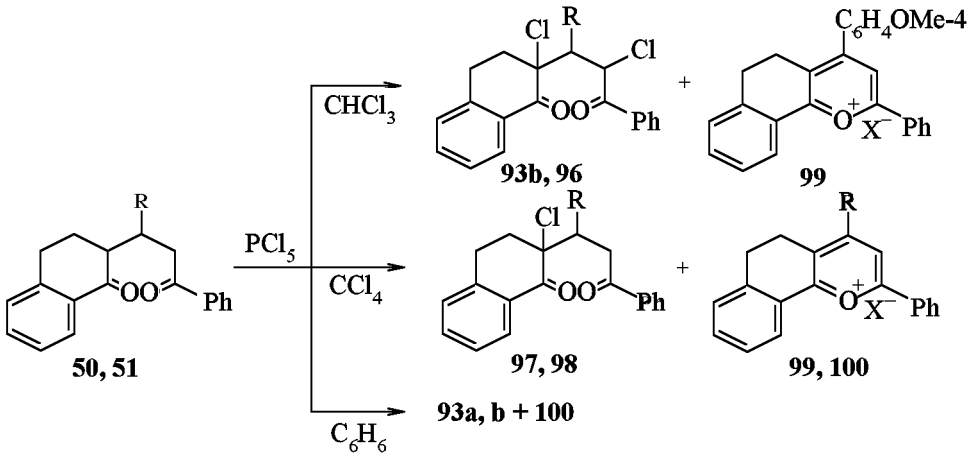


Scheme 10.



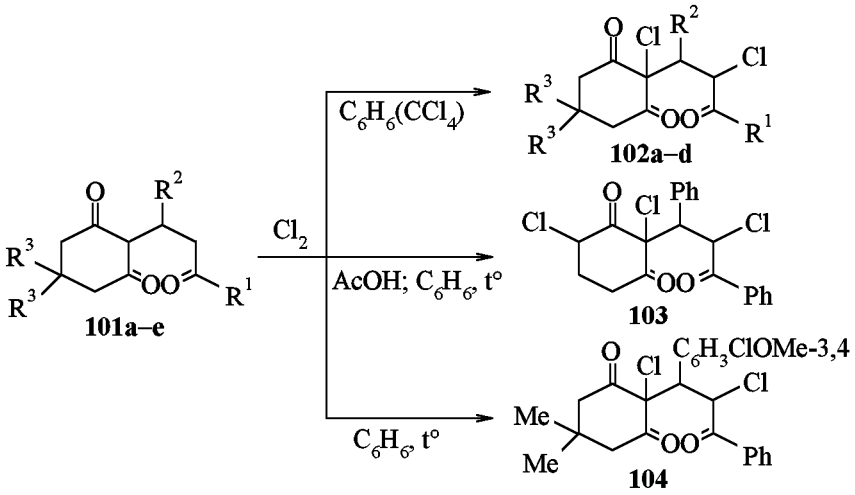
38, 83, 84, 88, R = Ar = Ph; **39, 85, 87**, R = 4-ClC_6H_4; Ar = Ph; **40, 86, 89**, R = Ph, Ar = 4-ClC_6H_4.

Scheme 11.



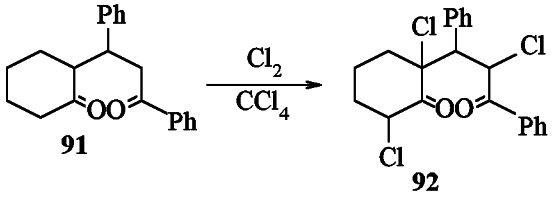
50, 93b, 97, 100, R = Ph, X^- = mixture of anions; **51, 96, 98, 99,** R = 4-$MeOC_6H_4$, X^- = Cl^-.

Scheme 12.



101, 102, R^1 = R^2 = Ph, R^3 = H (**a**); R^1 = R^2 = Ph, R^3 = Me (**b**); R^1 = Ph, R^2 = 4-$MeOC_6H_4$, R^3 = Me (**c**); R^1 = Ph, R^2 = 4-$NO_2C_6H_4$, R^3 = H (**d**); R^1 = R^3 = Me, R^2 = Ph (**e**).

atoms substitution in the three α-positions with respect to the carbonyl groups of the initial compound.



The reaction between chlorine and 2-(1,3-diphenylpropan-3-on-1-yl)-1,2,3,4-tetrahydronaphthalen-1-one (**50**) in tetrachloromethane, benzene or acetic acid at room temperature or at heating proceeded very slow. The initial compound was found in the reaction mixture even after 35 h [17]. The replacement for chlorine of iodobenzene dichloride which in polar solvents behaves as an electrophilic chlorinating agent and is successfully applied to halogenation of acyclic 1,5-dicarbonyl compounds [35, 36] results in conversion of diketone **50** within 4 h into α,α'-dichloro-substituted diketone **93a, b** in 70% yield. The product is a mixture of erythro- and threo-isomers, the latter prevailing (Scheme 11) [17].

A similar result was obtained by saturation with chlorine of a solution of dioxo compound **50** in acetic acid in the presence of iodobenzene; the latter acted as an agent of chlorine transfer, providing the reagent *in statu nascendi* [17]. In the chlorination of 1,5-diketone (**51**) under the above conditions occur two concurrent processes: electrophilic substitution

of hydrogens in α-positions with respect to carbonyls and in the methoxyphenyl substitutent. In 45 min as reaction product appears 2-[1-(3-chloro-4-methoxyphenyl)-3-phenylpropan-3-on-1-yl]-2-chloro-1,2,3,4-tetrahydronaphthalen-1-one (**94**), and after 4 h forms threo-2-[1-(3-chloro-4-methoxyphenyl)-3-phenyl-2-chloropropan-3-on-1-yl]-2-chloro-1,2,3,4-tetrahydronaphthalen-1-one (**95**).

The chlorination of diketones **50, 51** with phosphorus pentachloride in chloroform furnished in 30–50% yield α,α'-dichloro derivatives, 1,5-dioxo compounds **93b, 96** in erythro-configuration. Formation of a salt was observed in the case of diketone **51**. In tetrachloromethane were obtained monochloro derivatives, 2-(1,3-diphenylpropan-3-on-1-yl)- and 2-(1-(4-methoxyphenyl)-3-phenylpropan-3-on-1-yl)-2-chloro-1,2,3,4-tetrahydronaphthalen-1-ones **97, 98** and benzohydrochromylium salts **99, 100**.

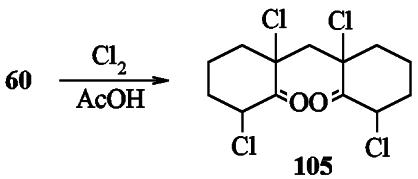
Identification of benzohydrochromylium salts **99, 100** was performed in the stable perchlorate form obtained by anion exchange [17].

The chlorination of semicyclic oxo-1,5-diketones (**101a–e**) is governed not only by the character of the substituents but also by the presence of three carbonyl groups [37].

Triketones **101a–e** react with chlorine in benzene or tetrachloromethane at room temperature yielding dichloro-containing oxo-1,5-diketones **102a–d**. In acetic acid at 25°C, and in benzene at 70°C arises trichloro derivative **103** (R^3 = H). Methyl groups attached to the alicycle produce a shielding effect, therefore even at heating no substitution with chlorine occurs at C^4 and C^6 atoms of the ring. The methoxyphenyl group in diketone **101c** facilitates the chlorination of the aryl substituent that results in a trichloro derivative **104**.

The halogenation of triketone **101e** in benzene, tetrachloromethane, and acetic acid is accompanied by retro-Michael cleavage giving rise to polyhalo-substituted decomposition products.

Whereas bromination and iodination of methylenebiscyclohexanone (**60**) results in formation of salts and carbocyclization into compounds **61–63**, its chlorination even in acetic acid yields only tetrachloromethylenebiscyclohexanone (**105**) [18, 19].



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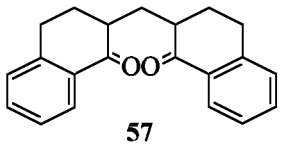
Methylenebis-2,2'-(1,2,3,4-tetrahydronaphthalen-1-one) (**57**) in reaction with phosphorus pentachloride behaved similarly to propanyltetrahydronaphthalenones **50, 51**; the obtained compound is the *meso*-form of methylenebis-2,2'-(2-chloro-1,2,3,4-tetrahydronaphthalen-1-one) (**106**). Yields of dichlorodiketone **106** and salt **107** were 41 and 5% respectively [17].



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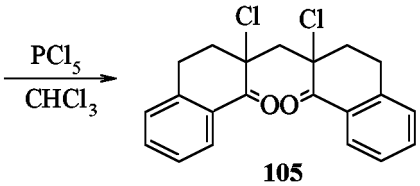

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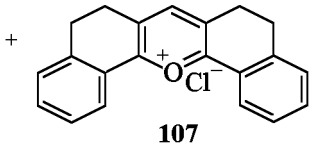

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