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Chemistry of cross-conjugated dienones

S Z Vatsadze, A G Golikov, A P Kriven'ko, N V Zyk

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Abstract. The review covers methods of synthesis, structure and properties of cross-conjugated dienones, *viz*., bis(arylmethylidene) derivatives of cyclic ketones and their heteroanalogues. The regio- and stereochemistry of the reactions of dienones depending on the ring size and the nature of substituents is analysed. The bibliography includes 234 references.

I. Introduction

The number of papers dealing with the synthesis, stereochemistry and properties of cross-conjugated bis(arylmethylidene) derivatives of cyclic ketones (hereinafter, dienones) has considerably increased in recent years. Keen interest in these systems is associated primarily with their availability and high reactivity, making them valuable starting compounds for organic synthesis. Lately, symmetrical conjugated dienones that are the condensation products of cyclic ketones with heteroaromatic aldehydes, have found use as *exo*-dentate ligands in the synthesis of coordination polymers. The latter hold promise in supramolecular chemistry for the design of catalytic, magnetic, luminescent, *etc*. practically important polymeric materials.[1]

Bis(arylmethylidene) derivatives of cyclic ketones have a broad spectrum of biological activities, such as androgenic,[2] antimicrobial,[3] hypocholesterolemic,[3–5] choleretic,[6] anti-inflammatory,[7] antimutagenic, antitumour[8] and antipyretic[9] activities. High cytotoxicity of bis(arylmethylidene)cyclohexanones and -piperidin-4-ones against murine and human leukemia cells was documented.[10–18] There are data on high antioxidant activity of hydroxybis(arylmethylidene)cyclanones, which are analogues of the natural antioxidant curcumin,[9,19,20] and the possibility of using these compounds as insecticides, acaricides, nematocides, fungicides and herbicides,[21] as well as for environmental purposes.[22]

Cross-conjugated dienones can find use in optics and rocket engineering where they can be used as optically active materials (for example, as sensitisers in highly sensitive composites[23–26]) and components of rocket fuels spontaneously inflammable in the presence of oxidants.[27,28] These compounds are used also in the synthesis of polymers[29–31] including those with high thermal stability (withstanding temperatures above 300 °C),[29,30] and in photolithography for the preparation of precision optical masks resistant to dry plasma etching.[32]

The vast literature on the chemistry of cross-conjugated dienones and their derivatives was not summarised and the data on this subject were reported in separate publications.[33–35] The present review covers the data published primarily in the last 15 years. Earlier literature is cited only if the data are of substantial importance. Conventional methods of synthesis of cross-conjugated dienones are outlined here. The structures of virtually all known compounds are considered. The main transformations of dienones are discussed. The problems of regio- and stereoselectivity of heterocyclisation reactions are analysed in detail.

Numerous reactions of cross-conjugated dienones can be classified into the following groups: reactions involving the conjugated system C=C–C=O (the addition of bis- and polynucleophiles, the formation of metal π complexes, *etc*.), reactions at the C=C bonds (cycloaddition, aziridination, cyclopropanation, dimerisation, isomerisation, *etc*.), the functionalisation of the central ring (allylic bromination) and reactions involving aromatic substituents (the Friedel–Crafts reaction, the formation of metal σ complexes) and the carbonyl group.

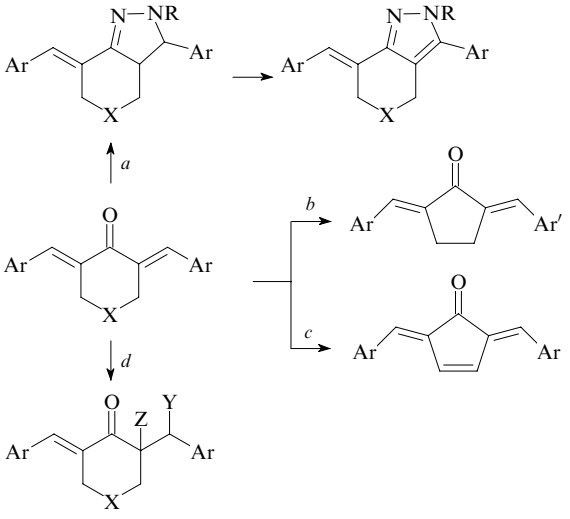
Of the possible modifications of symmetrical dienone structures (Scheme 1), most promising are construction of fused heterocyclic compounds (path *a*), ligands with the unsymmetrical arrangement of donor pairs (path *b*) and 'flattened' systems with a larger number of conjugated double

S Z Vatsadze, N V Zyk Department of Chemistry, M V Lomonosov Moscow State University, Leninskie Gory, 119991 Moscow, Russian Federation. Fax (7-495) 932 88 46, tel. (7-495) 939 40 20, e-mail: szv@org.chem.msu.ru (S Z Vatsadze), tel. (7-495) 939 46 52 (N V Zyk)
A G Golikov, A P Kriven'ko Department of Chemistry, N G Chernyshevskii Saratov State University, ul. Astrakhanskaya 83, 410012 Saratov, Russian Federation. Fax (7-8452) 27 14 91, tel. (7-8452) 51 69 51, e-mail: sorokinvv@info.sgu.ru

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bonds (path *c*), as well as the functionalisation of one of the double bonds (path *d*).

Scheme 1



X = $(CH_2)_n$ (n = 0, 1, 2, ...), NR, O, S.

In the published papers, most attention has been given to dienones based on five- and six-membered carbocyclic ketones and piperidone, tetrahydropyranone and tetrahydrothiopyranone derivatives. Their homologues containing larger or smaller rings have received little attention due, apparently, to the fact that the corresponding carbocyclic ketones (cyclanones) and heterocycles are difficult to prepare.

Dienone derivatives of cyclic ketones are divided into symmetrical and unsymmetrical according to the nature of the substituents in the α position with respect to the carbonyl group. The chemistry of symmetrical systems was described in sufficient detail due to their higher availability and unambiguity of their reactions. Unsymmetrical analogues have been studied to a lesser extent.[36] The introduction of heterocyclic fragments into the latter compounds gives rise to additional nonequivalent reaction centres. This fact not only calls for the solution of the problems concerned with the regioselectivity of reactions, but also extends the scope of application of transformation products of these compounds.

II. Methods of synthesis

1. Symmetrical dienones

Symmetrical cross-conjugated dienones are generally synthesised by the aldol condensation of cyclic ketones with two equivalents of aldehydes in the presence of alkalis,[1,4,5,37–44] alkali metal alkoxides,[3,45] anhydrous potassium carbonate[46] or magnesium hydrogensulfate (under solvent-free conditions).[47] In a series of studies,[7,9,19,27,48] these reactions were catalysed by hydrochloric acid. In particular, HCl was used in those reactions where basic catalysis is inapplicable (for example, in the synthesis of hydroxyphenyl-containing dienones).

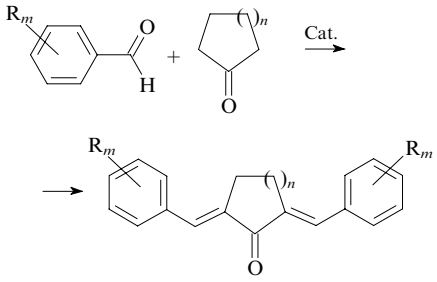
Lewis acids [$SOCl_2$ in anhydrous ethanol,[49] $Yb(OTf)_3$ and $Sc(OTf)_3$ (Ref. 50)], silicon compounds [$Me_3SiI-NaI$, $Me_3SiCl-NaI$,[51] $(MeO)_4Si-KF$, $(EtO)_4Si-CsF$[52] and $InCl_3\cdot 4H_2O-Me_3SiCl$ systems[53,54] and the complex $Pd\cdot Me_3SiCl$[55]], zirconium compounds ($Cp_2ZrH_2-NiCl_2$, Cp = η^5-C_5H_5)[56] and titanium compounds [Cp_2TiPh_2 (Ref. 57) and $TiCl_3OTf$[58]] have been used in numerous recent studies as catalysts for the aldol condensation. Complexes of copper(II), nickel(II), cobalt(II) and zinc(II) acetates with 2,2′-bipyridine proved to be efficient catalysts for the condensation of ketones with benzaldehyde.[59]

The catalytic properties of Lewis acids were compared in the synthesis of dibenzylidenecyclopentanone.[50] The highest yield of the product (93%) was achieved with the use of $Yb(OTf)_3$ at a concentration of 0.5 mol % – 5 mol %.

The aldol condensation can be performed in ionic liquids in the presence of $FeCl_3\cdot 6H_2O$[21,60] or SmI_3 as the catalysts.[61–64] In the presence of cationic surfactants, the condensation proceeds even in water;[65] the micellar catalysis is efficient in the step of aldol dehydration.

The products were obtained in high yields also under solvent-free conditions. These processes can be catalysed by acids,[66] anhydrous $RuCl_3$ (Ref. 67) or $InCl_3\cdot 4H_2O$ (upon heating of the reactants to 110 – 120 °C in a sealed tube).[68,69] These reactions can also be performed using microwave activation[26,70–75] (in the presence of boron trifluoride etherate[26] or ethoxyphenyltellurium oxide[74] as the catalyst; in this case, the reaction time decreases to a few minutes) or with sonication,[64] including the reactions in the presence of KF deposited on Al_2O_3.[76]

The above-described methods of synthesis were developed primarily for dienones prepared from cyclopentanone or cyclohexanone (more seldom, from cycloheptanone) and various aromatic aldehydes.



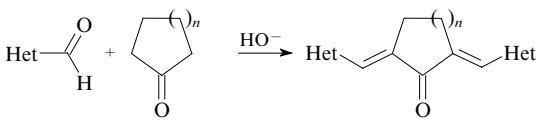
n = 1: R_m = H, 4-Me, 4-OH, 3-OMe, 4-OMe, 4-NMe_2, 4-NO_2, 4-F, 3-Cl, 4-Cl, 3,5-Me_2, 3,5-Et_2, 3,5-Pr^i_2, 3,5-Bu^t_2, 3,4-$(OMe)_2$, 3,5-$(OMe)_2$, 2,4-Cl_2, 3,5-Cl_2, 3-Me-4-OH, 3-Br-4-OH, 3,5-Me_2-4-OH, 3,5-Br_2-4-OH, 2-Cl-4-OH-5-OMe, 2,3,5-Br_3-4-OH;

n = 2: R_m = H, Me, 4-Bu^t, 4-Cy (Cy = cyclo-C_6H_{11}), 4-OH, 4-NMe_2, 4-NEt_2, 2-NO_2, 3-NO_2, 2-Cl, 4-Cl, 4-Br, 4-I, 3,4-Me_2, 3,5-Me_2, 3,5-Et_2, 3,5-Pr^i_2, 3,5-Bu^t_2, 3,5-$(OMe)_2$, 3-OMe-4-OH, 3,4-(OCH_2O), 2,4-Cl_2, 3,4-Cl_2, 2,6-Cl_2, 3,5-Cl_2;

n = 3: R_m = H, 4-OMe, 4-NMe_2, 3-NO_2, 4-Cl, 4-Br.

2,4-Dibenzylidenecyclobutanone is the only characterised cross-conjugated cyclobutanone derivative.[1,77,78] Cycloalkanone-based dienones containing seven- to ten-membered rings were documented.[1,3,39,42,79]

The reactions of alicyclic ketones with heteroaromatic aldehydes (furfural, thiophenecarbaldehyde and 2- and 3-pyridinecarbaldehydes) are generally performed in the presence of alkalis.



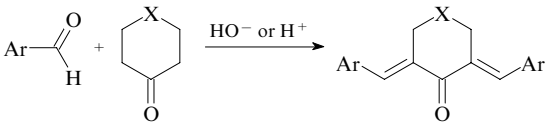
Het = Fu (2-furyl), Th (2-thienyl), 2-Py (pyridyl), 3-Py; n = 1 – 3.

The condensation reactions of furfural with cyclanonanes C_5-C_7 catalysed by various bases[1,39,50,56,80–84] or performed under solvent-free conditions,[46,52] with sonication[76,85] or

under microwave irradiation were described.[86,87] It should be noted that the synthesis of dienones containing the 5-nitrofuran fragment can be carried out only with acid catalyst. For example, 2,6-bis(5-nitrofurfurylidene)cyclohexanone was prepared by the reaction of commercial 5-nitrofurfural diacetate with cyclohexanone in 60% phosphoric acid.[88]

Dienones containing the thienylmethylidene groups are formed both in the presence of a basic catalyst (NaOH) and an acid catalyst $Yb(OTf)_3$.[1,39,50] The synthesis of bis(pyridylmethylidene)cycloalkanones in an alkaline medium was documented.[15,89] It should be noted that the data on the yields of hetaryldienones were not reported in the studies,[5,20,37,39] and the melting points given in different studies differ by 10–30 °C. Consequently, many of the published data should be revised. The most reliable data on the synthesis and interpretation of spectroscopic studies of hetaryl-substituted dienones were documented in our publication.[89]

The reactions of nitrogen-, oxygen- and sulfur-containing analogues of cyclohexanone (piperidin-4-one, tetrahydropyran-4-one and tetrahydrothiopyran-4-one) with aromatic and heteroaromatic aldehydes afford 3,5-bis(arylmethylidene) derivatives (hereinafter, the abbreviation Ar refers to both aryl and hetaryl substituents).[16–18,53,54,86–97]



X = NMe, NAc: Ar = RC_6H_4 (R = H, 4-Me, 2-Cl, 3-Cl, 4-Cl, 4-OMe, 4-NO_2), 2-naphthyl, 2-Py, 4-Py, Th, 2- and 4-quinolyl;

X = S: Ar = $R_nC_6H_{4-n}$ (R_n = H, 2-Me, 4-Me, 4-Pr^i, 4-NMe_2, 3-NO_2, 3-CF_3, 4-SMe, 4-S(O)Me, 3,4-$(OMe)_2$, 3,4-Cl_2), 1-naphthyl;

X = O: Ar = $R_nC_6H_{4-n}$ (R_n = H, 2-Me, 4-Me, 4-Pr^i, 4-OMe, 4-OEt, 4-NMe_2, 4-NO_2, 4-S(O)Me, 3,4-$(OMe)_2$, 2,3-$(OMe)_2$, 3,4-(OCH_2O), 3,4,5-$(OMe)_3$, 2,3-Me_2-4-OMe, 2,5-Me_2-4-OMe), 2-naphthyl.

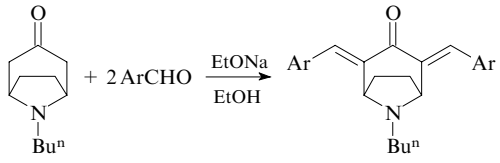
Among the above-considered heterocyclic ketones, the largest number of dienones was synthesised starting from piperidin-4-ones. 3,5-Bis(arylmethylidene)piperidin-4-ones prepared as free bases in the presence of basic catalysts were isolated[40,41,90,91] and as the corresponding salts in the presence of acid catalysts.[10,11,90,92]

In some cases, the condensation in the presence of bases in an aqueous ethanolic medium affords a complex mixture of products (mono- and dienones or mono- and dialdols).[90] For example, the reaction of 1-benzylpiperidin-4-one with benzaldehyde in the presence of NaOH affords a mixture consisting of the monobenzylidene derivative (16%), the addition product of the latter to the starting ketone (29%) and trace amounts of the dibenzylidene derivative.[93] By contrast, the reaction of 1-methylpiperidin-4-one with substituted benzaldehydes proceeds in anhydrous ethanol even in the absence of catalysts to form the corresponding bis(arylmethylidene)piperidinones.[93]

The condensation of tetrahydropyran-4-one[91,94,95] and its S-heteroanalogues[91,94–97] with aromatic aldehydes can be performed in an aqueous ethanolic solution of alkalis or HCl or in solution of piperidine in acetic acid.

The oxidation of 3,5-bis(arylmethylidene)tetrahydrothiopyran-4-ones with periodates in an aqueous ethanolic medium affords the respective sulfoxides[16–18] and sulfones under more drastic conditions (30% H_2O_2, refluxing in glacial acetic acid).[16–18,88] The oxidation of the starting tetrahydrothiopyran-4-one followed by condensation of the product with benzaldehyde gives similar results.[18]

Bis(arylmethylidene) derivatives **1**, which were prepared by the condensation of *N*-butyl-8-azabicyclo[3.2.1]octan-3-one with various aldehydes in the presence of sodium ethoxide,[98] can be mentioned as an example of bicyclic cross-conjugated dienones.



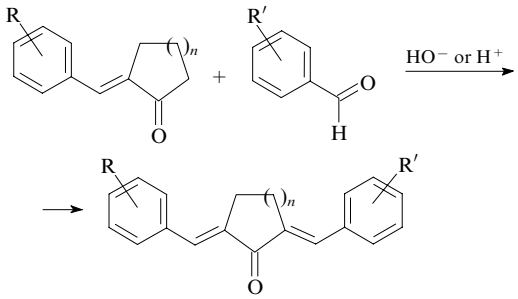
1

Ar = RC_6H_4 (R = H, 2-Cl, 3-Cl, 4-Cl, 4-Me, 4-NMe_2, 4-OMe, 4-NO_2), Fu, 3-Py, 4-Py.

2. Unsymmetrical dienones

Unlike the well-studied symmetrical cross-conjugated dienones, their unsymmetrical analogues have received much less attention. Unsymmetrical dienones are generally synthesised by the condensation of the corresponding monoenones with aldehydes containing another (hetero)aromatic ring under conditions of basic or acidic catalysis and by the condensation of cycloalkanone enamines with aldehydes.

For example, the reaction of 2-arylmethylidenecycloalkanones with carboaromatic aldehydes in an alkaline medium produced unsymmetrical bis(arylmethylidene)cycloalkanones.[99–101] The reactions of derivatives containing hydroxy or cyano groups and amidine substituents in the benzene ring were performed in the presence of acid catalysts.[9,102]



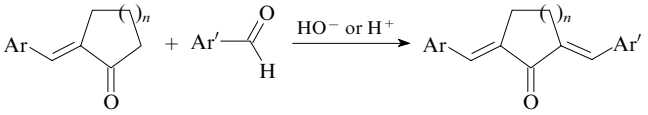
n = 1: R = H, 4-Cl, 4-Me; R′ = 4-Pr^i, 4-OMe, 4-C(=NH)NH_2·HCl, 3,4-$(OMe)_2$;

n = 2: R = H, 4-OMe, 4-Cl, 4-Br, 2-NO_2, 4-NO_2, 3,4-Cl_2; R′ = 4-Me, 4-OH, 4-OMe, 4-NMe_2, 4-NO_2, 4-Cl, 3-CN, 4-CN, 4-C(=NH)NH_2·HCl, 3-C(=NH)NH_2·HCl, 3,4-Cl_2.

The synthesis of dienones containing both aryl and 1- or 2-naphthyl substituents was documented.[103] In some reactions, the use of enamines instead of the corresponding cycloalkanones resulted in the increase in the yield of the products.[104]

Dienones containing simultaneously aryl and hetaryl substituents or two different heterocycles can be synthesised by analogous reactions.[39,101,103,105–110] For example, the condensation of monoenones with aldehydes in an alkaline medium afforded dienones containing 2-thienyl,[33,39,101,103,105] 2-furyl[39,101,103,105,106,107] or pyridyl fragments substituted in different positions.[33,108] In the synthesis of arylmethylidene(furfurylidene)cyclohexanones, the highest yields (79%–92%) were obtained for dienones containing electron-withdrawing (4-Br, 3-NO_2, 4-NO_2, 2-Cl or 2-F) groups in the benzene ring. It should be noted that the synthesis

of dienones containing the electron-donating 4-NMe_2 group requires the use of 20% – 40% aqueous NaOH.[106] The synthesis of 5-nitrofurfurylidene derivatives can be performed under conditions of acid catalysis.[2, 106]



n = 1: Ar = Ph, Fu, Th; Ar′ = Ph, 4-$OMeC_6H_4$, 4-$Pr^iC_6H_4$, 3,4-$(OMe)_2C_6H_3$, 1- and 2-naphthyl, Th, 5-bromo-2-thienyl, 2-Py, 3-Py, 4-Py;

n = 2: Ar = Ph, 4-$OMeC_6H_4$, Th, Fu, 5-methyl-2-furyl; Ar′ = Ph, 4-MeC_6H_4, 4-PhC_6H_4, 4-$OMeC_6H_4$, 2,4-$(OMe)_2C_6H_3$, 2-FC_6H_4, 2-ClC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 4-$NMe_2C_6H_4$, 1- and 2-naphthyl, Th, 5-bromo-2-thienyl, 5-nitro-2-furyl, 2-Py, 3-Py.

III. Properties and structures

1. Spectroscopic characteristics

The presence of the conjugated C=C–C(=O)–C=C group and the stereochemistry of substituents at C=C double bonds are responsible for the characteristic features in the IR and UV spectra, as well as in the NMR spectra of bis(arylmethylidene) derivatives of cyclic ketones. In this connection, the specific spectroscopic properties of close analogues of cross-conjugated dienones, *viz*., ω,ω′-bis(dialkylamino)polyenyl ketones (ketocyanines), are noteworthy. These properties were considered in detail in the review.[111] The electronic structures of these compounds are related to such properties as the pronounced solvatochromism, strong thermochromism, intense fluorescence and the generation of laser radiation, as well as the great ease of alkylation and protonation at the carbonyl group accompanied by a sharp change in the colour of their solutions. Analogous changes were observed in the spectra upon protonation of a series of cyclopentanone-containing arylpolyenes [112] and pyridine-containing dienones.[113]

In the IR spectra [105, 106–109] of cross-conjugated dienones, the carbonyl stretching bands are shifted to lower frequencies (1705 – 1648 cm^{-1}) compared to the bands of cyclanones due to conjugation. Lower intensities of these bands compared to the C=C stretching bands (1610 – 1526 cm^{-1}) is analytical evidence for *s-cis* orientation of these groups. The presence of out-of-plane bending vibrations of the =C–H bond (968 – 984 cm^{-1}) indicates that the aryl substituent and the carbonyl group are located on the opposite sides of the C=C double bond.[107–109] In the case of monosubstituted enones, this fact is attributed to the steric interaction between the carbonyl group and the aryl substituent, to be more precise, between the *ortho*-protons of the benzene ring, in the *Z* isomer.[110, 114] However, the stereochemistry of dienones cannot be unambiguously determined based only on the IR spectroscopic data, and further investigations are required.

It is commonly accepted [39] that the long-wavelength band of the n – π* transition (406 – 320 nm) in the UV spectra of the dienones under consideration characterises the degree of conjugation in the molecule. The position of this band depends on the size of the alicyclic moiety and the nature of the aryl substituents. According to this point of view, the highest degree of conjugation is observed for cyclopentanone derivatives (λ_{max} = 352 – 402 nm). The degree of conjugation decreases with the increase in the ring size. Thus the absorption bands of cyclohexanone derivatives (λ_{max} = 320 – 380 nm) and cycloheptanone derivatives (λ_{max} = 298 – 340 nm) are shifted to shorter wavelengths. The lowest degree of conjugation was observed for ketones containing carboaromatic substituents. The thiophene and furan rings in unsymmetrical systems containing a carbocycle as the second substituent are characterised by the highest degree of conjugation.[39]

The most unambiguous information on the configuration of the double bonds in dienones can be obtained from NMR spectroscopic data. For example, 1D ^1H and ^{13}C NMR spectra [97, 106] and 2D $^1H-^1H$ (COSY) NMR spectra [7] provide evidence that the chemical shifts of the vinyl protons in a series of dienones have similar values and vary from δ 7.35 to 7.85. The similarity of the chemical shifts of the methine protons in the =C(Ar)–H and =C(Het)–H fragments is indicative of the weak influence of the substituents at the double bonds on the conjugation. Only slight upfield shifts of the signals for these protons (δ 7.36 – 7.58) are observed in the presence of electron-donating groups (4-OMe or 4-NMe_2) in the aromatic ring; in the presence of electron-withdrawing substituents (4-NO_2, 3-NO_2 and 2-Cl, 2-F), these signals are slightly shifted downfield (δ 7.70 – 7.79).[106] The largest chemical shifts were found for 2-thienyl derivatives of dienones.

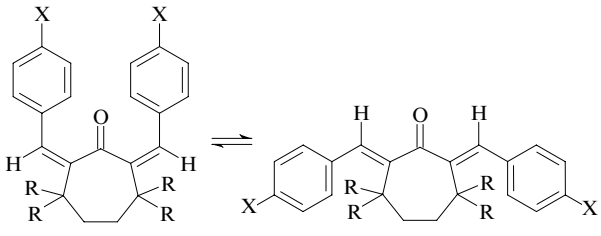
The chemical shifts of the vinyl protons in the spectra of monoenones with the *trans* configuration of the double bond are observed at δ > 7.0; those for the corresponding *cis* isomers are at higher field (δ ~ 6.5).[110, 114–117] Based on these data, it can be concluded that symmetrical and unsymmetrical dienones have an *E*,*E* configuration.

The X-ray diffraction data for five heterocyclic dienones were analysed,[89] and the configuration of the double bonds was correlated to the chemical shifts of the methine protons in the NMR spectra of these compounds. It was found that the signals for the vinyl protons in the *Z* isomers are characterised by upfield shifts up to δ 6.51 – 6.99 compared to the signals for the protons in the *E* isomers (δ 7.26 – 7.63).

2. Stability and interconversions of isomers

The stability of isomeric, bis(arylmethylidene) derivatives of cyclic ketones C_5 – C_7 was studied by quantum chemical methods. The relative conformational energies of three possible geometric isomers of 2,5-dibenzylidenecyclopentanone and -cyclohexanone were calculated.[118] These data suggest that the *E*,*E* isomers are the most stable. For cyclopentanone and cyclohexanone derivatives, the *Z*,*Z* and *E*,*Z* isomers, respectively, proved to be the least stable.

Ab initio calculations [119] (the Hartree – Fock method at the 3.21G level with the use of the Gaussian programme) showed that the (*E*,*E*)-bis(arylmethylidene) derivative of cycloheptanone **2a** is 2.1 kcal mol^{-1} more stable than the *Z*,*Z* isomer. In the presence of methyl substituents in positions 3 and 6 of the alicyclic moiety, *Z*,*Z* isomer **2b** is more stable due to steric factors (ΔE = –2.8 kcal mol^{-1}).

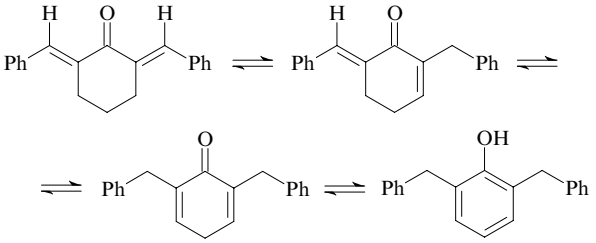


(*Z*,*Z*)-**2a**–**c** (*E*,*E*)-**2a**–**c**

R = H, X = C(=NH)NH_2 (**a**);
R = Me: X = C(=NH)NH_2 (**b**), CN (**c**).

The NMR spectroscopic and X-ray diffraction data for compound **2c** confirm the exclusive formation of *Z*,*Z* stereoisomers.[119]

Dibenzylidene derivatives of various carbocyclic ketones undergo isomerisation to form the *cis* isomers when exposed to light or under UV irradiation.[89, 116] Under UV irradiation, the exocyclic double bonds can also undergo isomerisation.[120] For example, the reaction with polyphosphoric acid under these conditions resulted in the transformation of 2,6-dibenzylidenecyclohexanone into 2,6-dibenzylphenol in 17% yield.[121, 122]



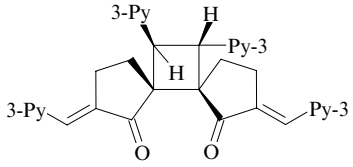
In some cases, the isomerisation proceeds in the course of mere distillation. Thus 2-benzyl-5-benzylidenecyclopent-2-enone was prepared from 2,5-dibenzylidenecyclopentanone as a result of migration of the exocyclic double bond to the ring, which was confirmed by the independent synthesis of the migration product.[123]

Other conditions under which alicyclic isomers are isomerised into aromatic products were also documented. For example, platinum black (the Adams catalyst) catalyses the isomerisation of 2,6-dibenzylidenecyclohexanone to 2,6-dibenzylphenol upon heating *in vacuo* at 255–265 °C for 5 h (the degree of conversion of the starting ketone is 34%). The conversion achieved in the reaction catalysed by Pd/C at 235–245 °C is 91%;[124] an analogous transformation proceeds in the presence of the complex $IrCl(CO)(PPh_3)_2$ at 250 °C.[125]

2,6-Dibenzylidenecycloheptanone (**2a**), which cannot be transformed into an aromatic structure without a loss of the hydrogen atom, undergoes only *Z*,*E* isomerisation. For example, a mixture of the *E*,*E* (66%), *Z*,*E* (33%) and *Z*,*Z* isomers (<1%) is present in the reaction mixture obtained under thermal conditions; after UV irradiation, the percentage of the *Z*,*E* isomer increases to 40% and the *Z*,*Z* isomer becomes the major product (55%).[125] In the photostationary state, 2,6-bis(4-cyanobenzylidene)cycloheptanone (**2c**) exists as a mixture of the *E*,*E* (5%), *Z*,*E* (45%) and *Z*,*Z* isomers (50%),[126] which is consistent with the data for dienone containing the unsubstituted benzene ring.

The isomerisation of derivatives of heterocyclic ketones proceeds under milder conditions. For example, 3,5-dibenzylidene-1-methylpiperidin-4-one is quantitatively isomerised into 3,5-dibenzyl-1-methylpyridin-4-one upon refluxing in ethylene glycol in the presence of palladium on carbon for 1 h.[93]

Recently, studies by NMR spectroscopy and X-ray diffraction[89] have shown that the aldol condensation affords all products as *E*,*E* isomers. Cross-conjugated dienones were found to undergo spontaneous photochemical equilibrium *trans*,*cis*-isomerisation in solution when exposed to scattered light. The degree of isomerisation was demonstrated to depend primarily on the nature of the central fragment in the dienone molecule. The percentage of the *Z*,*E* and *Z*,*Z* isomers increases with the increase in the size of the alicyclic moiety in the series C_5–C_8. The photochemical [2+2]-cycloadduct of 2,5-bis[(*E*)-3-pyridylmethylidene]cyclopentanone, *viz*., cyclobutane adduct **3** existing as one stereoisomer, was synthesised and characterised by spectroscopic methods and X-ray diffraction for the first time.



3

A series of N-donating heterocyclic ligands, including a large group of pyridine dienones, was studied by quantum chemical methods and electrochemistry.[127, 128] The correlation between the calculated energies of the lowest unoccupied molecular orbitals (LUMO) of the ligands in the gas phase and the first potentials of their electrochemical reduction in solution was established.

3. Molecular and crystal structures

The Cambridge Structural Database (CSD) contains a rather small number of bis(arylmethylidene) derivatives of cyclic ketones. It should be noted that all characterised dienones have the *E*,*E* configuration in the crystal structures.

In the 2,6-dibenzylidenecyclohexanone molecule, the central ring adopts a distorted chair conformation.[129] The corresponding ring in 3,5-dibenzylidenepiperidin-4-one has a boat conformation.[18] In the latter compound, the dihedral angle between the planes of the benzene ring and the C=C–C=O fragment is 49.50°, *i.e*., the substituents deviate from the plane of the molecule and make a small contribution to the conjugation.[18] This confirms the conclusion about the relationship between the degree of conjugation and the absorption wavelength, which was drawn[39] based on the UV spectra of this compound.

An analogous structure is typical also of unsymmetrical ketone, *viz*., 2-benzylidene-6-furfurylidenecyclohexanone (**4**) (Ref. 130). The benzene ring and the C=C bond are noncoplanar. The angle between these fragments is 36.32°, which characterises the incomplete conjugation in the benzylidene fragment, whereas the furan ring is coplanar with the C=C–C=O bond system (Fig. 1).

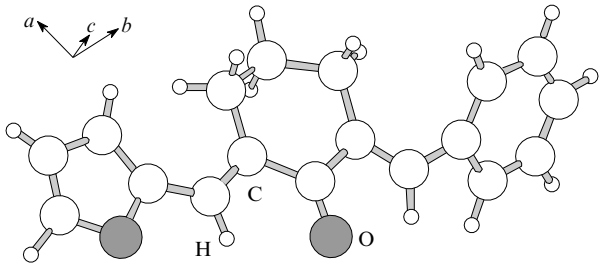


Figure 1. Molecular structure of 2-benzylidene-6-furfurylidenecyclohexanone (**4**).[130]

A research on the nonlinear optical properties of crystals of dibenzylidenecycloalkanones has recently been published.[129] The intermolecular =C–H···O bond (or several such bonds) between the carbonyl oxygen atom and the rather acidic hydrogen atom of the methylene group was found to be an important factor in determining the crystal structures of these compounds. Among the X-ray structures of five dienones,[89] the shortest =C–H···O [2.42(1) Å] contact was observed in

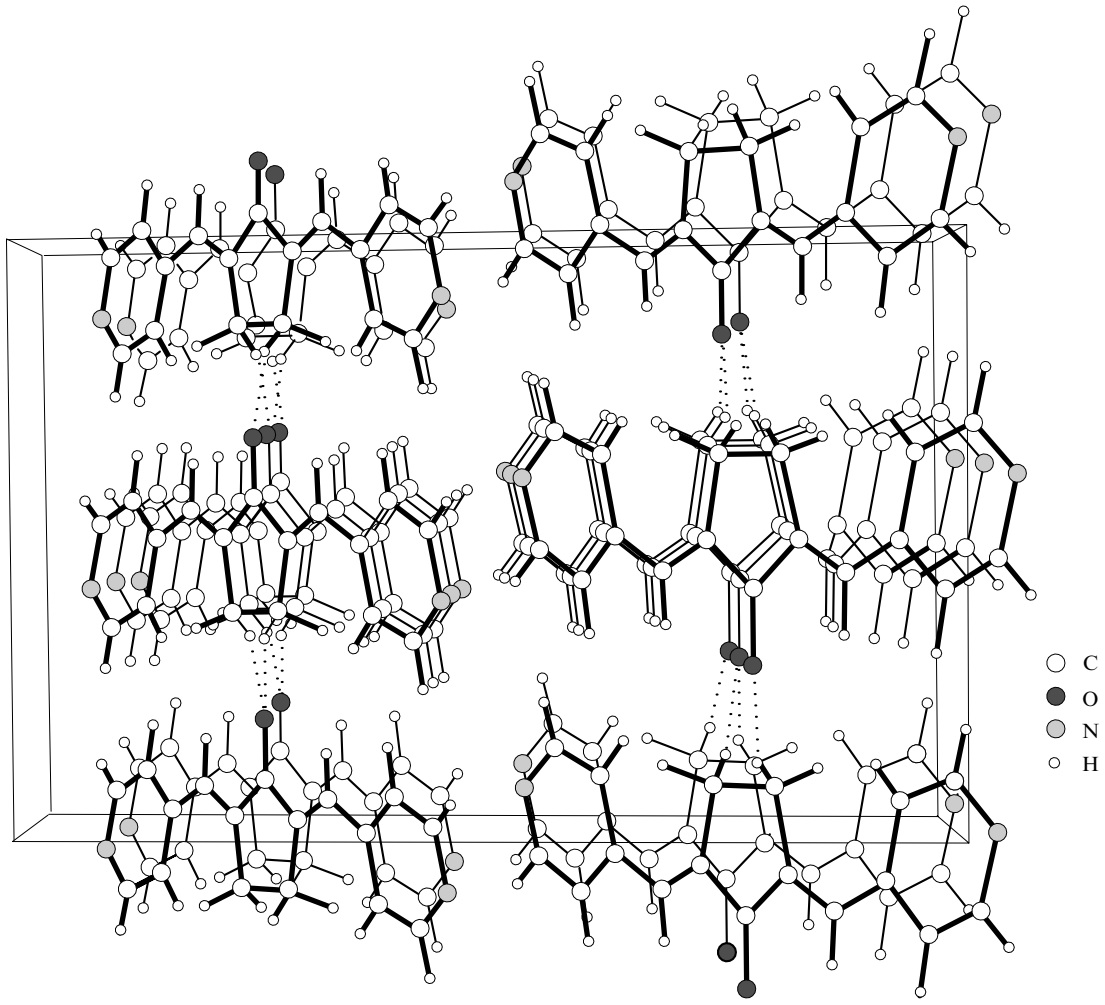


Figure 2. Fragment of the crystal structure of (*E*,*E*)-bis(4-pyridylmethylidene)cyclopentanone (**5**).[89]

the structure of (*E*,*E*)-2,4-bis(4-pyridylmethylidene)cyclopentanone (**5**). The oxygen atom of one molecule **5**, like that in the structure of the benzylidene analogue,[129] forms two hydrogen bonds with the methylene hydrogen atoms of two translationally related molecules. The hydrogen atoms of both methylene groups in the starting molecule form analogous bonds with two other adjacent molecules, resulting in two-dimensional networks (Fig. 2). In each network, the dienone molecules are aligned in a head-to-tail fashion.

An analogous packing mode was found in the crystals of (*E*,*E*)-5-benzylidene-2-(2-pyridylmethylidene)cyclopentanone (**6**). However, the intermolecular contact in the latter structure is somewhat weaker (C—H···O, 2.50 Å).[131]

The X-ray diffraction data for cross-conjugated dienones were used [130] to explain the regioselectivity of the reactions of unsymmetrical dienones with nucleophilic reagents.

IV. Reactions of dienones

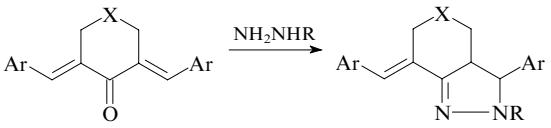
1. Reactions involving the C=C—C=O bonds

Among numerous transformations of bis(arylmethylidene) derivatives of cyclic ketones, reactions with nitrogen-containing bis- and polynucleophilic reagents [hydrazines, hydroxylamine, (thio)semicarbazides and guanidines] have been studied in most detail, whereas reactions with C-nucleophiles have received less attention. These reactions involve the C=C—C=O bonds of dienones and are used primarily for constructing new hetero- and carbocyclic systems.

a. Reactions with hydrazines and semicarbazides

The reactions of bis(arylmethylidene)cyclohexanones with hydrazine hydrate afford rather stable hexahydro-2*H*-indazoles in good yields regardless of the reactant ratio. Most of the studies concerned the reactions of symmetrical bis(arylmethylidene)cyclohexanones [40, 41, 132–142] or their heteroanalogues, such as piperidin-4-ones,[12, 40, 41, 92, 138, 143, 144] tetrahydropyranones [7, 14, 142] and tetrahydrothiopyranones,[14, 95, 97, 145] with hydrazine [40, 41] and its derivatives (phenylhydrazine,[135–139] 4-nitrophenylhydrazine,[139] alkylhydrazines,[36, 37, 140, 143, 145] alkylaminohydrazines [141–143] and 2- and 3-pyridylhydrazines [138]).

In the reactions with substituted hydrazines, dienones undergo heterocyclisation to form hexahydroindazoles **7**. In all cases, the adducts of substituted hydrazines are the most stable.[35]



7

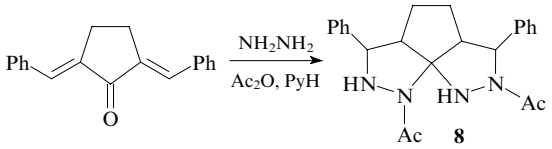
X = CH_2, S, NH, NMe, NCH_2OH, $N(CH_2)_2Ph$, $N(CH_2)_2Ac$, NAc, NC(O)Et, $NC(O)NH_2$, NC(O)NHMe, NC(=NH)NH_2;
R = H, Me, Pr^n, Bu^n, $(CH_2)_2OH$, CH_2CF_3, Ac, $(CH_2)_2NMe_2$, $(CH_2)_3NMe_2$;
Ar = Ph, 2-ClC_6H_4, 3-ClC_6H_4, 4-ClC_6H_4, 4-$OMeC_6H_4$, 3,4-$(OMe)_2C_6H_3$, 4-$NMe_2C_6H_4$, 3,4-$(OCH_2O)C_6H_3$, 1- and 2-naphthyl, Fu, Th, 2-Py.

The only example of the microwave-assisted synthesis of hexahydroindazoles from bis(arylmethylidene)cyclohexanones and methylhydrazine was documented.[140]

It was suggested[36, 146, 147] that hexahydroindazoles are formed *via* the hydrazone followed by the five-membered ring closure (path *a* in Scheme 2). Only in some cases,[97, 139] did reactions with substituted hydrazines (R = Ph or Pr^n) give isomeric indazoles as minor products due to steric factors. These products are formed as a result of the Michael addition of the primary amino group (path *b* in Scheme 2). The latter compounds readily undergo aromatisation to give tetrahydroindazoles.

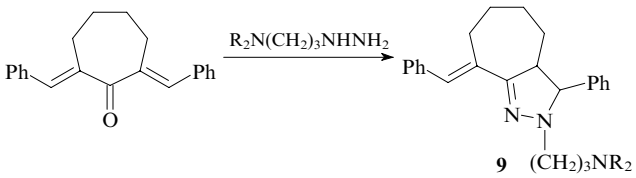
The reactions of cyclopentanone derivatives with hydrazines have been little studied.[132, 137, 148, 149] Unambiguous spectroscopic evidence for the structures and stereochemistry of such products are lacking in the literature; for the exception see Ref. 137.

For example, it was demonstrated[132] that 2,4-dibenzylidenecyclopentanone, unlike 2,5-dibenzylidenecyclohexanone, is transformed into product **8** as a result of the addition of two hydrazine molecules at the carbonyl group and both double bonds. However, the spectroscopic data reported in this study are contradictory, and the formation of this structure has not been confirmed in more recent studies.



8

The reactions of dienones containing the seven-membered ring with hydrazines were covered by a patent.[150] The reactions of 2,6-dibenzylidenecycloheptanone with aminoalkylhydrazines afford cyclohepta[*c*]pyrazolines **9** as free bases. The latter were used as the starting compounds in the synthesis of the corresponding salts (oxalates and maleates). These heterocyclic systems have antimicrobial activity.

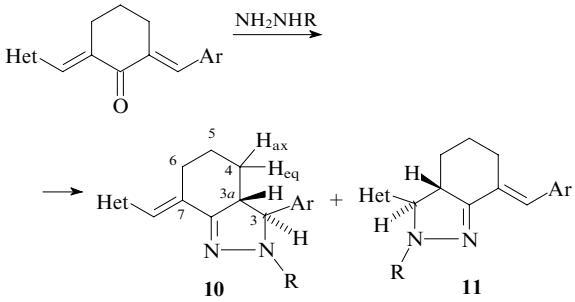


9

NR_2 = NH_2, NHAlk, $NAlk_2$, NAlkAr.

The reactions of hydrazines with unsymmetrical dienones raise a problem of regiospecificity and regioselectivity. The regiospecificity and regioselectivity of these reactions are determined by the nature of heterocyclic substituents and the geometry of substrates.[2, 115, 151–156] For example, in the reactions of dienones containing the furfurylidene fragment with hydrazine and phenylhydrazine, this fragment remains intact regardless of the nature of another substituent, even in the presence of electron-donating or electron-withdrawing groups in the carboaromatic rings. This regiospecificity is attributed to the fact that the furfurylidene fragment is coplanar with the C=C–C=O bonds (X-ray diffraction data), whereas another substituent deviates from this plane. This arrangement leads to a substantial difference in the activity of two electrophilic β-carbon centres and determines the direction of the nucleophilic attack.

In the presence of the carboaromatic, thienyl, 2- or 3-pyridyl substituent instead of the furyl group, the heterocyclisation follows both possible pathways. The ratios of the resulting regioisomeric hexahydroindazoles **10** and **11** are generally estimated by ^{1}H NMR spectroscopy.[115]

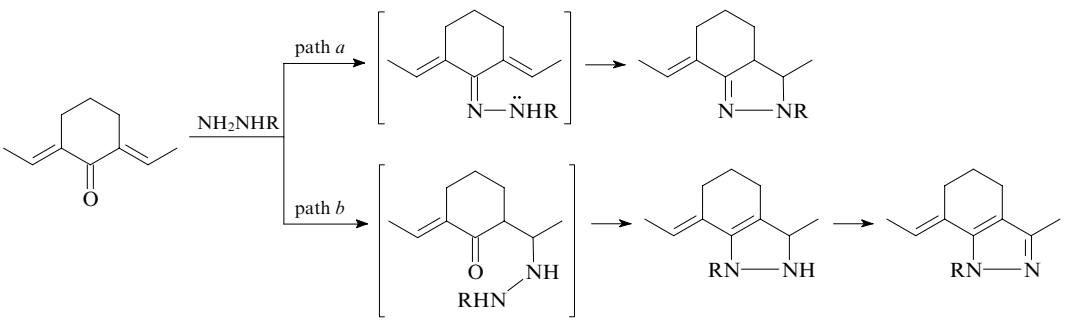


10 **11**

Het = Fu, 5-nitro-2-furyl, 5-methyl-2-furyl, Th, 2-Py, 3-Py;
Ar = 2-Py, 3-Py, XC_6H_4 (X = H, 4-OMe, 4-NMe_2, 3-NO_2, 4-NO_2, 2-Cl, 2-F, 4-Br) ; R = H, Ph.

The stereochemistry of the adducts of hydrazine to dienones (*cis* or *trans* positions of the protons at the chiral centres of pyrazoline) often depends on the conditions of cyclocondensation. Thus the reactions in basic media afford *trans* isomers, whereas acidic media generally favour the formation of *cis* isomers. For example, the acid-catalysed reactions of bis(arylmethylidene)cyclohexanones with unsubstituted

Scheme 2



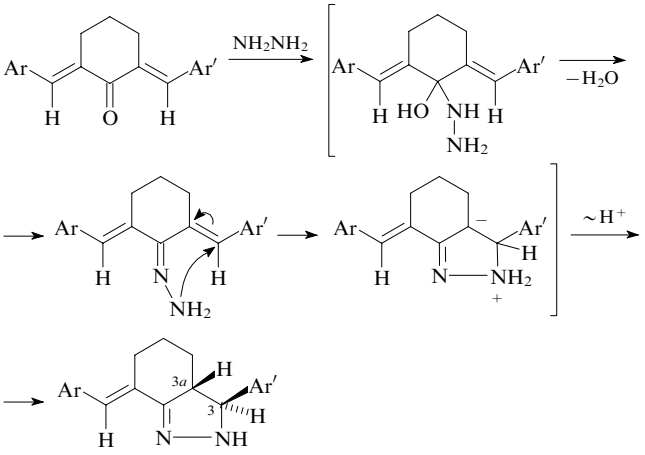
hydrazine or 4-nitrophenylhydrazine gave hexahydroindazoles as *cis* isomers or mixtures of *cis* and *trans* isomers, respectively.[139] However, the reactions of dibenzylidenecyclohexanone with phenylhydrazine afforded only *trans* isomers in both acidic and basic media.[139] These data remain to be explained. It should be noted that the stereochemistry of the reaction products has not been considered at all in some publications (see, for example, Refs 132, 142 and 157).

The choice of the criterion for the assignment of hexahydroindazoles **10** and **11** to *cis* or *trans* isomers has long been debated. The spin–spin coupling constants (J) of the methine protons at the C(3) and C(3*a*) atoms of the pyrazoline ring in the ^{1}H NMR spectra were used as this criterion. The constants $J_{3,3a}$ for the *cis* and *trans* isomers are 10–14 and 3–10 Hz, respectively.[158] At the same time, the *trans* configuration was assigned to systems with $J_{3,3a}$ = 13 Hz.[40,41,92,133] More recently, it has been demonstrated[159,160] that the unambiguous assignment of isomers cannot be made based on the spin–spin coupling constants because these constants can be different, equal or only slightly different for the *trans* and *cis* isomers. This fact was established based on the analysis of the ^{1}H NMR spectra of 2-acetyl- and 2-carbamoylhexahydroindazoles with a known configuration.

The assignment of stereoisomers based on the difference in the chemical shifts of the protons H(3), H(3*a*) and H_{ax}(4) proved to be more reliable. These differences are determined to a large extent by the diamagnetic anisotropy of the substituent at the C(3) atom. The signals for the protons H(3) and H(3*a*) in the *trans* isomer are shifted upfield by 0.5–0.7 ppm with respect to the signals of the *cis* isomers. The proton H_{ax}(4) is more sensitive to the stereochemistry of compounds. In the spectra of the *cis* isomers, this signal is shifted upfield by 0.9–1.0 ppm compared to that of the *trans* isomers.[139]

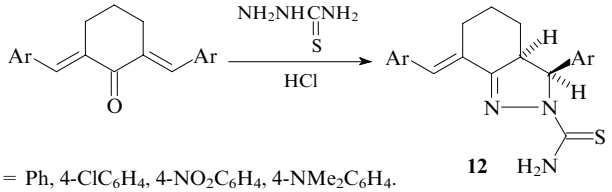
Therefore, the signal for the proton H(3) at δ 4.30–5.10, the signal for the proton H(3*a*) at δ 2.94–3.25 and the signal for the proton H_{ax}(4) at δ 1.35–1.75 serve as the reliable criterion for assigning the *trans* configuration to hexahydroindazoles **10**. The X-ray diffraction data[156,159] confirmed the conclusions drawn from the analysis of NMR spectra.

An adequate explanation for the formation of the observed isomeric hexahydroindazoles is lacking. It was hypothesised[115] that the azacyclisation affords the planar carbanion stabilised by the intramolecular 1,3-proton transfer. This gives rise to a heterocycle containing a bulky substituent in the pseudoequatorial *trans* position and pseudoequatorial protons H(3) and H(3*a*).

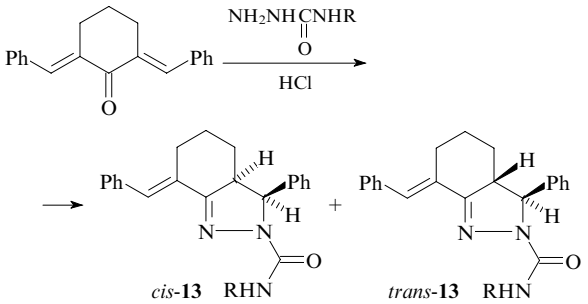


Apparently, one of the C=C double bonds is protonated in an acidic medium to form a carbocation, which can be attacked by a nucleophile from both sides to give finally both the *cis* and *trans* isomers.

The reactions of 2,6-dibenzylidenecyclohexanones with thiosemicarbazide[159,161–163] or semicarbazides[159,161] proceed with the involvement of the hydrazine group of the reagents to give *cis*-2-thiocarbamoylhexahydroindazoles **12** (Refs 159, 161 and 162) or a mixture of *cis*- and *trans*-2-carbamoylhexahydroindazoles **13**.[163] The lower nucleophilicity of semicarbazides compared to hydrazines requires the use of acidic catalysts. The stereochemistry of products **12** and **13** was established by ^{1}H and ^{13}C NMR spectroscopy and X-ray diffraction.[159]

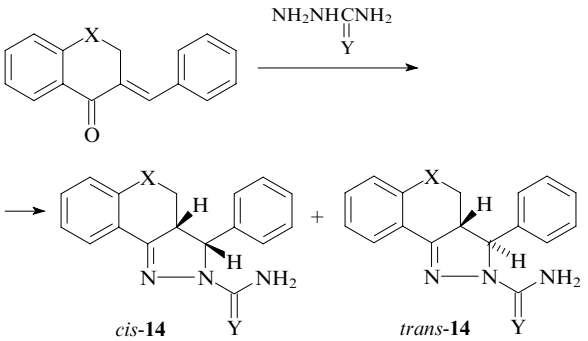


Ar = Ph, 4-ClC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$, 4-NMe$_2$C$_6$H$_4$.



R = H, Ph.

The stereoselective synthesis of *trans*- and *cis*-isomeric benzocyclohexa(hepta)-, benzopyrano- and benzothiopyrano[*c*]pyrazolines **14** was documented.[164] The *trans* isomer is formed only in hot pyridine, whereas the reactions in refluxing ethanol in the presence of HCl afford *cis*-pyrazolines and small amounts of the *trans* isomers.

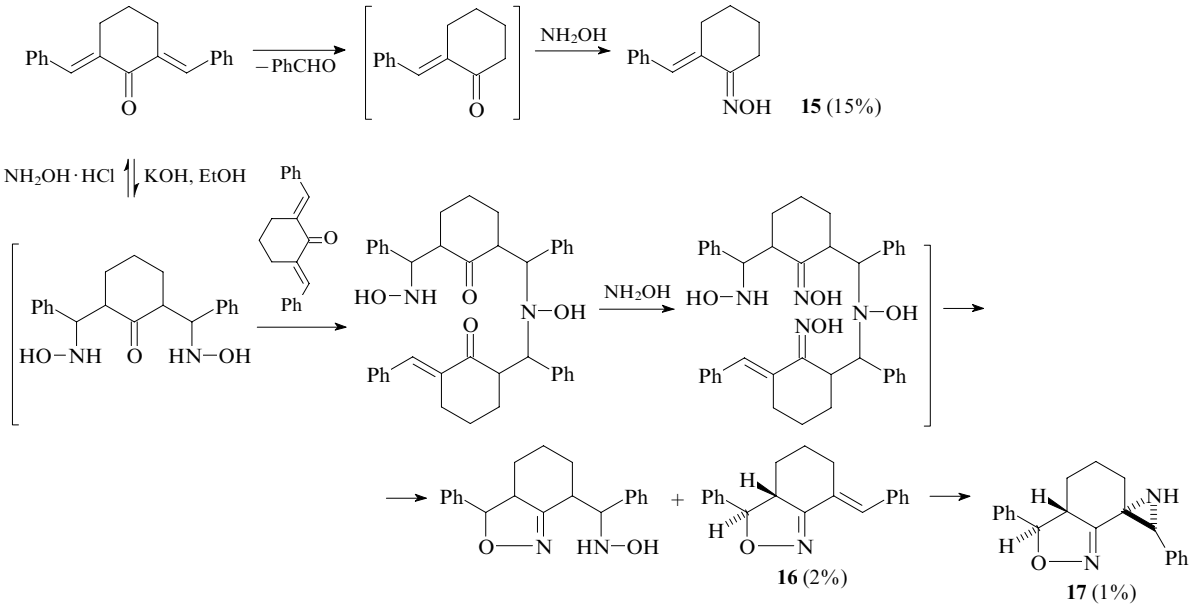


X = CH$_2$, (CH$_2$)$_2$, O, S, SO$_2$; Y = O, S.

b . Reactions with hydroxylamine

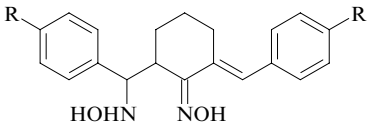
The reactions of dienones with hydroxylamine are complex and follow different pathways. For example, 2,6-dibenzylidenecyclohexanone underwent an unusual transformation when refluxed with hydroxylamine hydrochloride in a 3.5 M ethanolic KOH solution.[165] The reaction afforded a mixture of the following three products in a total yield of 18%: 2-benzylide-

Scheme 3



necyclohexanone oxime (**15**), 7-benzylidene-3-phenylcyclohexahydrobenzisoxazole (**16**) and 3-phenylhexahydrobenzisoxazole-7-spiro-2-(3-phenylaziridine) (**17**). In these heterocyclic systems, the *trans* arrangement of the protons was established by two-dimensional ^{1}H and ^{13}C NMR spectroscopy. Heterospirane **17** was characterised by X-ray diffraction. The reaction mechanism proposed by the authors is presented in Scheme 3.

According to other studies,[166–168] the reactions of substituted 2,5-dibenzylidenecyclohexanones with a fourfold excess of hydroxylamine hydrochloride and sodium acetate afford hydroxylaminooximes **18**. The latter can be considered as the nucleophilic addition and nucleophilic substitution products. It should be noted that the structures of products **18** were confirmed only by elemental analysis data and IR spectra.



18

R = H, Me, Cl.

c. Reactions with thioureas and guanidines

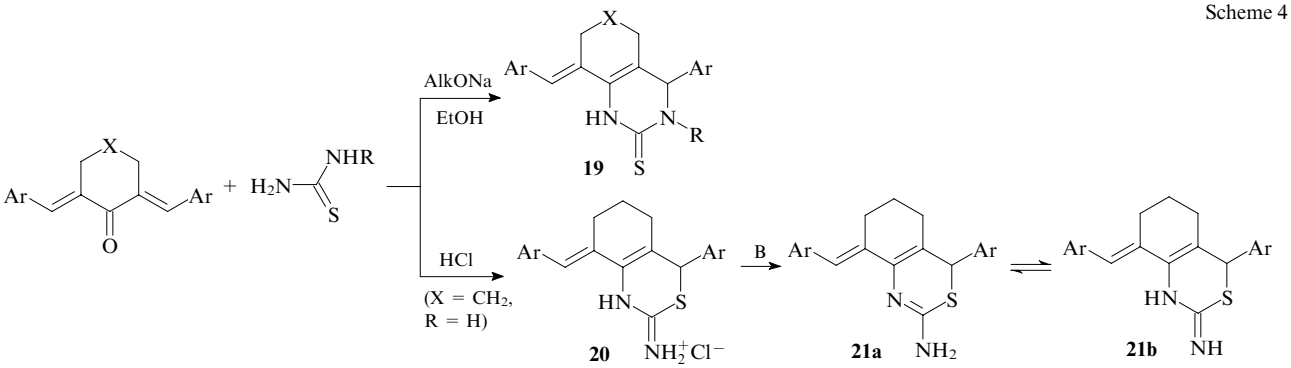
The reactions of thiourea with α,β-unsaturated ketones involve either the S,N- or N,N-nucleophilic sites depending on the reaction conditions. In an acidic media, the reactions afford 1,3-thiazines as the major products; in alkaline media, pyrimidine-2-thiones are formed as the major products.[169, 170] The same situation is observed for dienone derivatives of cyclic ketones.

In alkaline media, the reactions of bis(arylmethylidene)-cyclohexanones, -piperidin-4-ones and -tetrahydropyran-4-ones afford fused pyrimidinethiones **19** as a result of the addition of thiourea at the C=C–C=O bonds.[12, 136, 171, 172] 2,5-Bis(arylmethylidene)cyclopentanones behave analogously.[171, 173] In acidic media, thiourea reacts in the thiol form, and the heterocyclisation with dienones involves the sulfur atom to give benzothiazinium salts **20**. Neutralisation of the latter affords free bases[174] existing as the amino (**21a**) and imino (**21b**) tautomers (Scheme 4).

Data on the use of urea as the bis-nucleophile in the reactions with cross-conjugated dienones are lacking in the literature.

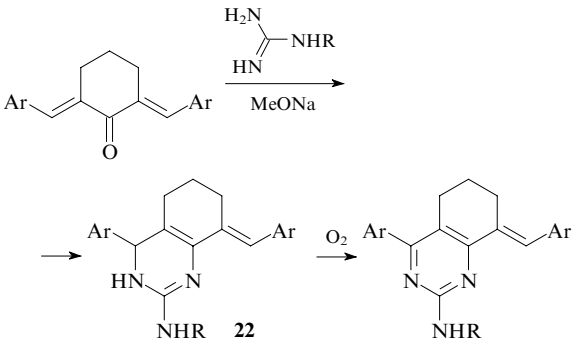
Heating of bis(arylmethylidene)cyclohexanones with guanidinium hydrochloride or alkylguanidines in basic media

Scheme 4



X = O, CH_2, NH; R = H, Me; Ar = XC_6H_4 (X = H, 2-Cl, 4-Cl, 4-Me, 4-OMe, 4-NMe_2), 3,4-$(OCH_2O)C_6H_3$, Fu, Th; B is a base.

affords hexahydroquinazolines **22**, which readily undergo aromatisation during isolation.[175, 176]

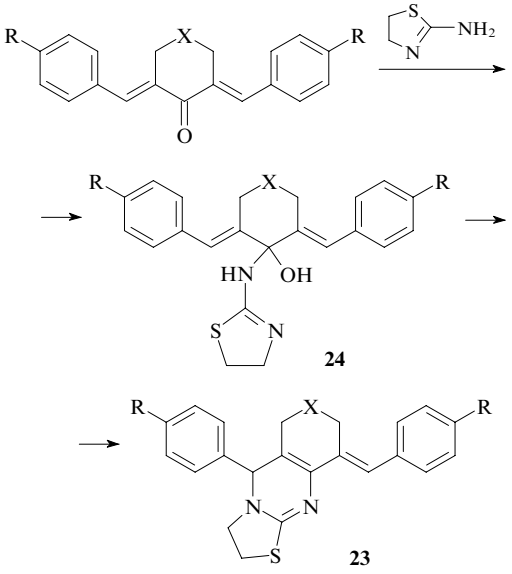


R = H, Et, Bu^n, Bn; Ar = Ph, 4-OMeC$_6$H$_4$, 4-NMe$_2$C$_6$H$_4$, 3,4-Cl$_2$C$_6$H$_3$.

d. Reactions with hetarylamines

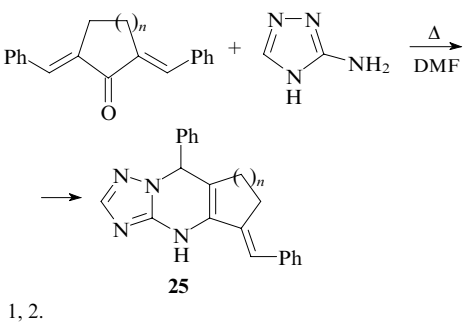
Polyfused heterocyclic systems are constructed by cyclocondensation of dienones with hetarylamines. The annulation proceeds with the involvement of the exocyclic primary amino group and the heterocycle of the reagent.

For example, annelated thiazolopyrimidines **23** were synthesised by cyclocondensation of 2-aminothiazoline with the corresponding dienones.[91] The authors succeeded in isolating and characterising the initially formed hemiaminals **24**.



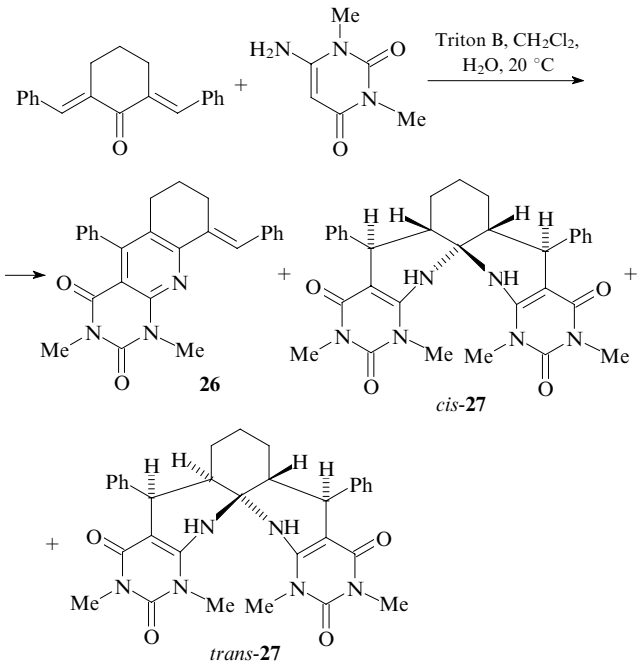
X = S, SO$_2$, O; R = H, Me, OMe.

Dihydro-1,2,4-triazolo[1,5-*a*]pyrimidine derivatives **25** annelated with carbocycles were synthesised analogously starting from 3-amino-1,2,4-triazole and dibenzylidenecycloalkanones.[177]



n = 1, 2.

The reactions of 6-amino-1,3-dimethyluracil with 2,6-dibenzylidenecyclohexanone under conditions of phase-transfer catalysis afford three products: monoadduct **26** and two isomeric bisadducts **27**. Their structures were confirmed by two-dimensional NMR spectroscopy and X-ray diffraction analysis.[178] According to the reaction mechanism proposed by the authors, the first step involves the Michael addition of the enamine to the dienone followed by the addition of the second uracil molecule to the adduct.

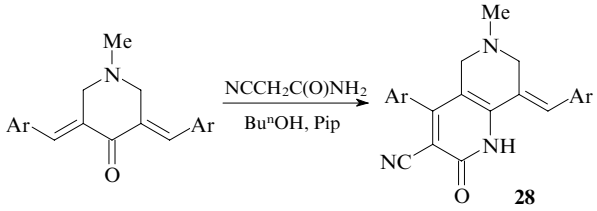


Examples of the construction of fused polycyclic systems by cyclocondensation of bis(arylmethylidene) derivatives of cyclohexanone with 5-aminopyrazole and 1-amino-4-azafluorene are documented.[179, 180]

e. Reactions with C-nucleophilic reagents

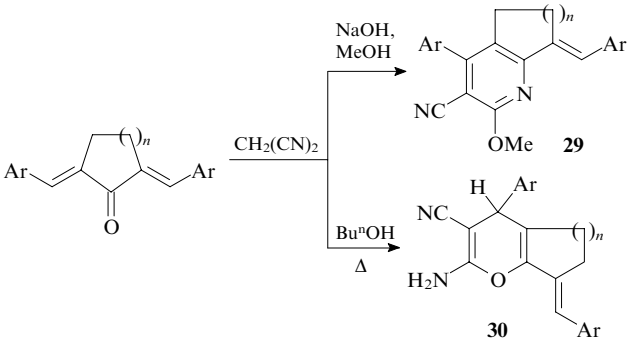
Dienones are active as substrates in reactions with compounds having high CH-acidity (cyanoacetamide, malononitrile, β-keto anilides, enamines and ynamines). These reactions afford fused carbo- and N,O-heterocyclic compounds.

This method was used to prepare substituted 1,6-naphthyridines **28** starting from bis(arylmethylidene) derivatives of piperidin-4-one and cyanoacetamide.[12]



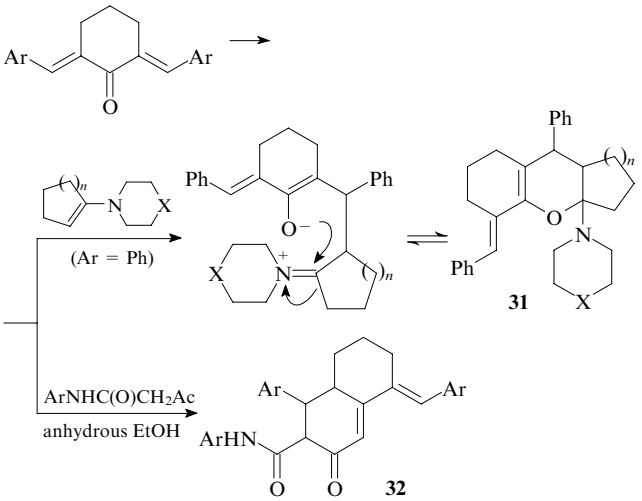
Ar = 4-MeC$_6$H$_4$, 4-OMeC$_6$H$_4$, Th; Pip is piperidine.

The reactions of bis(arylmethylidene) derivatives of cyclohexanone and cyclopentanone with malononitrile in alkaline media give 3-cyano-2-methoxypyridines **29** annulated with the corresponding carbocycles.[157, 181] The analogous condensation performed in refluxing butanol in the absence of bases afforded 2-amino-3-cyano-4*H*-pyran derivatives **30**.[12, 182, 183]



n = 1, 2; Ar = Ph, 4-ClC_6H_4, 4-$OMeC_6H_4$, Fu, Th.

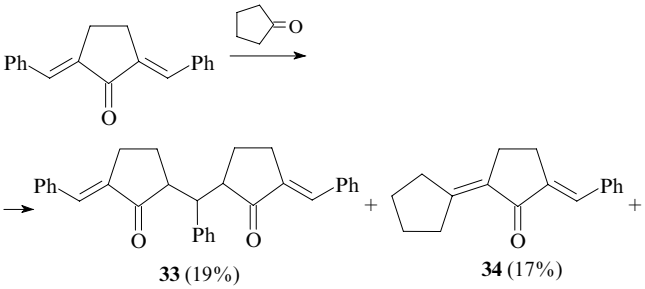
Bis(arylmethylidene)cyclohexanones react with cyclopentanone-[184] and cyclohexanone-derived[185] enamines, as well as with β-keto anilides,[186] to form hetero- and carbocyclic adducts, *viz*., dihydropyrans **31** and hexahydronaphthalenones **32**, respectively. Analogous hydronaphthalenones were synthesised by condensation of 2,6-bis(arylmethylidene)cyclohexanone with cyclohexanone in the presence of a 50% aqueous NaOH in a DMSO–ethanol mixture as the solvent.[186]



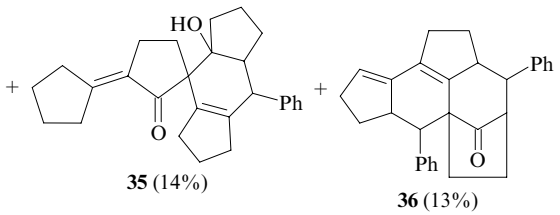
n = 1, 2; X = CH_2, O; Ar = Ph, 4-$OMeC_6H_4$.

The use of ynamines as the CH-acids in these reactions was documented.[187] However, the data confirming the structures of the resulting substituted 4*H*-pyrans were not convincing.

The unusual reaction of cyclopentanone with 2,5-dibenzylidenecyclopentanone (in DMSO, EtOH or aqueous NaOH) was described.[188] 1,5-Diketone **33**, unsymmetrical chalcone **34**, spiro compound **35** and fused polycyclic compound **36** were isolated from the reaction mixture by chromatography.

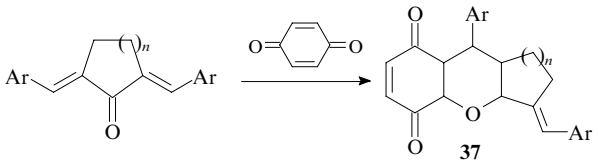


33 (19%) **34** (17%)



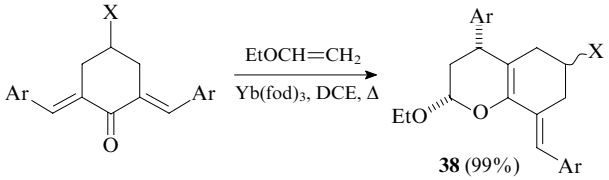
35 (14%) **36** (13%)

It was shown[189] that bis(arylmethylidene)cyclopentanones and -cyclohexanones react with 1,4-benzoquinone as dienes to form annulated chromanediones **37**. The compositions and structures of the reaction products were determined only by IR and UV spectroscopy and elemental analysis.



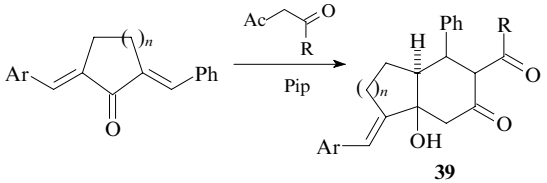
n = 1, 2; Ar = Ph, 2-OHC_6H_4, 4-MeC_6H_4, 2-ClC_6H_4, Fu.

The analogous [4 + 2]-cycloaddition reaction of ethyl vinyl ether with dienone affords tetrahydrobenzopyran **38** containing the aryl and ethoxy groups in *cis* positions.[190]



Ar = 2-$N_3C_6H_4$; X = $(CH_2)_2OMs$ (Ms = SO_2Me); DCE is 1,2-dichloroethane; fod is 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione.

The reactions of bis(arylmethylidene) derivatives of cyclohexanone and cyclopentanone with acetylacetone or ethyl acetoacetate in the presence of piperidine give tetrahydronaphthalenones and hydroindanones **39**, respectively, as a result of carbocyclisation. The reaction of unsymmetrical dienones proceeds exclusively at the carbon atom of the unsubstituted benzylidene fragment. The structures of products **39** were established by ^1H and ^{13}C NMR spectroscopy.[191]

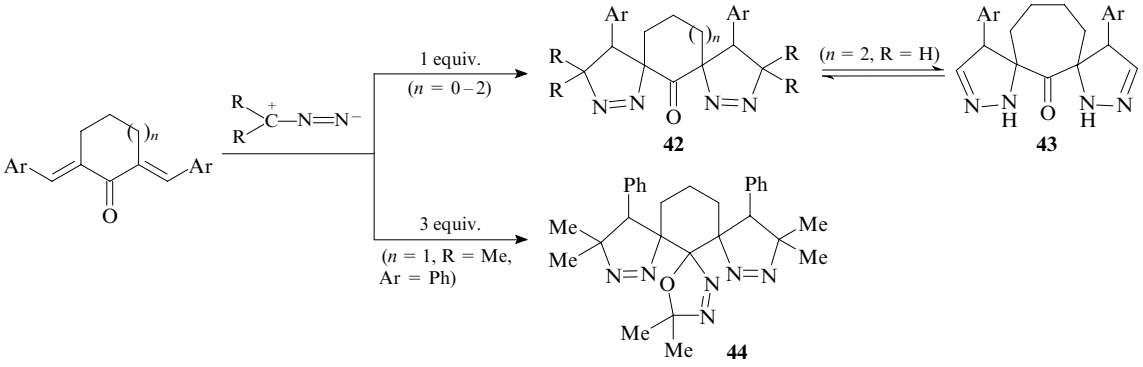


n = 1, 2; Ar = Ph, 2-OHC_6H_4, 4-MeC_6H_4, 2-ClC_6H_4, Fu; R = Me, OEt.

2. Reactions involving the C=C bonds

Bis(arylmethylidene) derivatives of cyclic ketones are involved in various reactions at one or two C=C double bonds ([3 + 2]- and [2 + 2]-cycloaddition reactions giving rise to mono- or bisadducts, bromination, aziridination, cyclopropanation and oxidation). In some cases, the carbonyl group is also involved in these reactions.

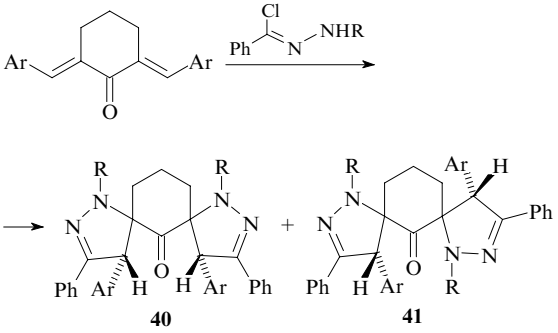
Scheme 5



R = H, Me; Ar = Ph, 4-$NO_2C_6H_4$, 2-ClC_6H_4, 4-ClC_6H_4, 4-$NH_2C_6H_4$, 3,4-$(OMe)_2C_6H_3$, 2,4-$(OMe)_2C_6H_3$, Fu.

a. Cycloaddition

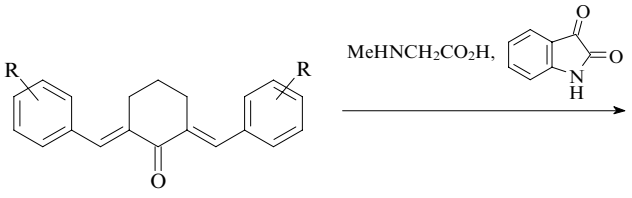
The dipolar [3 + 2]-cycloaddition of 1,3-dipoles to dienones affords spiro compounds.[42, 192–202] For example, the addition reactions of substituted hydrazones to 2,6-bis(arylmethylidene)cyclohexanones give mixtures of isomeric bisadducts **40** and 41.[192]

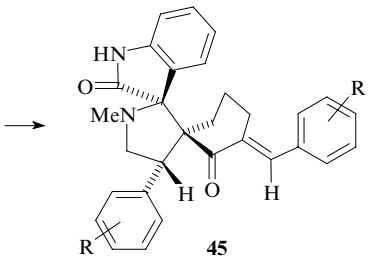


Ar = Ph, 4-MeC_6H_4, 4-FC_6H_4, 4-ClC_6H_4; R = Ph, 4-MeC_6H_4.

The reactions of cyclanone derivatives C_5–C_7 with diazomethanes proceed analogously to form spiranes **42**.[42, 200–202] The reaction of dibenzylidenecyclohexanone with unsubstituted diazomethane affords products **42** (*n* = 1, Ar = Ph), which are in tautomeric equilibrium with compounds **43**. In the presence of a threefold excess of diazo compounds, the keto group is also involved in this reaction, resulting in the formation of the spirooxadiazoline ring in spirane **44** (Scheme 5).[202]

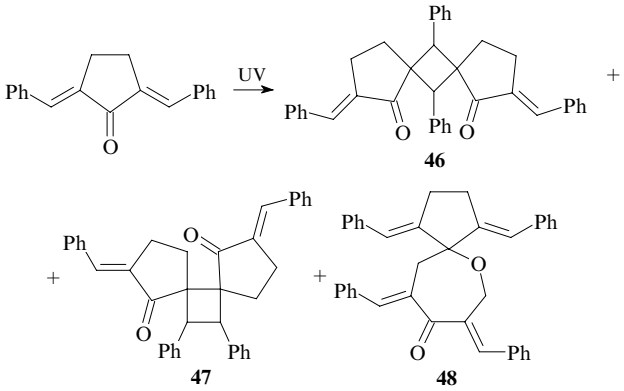
Azomethine ylide generated from isatin and sarcosine reacts with 2,6-dibenzylidenecyclohexanone to form cycloadduct **45.** The addition of the ylide to the dienone occurs only at one of the exocyclic double bonds.[203] Bisadducts are not produced in this reaction even when an excess of the 1,3-dipole is used. This is apparently attributed to steric hindrance caused by the spiropyrrolidine ring. Under these conditions, simpler dipoles (for example, the dipole prepared from formaldehyde and sarcosine) give bisadducts.[195]



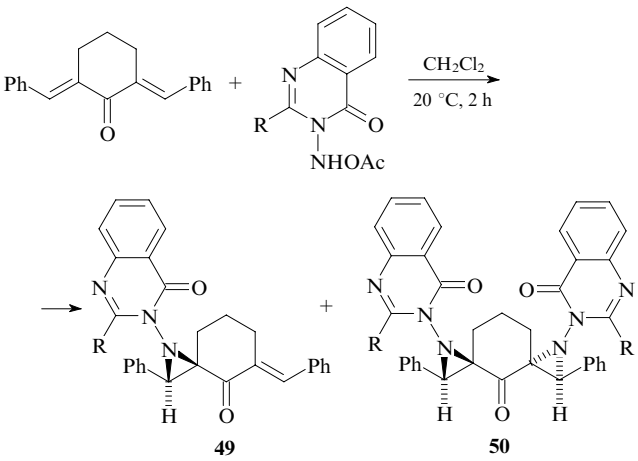


R = H, 4-Cl, 4-Me, 4-OMe, 4-NMe_2, 3-NO_2.

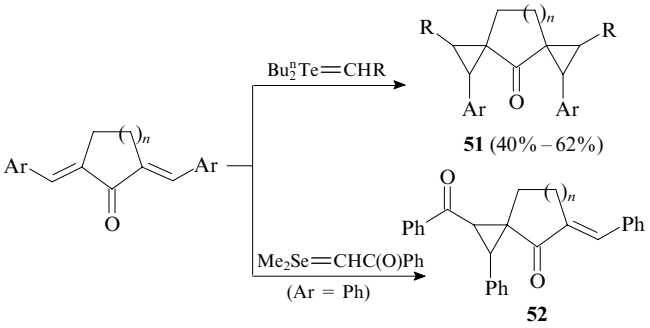
The dimerisation at the C=C bond induced by UV radiation was performed only for cyclopentanone derivatives.[89, 204, 205] This reaction gives different products depending on the reaction conditions (solid-state or solution dimerisation). The [2 + 2]-cycloaddition of 2,5-dibenzylidenecyclopentanone affords spiro compounds **46**–**48** (38 : 26 : 8 ratio); the conversion of the starting dienone is 90%.[205, 206] Similar results were obtained in the other studies.[38, 207, 208] It should be noted that under these conditions (+)-2,5-dibenzylidene-3-methylcyclopentanone appeared to be photostable and did not undergo dimerisation.[207, 208]



Spiro compounds containing three-membered rings were synthesised by aziridination and cyclopropanation.[203,209,210] For example, the reaction of equimolar amounts of 2,6-dibenzylidenecyclohexanone and 3-acetoxyaminoquinazolinone affords a mixture of mono- (**49**) and bisadducts (**50**) in a ratio of 7 : 3. The reaction with two equivalents of 3-acetoxyaminoquinazolinone directly affords compound **50**. The second C=C bond in compound **49** can be modified by the 1,3-dipolar cycloaddition with azomethines.[203]



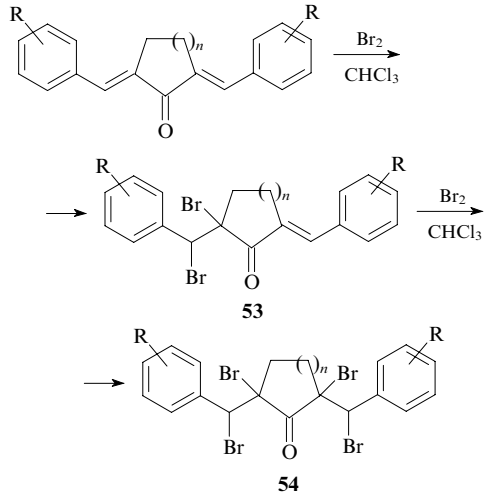
Dispirononanones and -decanones **51** were synthesised by the reactions of telluronium ylides with dibenzylidenecyclopentanone and -cyclohexanone, respectively.[209] The reactions of dienones with selenonium oxo ylide $Me_2Se{=}CHC(O)Ph$ proceed analogously to form monocyclopropanation products of bis(arylmethylidene)cycloalkanones (compounds **52**).[210]



n = 1, 2; Ar = Ph, 4-$OMeC_6H_4$; R = Ph, 4-ClC_6H_4, PhC(O).

b. Bromination. Synthesis of trienones

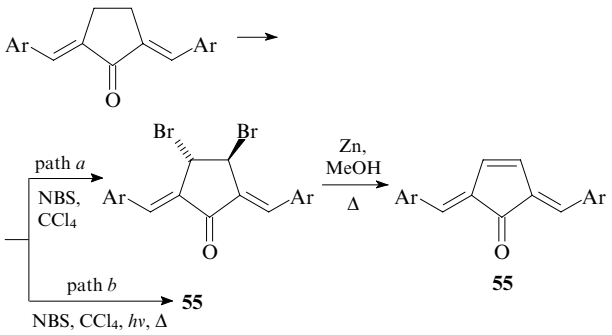
Bis(arylmethylidene)cycloalkanones are easily transformed into di- (**53**) or tetrabromo derivatives (**54**) when treated with one or two equivalents of bromine, respectively.[42, 79, 211, 212]



n = 2, 3; R = H, 4-OMe, 4-NMe_2, 3-NO_2.

The ability of bromine atoms (particularly, in the β position with respect to the carbonyl group) to undergo nucleophilic substitution was used to perform further transformations of polybromides **53** and **54**.[211–213] This method allows the successive introduction of one to four substituents (acyl, alkoxy or amino groups) into cyclanone molecules. It should be noted that electron-donating groups (4-OMe or 4-NMe_2) in the benzene rings of dienones facilitate the substitution, whereas electron-withdrawing groups (3-NO_2) inhibit the reactions. Despite the abundance of experimental details,[211–213] the stereochemistry of neither the bromination nor substitution products was discussed.

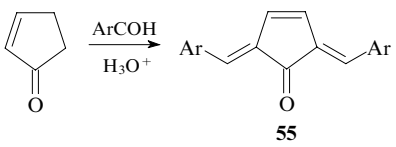
Bromine atoms can be introduced at the allylic position of the alicyclic moiety using *N*-bromosuccinimide (NBS) as the brominating agent. The subsequent elimination of bromine atoms with zinc dust affords trienone derivatives of cyclopentanone **55** (path *a*). The latter contain a larger number of conjugated double bonds compared to the starting dienones. As a result, there are strong π–π interactions between the molecules in the crystalline state due to flattening of the system.[214, 215]



Ar = Ph, 4-ClC_6H_4, 4-$OMeC_6H_4$.

The one-step transformation of dienones into trienones **55** without isolation of dibromides was carried out under irradiation and heating of a mixture of dienone and NBS in CCl_4 (path *b*).[216–219] This method was used to synthesise 2,5-bis(arylmethylidene)cyclopent-3-enones (**55**, Ar = Ph or 4-$OMeC_6H_4$). According to X-ray diffraction data,[216] the 2,5-di[(*E*)-benzylidene]cyclopent-3-enone molecules (**55**, Ar = Ph) are packed in the crystals in a head-to-tail fashion, which is typical of dienones. The adjacent layers are linked by interactions between the hydrogen atoms at the double bonds in the rings and the carbonyl oxygen atoms (CH···O, 2.5 Å).

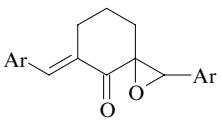
Attempts to use NBS for the synthesis of trienones containing pyridine fragments as the aryl component failed. Nevertheless, hetaryl-substituted trienones **55** (Ar = Th, 2-Py or 3-Py) were synthesised in good yields starting from cyclopent-2-enone and heteroaromatic aldehydes.[131]



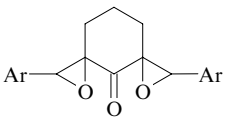
Ar = Th, 2-Py, 3-Py.

c. Oxidation

Dienones react with hydrogen peroxide in the presence of alkalis to form mono- (**56a**,**b**) and bis-epoxides (**57a**,**b**) as a result of oxidation of the C=C double bond.[220–223]



56a,b

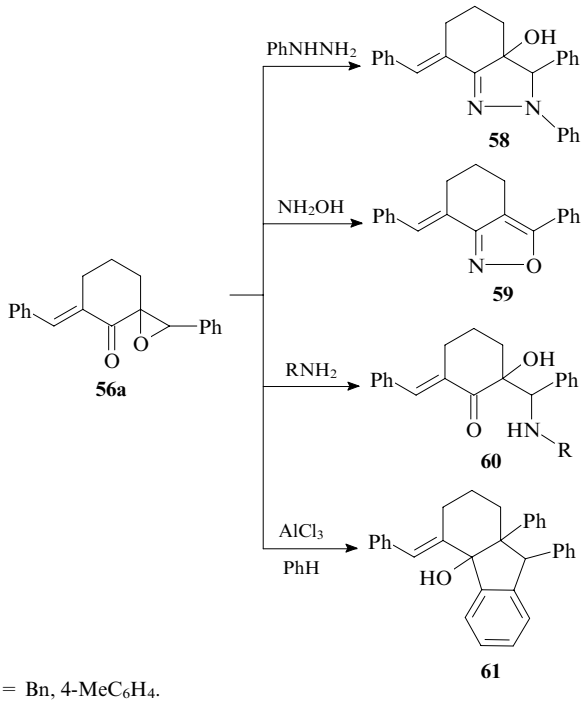


57a,b

Ar = Ph (**a**), 4-ClC_6H_4 (**b**).

The ability of the oxirane ring to undergo opening was used for the preparation of a series of compounds based on these products, which are difficult to synthesise by other methods (Scheme 6). For example, heterocyclic compounds, such as hydroxyhydroindazole **58** and tetrahydrobenzoisoxazole **59**, were synthesised from monoepoxide **56a** by the reactions with bis-nucleophiles (phenylhydrazine or hydroxylamine), whereas the reactions with amines (benzylamine or *p*-toluidine) afford ammonolysis products **60**. It was demonstrated [222] that compound **56a** is involved in the Friedel–Crafts reaction to form tricyclic compound **61**. However, no convincing proof of the structure of this product was offered.

Scheme 6



56a

58

59

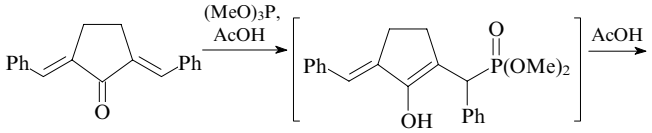
60

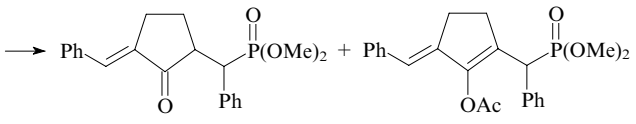
61

R = Bn, 4-MeC_6H_4.

d. Reactions with trialkyl phosphites

The reactions of trimethyl phosphite $P(OMe)_3$ with α,β-unsaturated ketones (including 2,6-dibenzylidenecyclohexanone) afford bipolar adducts, which are transformed into more stable cyclic phosphoranes or enol esters.[224] However, 2,5-dibenzylidenecyclopentanone does not give the expected product under these conditions; in the presence of acetic acid or acetic anhydride, this compound forms γ-keto phosphonate **62** and enol acetate **63**.[224]





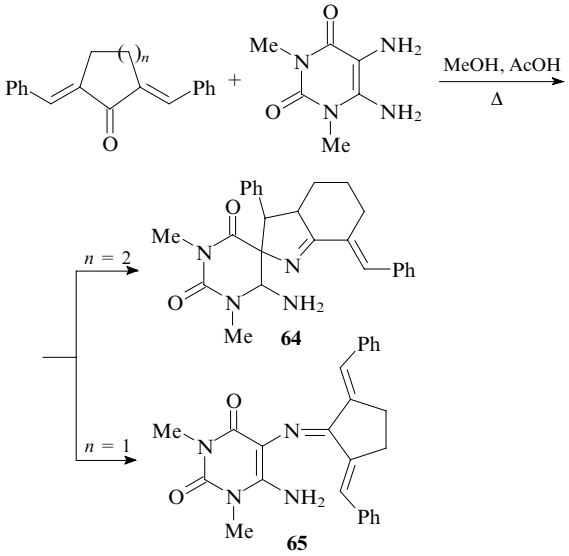
62

63

3. Reactions involving the C=O bond

The reactions of dienones at the carbonyl group are scarce due apparently to the conjugation in the C=C=O system and the fact that the attack of the reagents occurs predominantly on the β-carbon atoms.

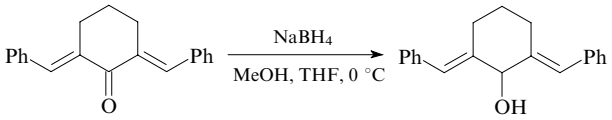
Unusual results were obtained in the study of the reactions of cyclic dienones with 5,6-diamino-1,3-dimethyluracil. In particular, 2,6-dibenzylidenecyclohexanone gives spirane **64**, whereas the reaction with 2,5-dibenzylidenecyclopentanone stops at the formation of azomethine **65**.[225] The structure of spiro compound **64** was unambiguously established by spectroscopic methods and X-ray diffraction analysis.



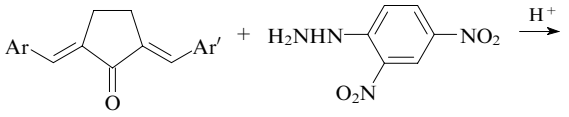
64

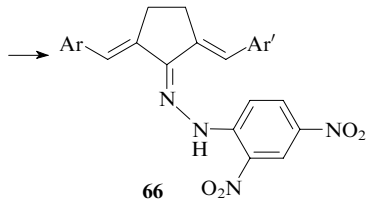
65

Under mild conditions (0 °C), the carbonyl group in 2,5-dibenzylidenecyclohexanone was selectively reduced to the hydroxy group.[226]



In the only study [103] on the reactions of unsymmetrical bis(arylmethylidene)cyclopentanones with hydrazines, it was reported that the reaction of 2,4-dinitrophenylhydrazine with these dienones in an acidic medium gave hydrazones **66**. However, no data confirming the structures of these products were reported.

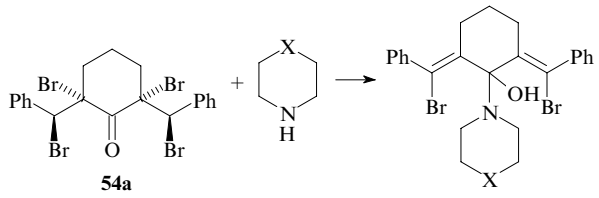




66

Ar = Ph, Fu, 1- and 2-naphthyl; Ar′ = Ph, Th, Fu, 1- and 2-naphthyl.

The non-conjugated carbonyl group in tetrabromo derivatives **54** can add to N-nucleophiles (for example, to piperidine or morpholine). In the presence of strong bases, the dehydrobromination of compounds **54** competes with the reaction with nucleophiles giving rise to addition – elimination products, *viz.*, 1-amino-2,6-bis(α-bromobenzylidene)cyclohexanols (**67**).[227]



54a **67**

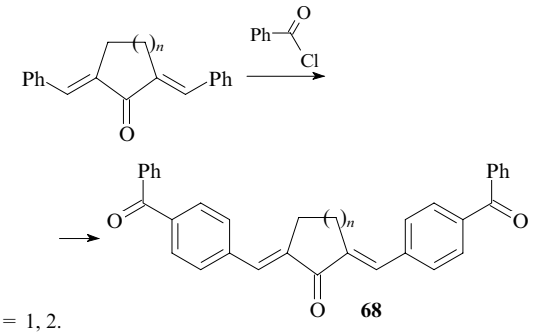
X = CH_2, O.

However, the reported structural formulas give rise to doubt. In our opinion, it is more likely that this reaction involves the addition of the amine at one or two double bonds and the nucleophilic substitution of bromine atoms.

4. Miscellaneous reactions

The present section deals with reactions of dienones, which proceed with the involvement of alicyclic moieties and aryl substituents. For bis(arylmethylidene) derivatives of heterocyclic ketones (piperidin-4-ones and thiopyran-4-ones), the following reactions at the heteroatom were documented: acylation at the NH group [18] and oxidation at the sulfur atom giving rise to the corresponding sulfoxides and sulfodioxides.[16–18, 88]

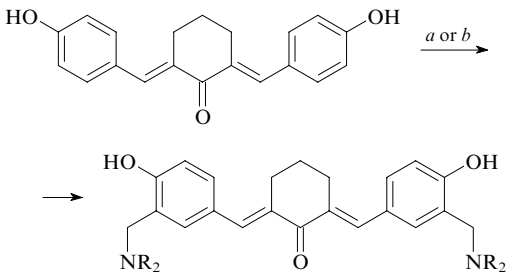
Aryl substituents can be modified by electrophilic substitution reactions. For example, compounds **68** were synthesised by acylation of dibenzylidenecycloalkanones.[228]



68

n = 1, 2.

Dienones **69a**,**b** containing hydroxy and dialkylaminomethyl groups in the aryl rings can be synthesised by aminomethylation of 2,6-bis(4-hydroxybenzylidene)cyclohexanone with dipiperidylmethane or tetramethyldiaminomethane in acetonitrile.[9]



69a,**b**

(*a*) $(CH_2)_5NCH_2N(CH_2)_5$, (*b*) $(Me_2N)_2CH_2$;
R_2 = $(CH_2)_5$ (**a**); R = Me (**b**).

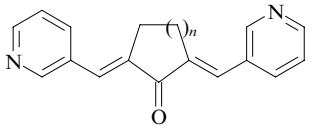
V. Dienone-based complex compounds

The field of supramolecular chemistry concerned with infinite supramolecular ensembles that are formed through coordination of ligands to complex-forming metals has been actively developed. It is advantageous to use polydentate ligands containing at least one carbon atom between donor heteroatoms (O, N, S, Se, *etc.*) for the construction of coordination polymers.[229] In this respect, cross-conjugated derivatives of cyclic ketones containing pyridine substituents, *viz.*, *exo*-bidentate systems Py–X–Py (X is a dienone bridge), are promising compounds.[89, 131, 230–234]

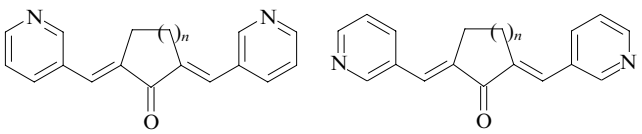
Compared to conventional *exo*-polydentate ligands (*i.e.*, non-chelating ligands), pyridine-containing dienones have a number of advantages. First, the angle between the electron pairs of the nitrogen atoms can be changed by varying the size and nature of the central ring. This angle is of importance for the construction of various metal – ligand combinations (cyclic dimers, cyclic oligomers, infinite chains, *etc.*). Second, these dienones are photosensitive materials.[11] This property can be used to stabilise polymers using radiation and to influence both the geometry and the degree of bond conjugation in the ligand molecules. Third, the structures of the complex products depend on the nature of the substituent at the aliphatic nitrogen atom in piperidin-4-one derivatives. Fourth, the nitrogen atom of the heterocycle can be involved in coordination to metal ions, thus increasing the ligand denticity to 3. This type of compounds can be assigned to monoheterotopic (identical substituents are present in aromatic fragments) or heterotritopic ligands (different substituents).

exo-Dentate cross-conjugated dienones were used (Refs 89, 131, 230–232) in the synthesis of supramolecular ensembles, Ag(I) served as the complexing metal ion and symmetrical derivatives of cyclopentanone, cyclohexanone and piperidin-4-one containing two 3- or 4-pyridylmethylidene fragments were chosen as ligands. For an adequate comparison of the experimental results, all complexation reactions were carried out under identical conditions (slow diffusion of a solution of metal salts in alcohols or acetonitrile into a solution of the ligand in chloroform or dichloromethane).

Different primary structural motifs were suggested for conformationally flexible ligand **70** containing 3-substituted pyridyl fragments. These motifs are determined by the conformation of the ligand in the complex (transoid or two cisoid).



transoid-**70**



cisoid-**70a** *cisoid*-**70b**

Three structural motifs for the complexation of metal (M) to ligand **70** are presented in Fig. 3 *a*–*c*. The *cisoid*-**70a**/*anti*, *transoid*-**70**/*syn* and *cisoid*-**70b**/*syn* combinations are also possible (the terms '*syn*' and '*anti*' refer to the orientation of the ligands with respect to the metal ion).

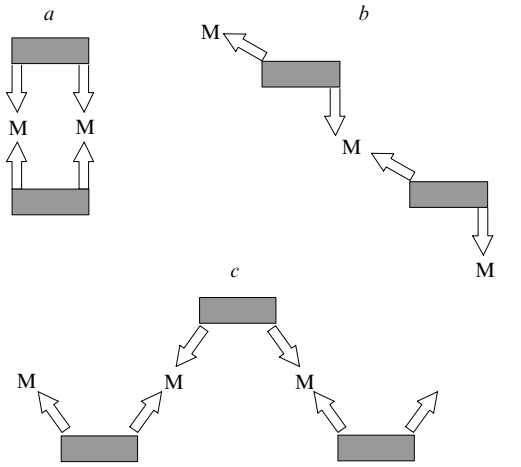


Figure 3. Schematic representation of the primary structural motifs for the complexation of ligand **70** with metal: *cisoid*-**70a**/*syn* (*a*), *transoid*-**70**/*anti* (*b*), *cisoid*-**70b**/*anti* (*c*).[231]
(Here and in Figs 5–7, the shaded rectangle indicates the ligand.)

Interactions between the primary motifs, which are responsible for the packing mode in the crystal structure, are determined by the balance between the interaction energies of the corresponding supramolecular synthons. These interactions depend on the nature of the anion and involve hydrogen bonds, dipole–dipole interactions, stacking interactions and metallophilic contacts.[234]

The reactions of 2,5-bis(3-pyridylmethylidene)cyclopentanone **70** ($n = 1$) with silver perchlorate or tetrafluoroborate in acetonitrile afford the isostructural discrete dinuclear metallacycles $[LAg \cdot NCMe]_2X_2$, where $X = ClO_4$ or BF_4 (Fig. 4).[231]

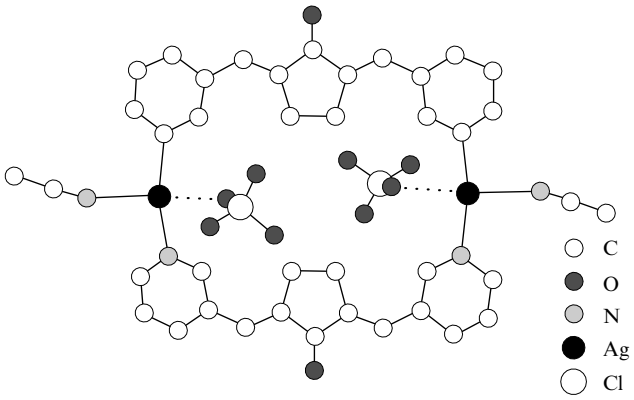


Figure 4. Molecular structure of the dinuclear metallacycle $[LAg \cdot NCMe]_2(ClO_4)_2$ prepared from (*E*,*E*)-2,5-bis(3-pyridylmethylidene)cyclopentanone (L = **70**, $n = 1$).[231]

Ligands containing the six-membered central ring (cyclohexanone and piperidin-4-one) do not form dimeric metallacycles (at least, in the crystalline state); instead, polymeric motifs of complexation are observed. X-Ray diffraction studies of polymeric complexes showed that the structural motif is determined primarily by the position of the nitrogen atom in the pyridine ring. Thus, 4-substituted pyridines form single chains, whereas 3-substituted pyridines form 'double chains', 'ladders' and more complex structures. In the complexation products, the Ag(I) ion is generally coordinated by two pyridine nitrogen atoms belonging to two different ligand molecules. This coordination results in the formation of angular structures, in which the ligands are predominantly in the *syn* orientation with respect to the metal centre [the so-called '*syn* chains' (Fig. 5 *a*)]. This structure is typical of the complex of 2,6-bis(3-pyridylmethylidene)cyclohexanone **70** ($n = 2$) with silver nitrate [230] (see Fig. 5 *b*).

It was demonstrated [227] that two adjacent *syn* chains are linked by short Ag···Ag contacts in a head-to-tail fashion. These interactions give rise to the ladder-type topology (Fig. 6 *a*,*b*).

In the silver complexes with 3,5-bis(3-pyridylmethylidene)-piperidin-4-ones,[232] all three nitrogen atoms are coordinated to

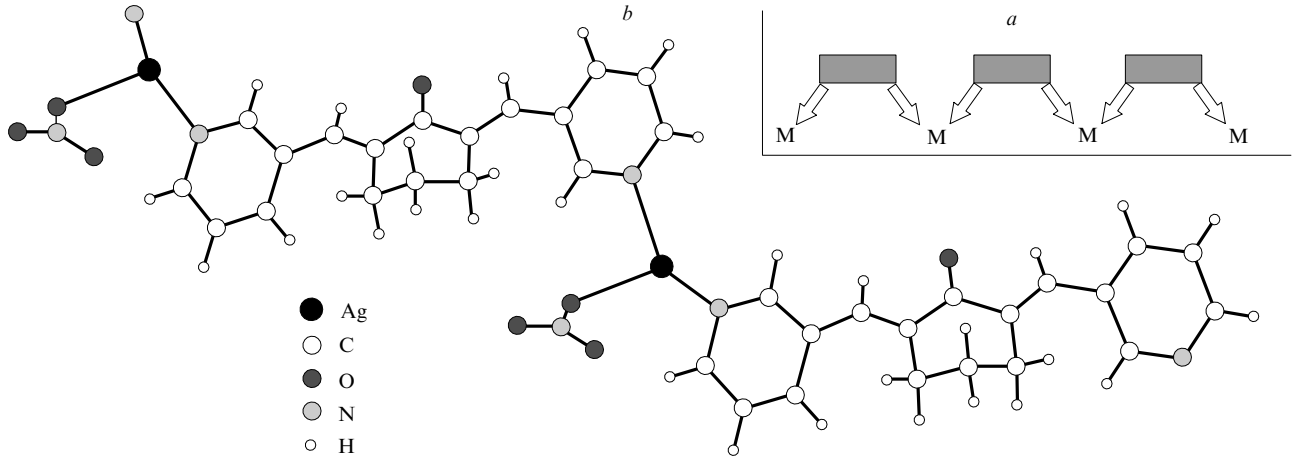


Figure 5. Schematic representation of the '*syn* chain' (*a*) and the molecular structure of the complex of 2,6-bis(3-pyridylmethylidene)cyclohexanone (**70**, $n = 2$) with silver nitrate (*b*).[230]

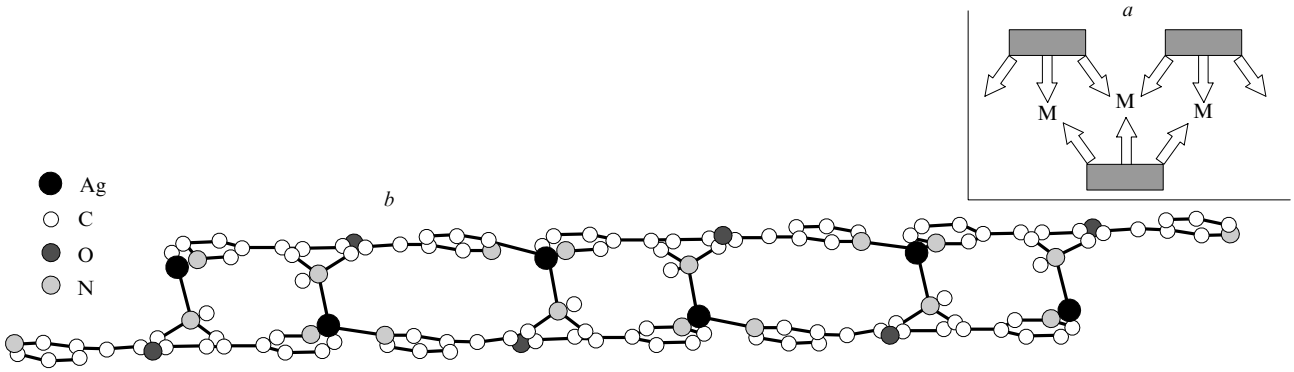


Figure 6. Schematic representation of the ladder-type structure (*a*) and the crystal structure of the complex of 2,6-bis(3-pyridylmethylidene)cyclohexanone (**70**, $n = 2$) with silver nitrate (*b*).[227]

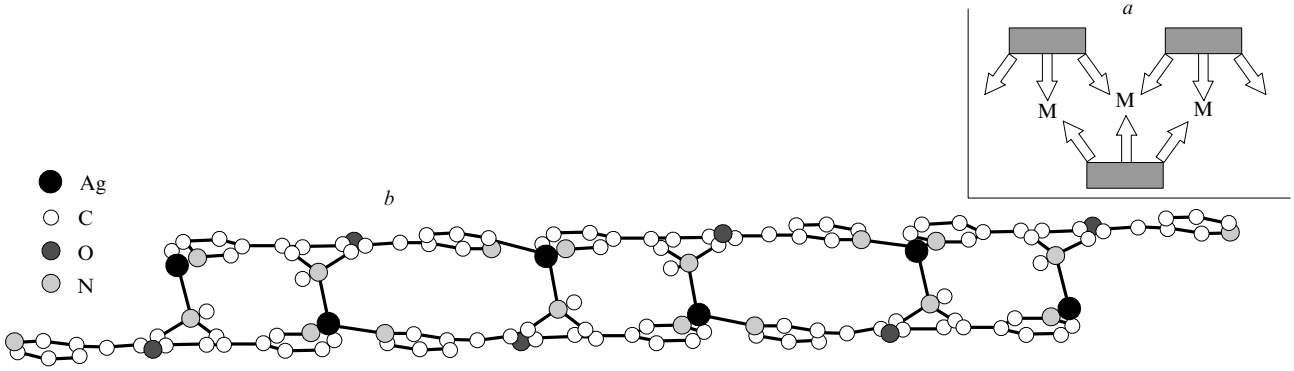


Figure 7. Schematic representation of the double-chain-type structure (*a*) and the structure of the complex of *N*-methyl-3,5-bis(3-pyridylmethylidene)piperidin-4-one (**71**) with silver nitrate (*b*).[232]

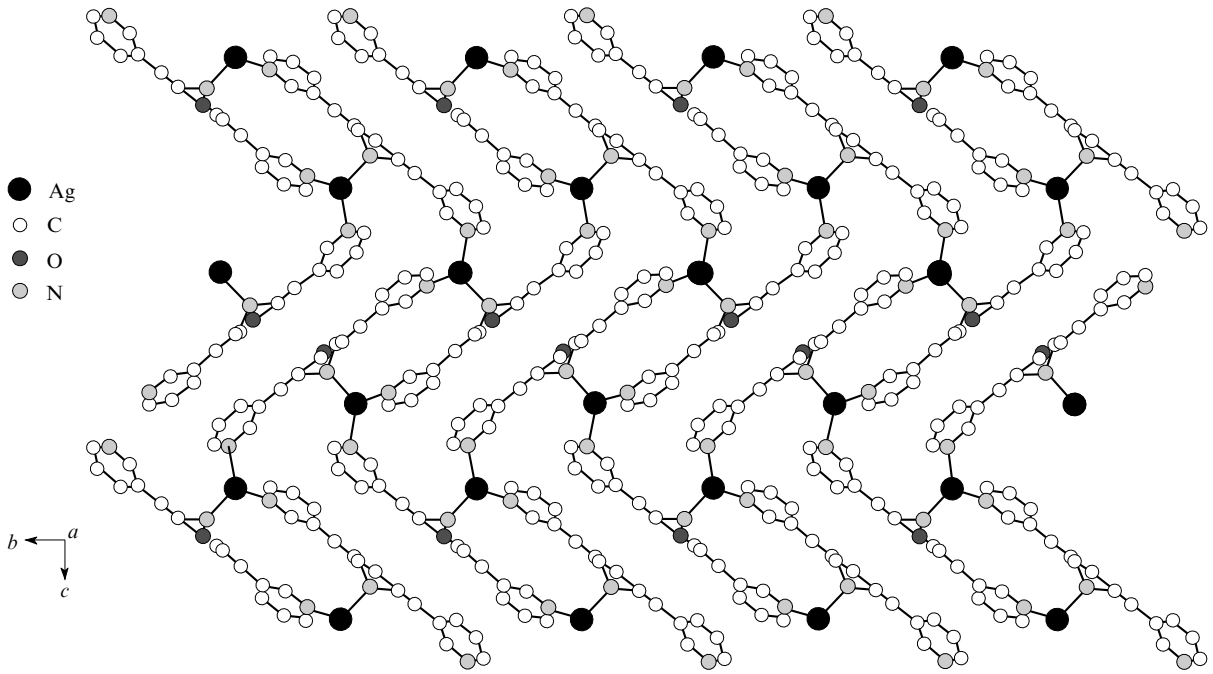


Figure 8. Two-dimensional network structure of the complex of *N*-benzyl-3,5-bis(3-pyridylmethylidene)piperidin-4-one (**72**) with silver nitrate.[232]

three different metal atoms. The silver ion is in a distorted tetrahedral environment as a result of the additional coordination by the nitrate anion. Changes in the nature of the substituent at the piperidine nitrogen atom lead to dramatic differences in the crystal structures of these complexes.

For example, interactions between the complementary components in the complex of *N*-methyl-3,5-bis(3-pyridylmethylidene)piperidin-4-one (**71**) with silver nitrate give rise to polymeric structures in the crystal. According to the topology, these structures can be assigned to 'double chains' (Fig. 7 *a*,*b*).

The product formed by *N*-benzyl-3,5-bis(3-pyridylmethylidene)piperidin-4-one (**72**) is characterised by a two-dimensional network structure (Fig. 8). In the crystal structure, the layers are located one above another. There is one chloroform solvent molecule and one acetonitrile solvent molecule per silver atom. These solvent molecules are located between the layers formed by the complexes. The topological analysis of the bond between the silver ions reveals a two-dimensional 4.8^2-type network consisting of 16- and 40-membered metallamacrocycles in the crystal structure of this complex.

The schematic representations of the structural topologies of the products [232] show that the above-mentioned motifs (double chains and two-dimensional networks) are formed by different combinations of two 16-membered metallamacrocyclic fragments $[AgL]_2$. Apparently, the aggregate growth in solution proceeds with the involvement of such building blocks. In addition, solvent molecules are involved in the crystal growth. The aim of future research will be to elucidate the mechanism of formation of coordination polymers in solution.

Pyridine-containing dienones were used [233] as *exo*-dentate linking ligands to synthesise tetranuclear complexes containing titanium, silver and copper ions. Taking into account the extended conjugated π system of dienones and their ability to undergo photochemical transformations, coordination compounds based on this type of ligands would be very promising for the construction of materials having high conductivity and unusual photophysical properties.

* * *

The analysis of the published data shows that considerable progress has been made in recent years in the chemistry of cross-conjugated derivatives of cyclic ketones. This refers primarily to new fields of use of these compounds as versatile building blocks and increasing attention to unsymmetrical analogues. The available data concerning this problem provide a deeper insight into the electronic and structural factors controlling the reactions of dienones and will be useful in studies of the mechanisms and quantitative characteristics of the directed synthesis of new compounds, including those with practically valuable properties.

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