Synthesis and spectra of some diarylidenecyclanones

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The synthesis and spectra (ultraviolet, infrared, and nuclear magnetic resonance) of some previously unknown 2,*n*-dibenzylidene and dicinnamylidenecyclanones where $n = 5$–10 are described. The spectra are in accord with the expected decrease in coplanarity of the conjugated groups with increasing ring size. *trans*-Ring hydrogen bonding may occur in 2,10-dibenzylidenecyclodecanone but no evidence is found for this effect in the parent cyclanone.

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Introduction

The symmetrical diarylidene derivatives of α,α′-dimethylene ketones have been frequently used for characterization and identification (1) but there are few reports of such derivatives of the cyclic ketones $C_nH_{2n-2}O$ where $n > 7$. 2,8-Dibenzylidenecyclooctanone was reported as a liquid obtained from the dehydration of 2-benzylidene, 8-(α-hydroxybenzyl) cyclooctanone but no characteristics of this other than an analysis were recorded (2). Braude *et al.* (3, 4) have synthesized the monobenzylidene derivatives of the cyclanones with $n = 8$, 9, and 10 and also succeeded in isolating a small amount of a compound which they considered to be 2,10-dibenzylidenecyclodecanone. The monobenzylidene derivative of cyclopentadecanone has been reported but attempts to form the dibenzylidene compound were unsuccessful and yielded only starting materials (5, 6). We are unable to find any records of the corresponding cinnamylidene compounds or higher homologues.

Results

Alkaline condensation of cyclooctanone with benzaldehyde resulted initially in a yellow oil (c.f. (2)) which, after separation and solution in hot methanol, gave white crystals of the required product.

Our attempts to make 2,10-dibenzylidenecyclodecanone by a similar method to that employed by Braude and Gofton (4) resulted always in the isolation of a white crystalline solid differing in melting point and spectral properties from those reported by these authors for the compound. A molecular weight determination gave a mean value of 340 (theory 330). The nuclear magnetic resonance (n.m.r.) spectrum showed absorption bands whose positions and areas are in accord with those expected for dibenzylidenecyclodecanone (see Table I). Attempts to reduce this ketone or to make a 2,4-dinitrophenylhydrazone were unsuccessful, possibly due to the preferred "*O*-inside" conformation of cyclodecanones (7). (See (7) for a discussion of this terminology.) On attempted reduction the formation of a tetrahedral carbon atom from the carbonyl group is energetically unfavorable in this system (8), whereas steric factors may well mitigate against 2,4-dinitrophenylhydrazone formation.

Attempted syntheses of 2,15-dibenzylidenecyclopentadecanone resulted only in the rapid formation of a white solid, identified from its n.m.r. spectrum, analysis as 2-(α-hydroxybenzyl) cyclopentadecanone, which we were unable to dehydrate to the monobenzylidene compound. Reactions involving cinnamaldehyde yielded only starting materials, together with resinous materials from which no products were isolated.

Discussion

In Table I are shown the C=O and C=C stretching frequency values, together with the maximum electronic absorption wavelengths, for the dibenzylidene- and dicinnamylidenecyclanones ($n = 5$–10), and in Table II the chemical

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TABLE I

Spectroscopic data for dibenzylidene and dicinnamylidenecyclanones and related compounds

Ring size n	Cyclanone* $\nu_{C=O}$ (cm^{-1})	Dibenzylidene derivatives† $\nu_{C=O}$ (cm^{-1})	$\nu_{C=C}$ (cm^{-1})	λ_{max}(mμ), (ε)	Dicinnamylidene derivatives† $\nu_{C=O}$ (cm^{-1})	$\nu_{C=C}$ (cm^{-1})	λ_{max}(mμ), (ε)
5	1751	1691	1625	337(32,000)	1670	1617	380(58,000)
6	1718	1661	1610	315(25,000)	1650	1615	369(58,000)
7	1706	1663	1610	250(12,500); 289(25,000)	1655	1615	290(22,500); 335(52,000)
8	1704	1663	1610	250(14,500); 284(22,000)	1657	1613	290(47,000); 333(50,500)
9	1703	1661	1615	250(15,500); 280(22,000)	1644	1607	290(30,000); 330(50,000)
10	1705	1650	1610	250(13,500); 284(23,000)			
5E‡		1711	1616	303(35,000); 340(26,000)	1685	1607	353(70,000); 394(40,000)
Acetone	1720	1645	1620	331(35,800)§	1634	1608	376(54,900)§

*Values taken from ref. 12.
†Infrared measurements in KBr discs; u.v. measurements in n-hexane.
‡5E = cyclopent-3-ene-1-one.
§Values taken from R. N Beale, Nature, 178, 37 (1956).

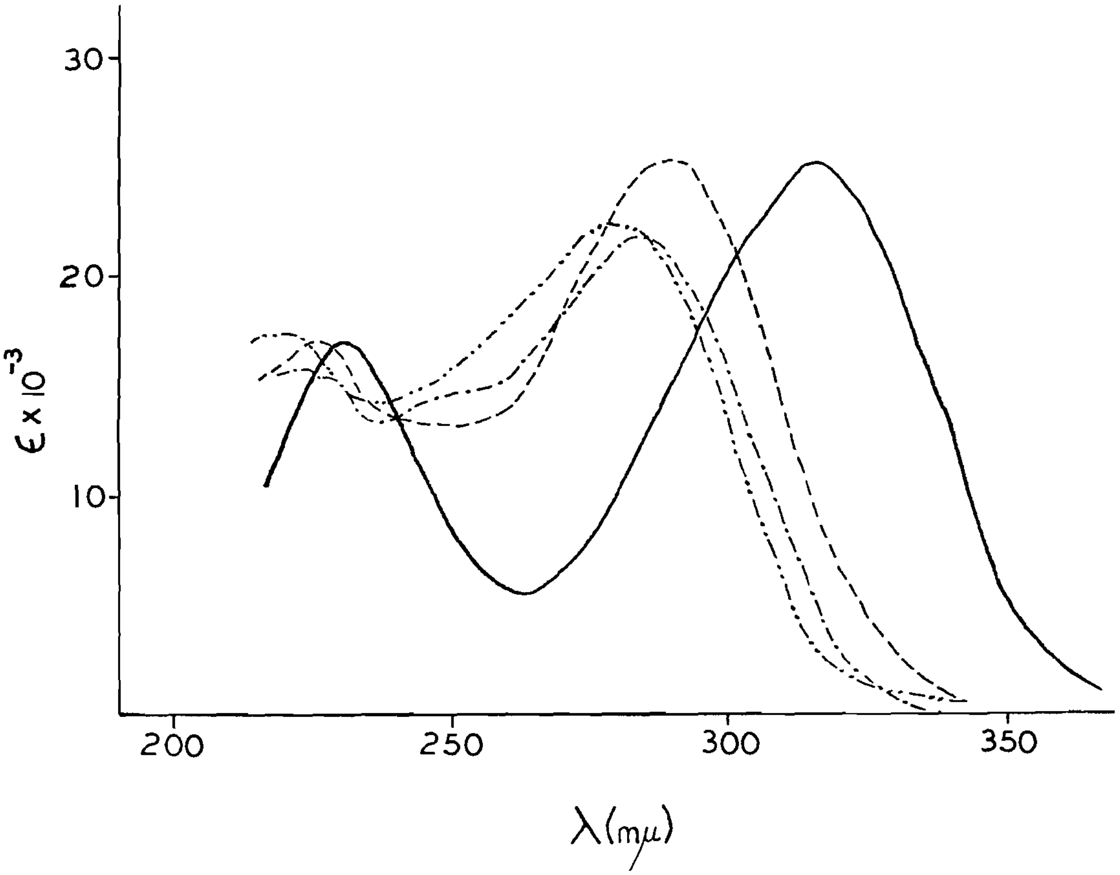

FIG. 1. The electronic spectra of —— 2,6-dibenzylidenecyclohexanone, ----- 2,7-dibenzylidenecycloheptanone, —·—·—· 2,8-dibenzylidenecyclooctanone, and —··—··— 2,9-dibenzylidenecyclononanone measured in n-hexane solution.

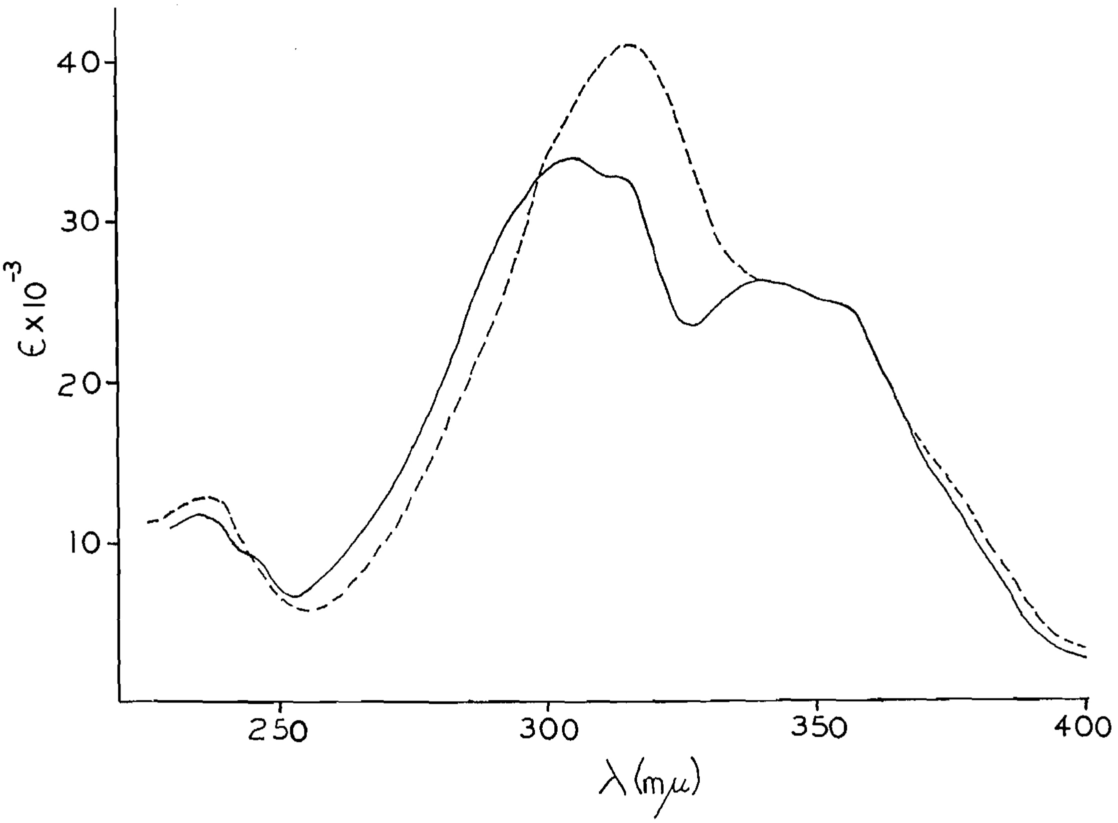

FIG. 2. The electronic spectrum of 2,5-dibenzylidenecyclopent-3-ene-1-one measured in —— *n*-hexane and ---- ethanol solutions.

shift values for the protons in the dibenzylidenecyclanones. The electronic spectra for some of the compounds are shown in Figs. 1 and 2.

The variation of the infrared C═O stretching frequencies of the cyclanones has been studied by various workers (9) who showed that the values reach a minimum when $n = 9$ and then rise with increasing n to approach the value for the open chain ketones (acetone = 1720 cm^{-1}). In the series studied here this frequency decreases for the small ring compounds, increases slightly for $n = 7$ and $n = 8$ and then decreases further. Values for the diarylideneacetone derivatives are lower than those for the cyclic analogues as would be expected. Although the differences are small they are consistent and the intensity variations of the long-wavelength electronic absorption bands are in qualitative accord with them. Such variations would be anticipated from the strain introduced into these systems by the two exocyclic C═C bonds. The high values for the cyclopent-3-enone derivatives reflect the increased '*s*' character of the carbonyl bond in these compounds, relative to the cyclopentanones, resulting from the more rigid geometrical requirements of the unsaturated-ring compounds.

It was suggested by Prelog (7) that some hydrogen bonding may exist in the medium-sized ring ketones between one or more of the intra-annular hydrogen atoms and the carbonyl group. This was considered as a possible reason for the lack of reactivity of cyclodecanone with respect to addition reactions but the effect of hydrogen bonding would lead to only small energy changes and could hardly be responsible entirely for the large rate changes observed. Sutherland (10) has suggested that evidence for hydrogen bonding of this type is found from the position of the first overtone of the C—H stretching vibration. If this is important one would expect that the carbonyl stretching frequency of cyclodecanone would be lower than that of the preceding member of the series. In the case of 2,10-dibenzylidenecyclodecanone it is possible that the constraints imposed upon the system by the three trigonal carbon atoms are such that the molecule takes up a conformation in which the carbonyl oxygen is much nearer to the intraannular hydrogen atoms than in the parent ketone. Hydrogen bonding in this compound would explain the lower infrared absorption frequency and also the failure to reduce it or to form a 2,4-dinitrophenylhydrazone. In both of these reactions the reactant would have great difficulty in approaching the carbonyl group. Further the relative intensities of the C=C and C=O stretching absorptions for 2,10-dibenzylidenecyclodecanone do not obey the rule of Erskine and Waight (11). If no other factor were involved these absorptions should have very similar intensities as in 2,9-dibenzylidenecyclononanone, or the C=O intensity should be greater than the C=C intensity. Hydrogen bonding would reduce the intensity of the carbonyl vibration as is observed, and it would thus seem to be possible in this compound.

The influence of ring size upon the delocalization of the π electrons over the conjugated system is also illustrated in Table I, where it can be seen that the intense long-wavelength band in the electronic spectrum shifts to the blue with increasing n. The effect of increasing ring size is to twist part of the conjugated system until the *effective* conjugation extends over only one-half of the chromophore, i.e. the wavelength of maximum absorption approaches that of monobenzylideneacetone (278 mμ) (12). The long-wavelength band has its maximum value and intensity in the cyclopentanone derivatives and not in the expected cyclohexanone derivatives. This '5-membered ring effect' has been adduced by other workers as indicative of a greater degree of conjugation in these compounds (13). This enhancement of conjugation of the 5-membered ring compounds is also shown by comparison with the corresponding acetone derivatives (Table I).

The spectra of the 2,5-diarylidenecyclopentenones show two distinct bands at long wavelengths, only the lower wavelength band being sensitive to solvent changes and shifting to the blue with decreasing solvent polarity (Fig. 2). This may be explained by consideration of the two π-electron "pathways" within the molecule, i.e. the upper part of the molecule containing the exocyclic conjugation and the carbonyl group giving rise to a solvent sensitive band, and the lower part of the molecule corresponding to *cis*,-*cis*-1,6-diphenylhexatriene giving rise to a solvent independent band similar in shape and position to the long-wavelength band of all-*trans*-1,6-diphenylhexatriene. The decrease in intensity and smearing out of the fine structure on the long-wavelength band corresponding to that of all-*trans*-1,6-diphenylhexatriene results from the introduction of the central *cis*-linkage (14).

From a consideration of Table II it is of interest to note that the chemical shift for the methine protons of 2,6-dibenzylidenecyclohexanone occurs at lower field than that for any other cyclanone derivative. This would be anticipated if the formation of an all-*trans* planar conjugated system within the molecule is favored, the electron withdrawing influence of the carbonyl group thus being maximized.

TABLE II

^{1}H Chemical shifts of dibenzylidenecyclanones (relative to TMS)

Cyclanone ring size	Exocyclic methine proton τ (p.p.m.)	Ring protons α to C=C τ (p.p.m.)*	Remaining cyclanone ring protons τ (p.p.m.)*
5	2.40	6.90	—
6	2.20	7.10	8.24
7	2.70	7.34	8.06
8	2.96	7.23	8.28
9	3.09	7.25	8.40, 8.60
10	2.90	7.14	8.26, 8.53

*Centers of multiplets

For rings where $n > 7$ the non-equivalence of the ring protons, other than those α to the exocyclic double bond, is shown by the asymmetry and eventual splitting of the highest-field absorption. In the spectrum of 2,9-dibenzylidenecyclononanone the ring protons, other than those α to the C=C bonds, give rise to a broad band split into two parts, centered on $\tau = 8.40$ and $\tau = 8.60$, integration showing each part to be due to four protons. This non-equivalence is also shown in the spectrum of 2,10-dibenzylidenecyclodecanone where those ring protons give rise to bands at $\tau = 8.26$ and $\tau = 8.53$. The integration of these bands suggests that each is due to five protons, rather than one group of four and one group of six protons. If the carbonyl group is hydrogen bonded to one of the six ring protons then this would be environmentally different from the remainder and its absorption could shift to lower field thus producing the observed spectrum which is equivalent to deshielding of one proton by the anisotropic carbonyl group. Again in agreement with previous arguments the n.m.r. spectrum of cyclodecanone does not support the idea of hydrogen bonding in this compound.

Experimental

General

Melting points were determined using a Koffler hot stage apparatus and are uncorrected.

All compounds were shown to be single substances using thin-layer chromatography.

Infrared spectra were measured on a Perkin–Elmer model 21 spectrometer. Ultraviolet/visible spectra were measured on a Cary 14 spectrometer. Nuclear magnetic resonance spectra were measured in deuteriochloroform on a Varian 100Mc.p.s. spectrometer equipped with a spin decoupler.

Molecular weights were determined in benzene using a 'Mechrolab Inc.' vapor pressure osmometer, average values of at least 3 determinations being taken.

The diarylidene ketones were all prepared in methanolic solution by the standard alkaline condensation procedure as used for the cyclanones where $n = 5$–7 (1). To minimize self-condensation of cinnamaldehyde in the presence of base it was found necessary to add the aldehyde slowly to the alkaline methanolic solution of the ketone, especially for 9- and 10-membered ring ketones. In most cases the yields were extremely low (1–2%) and have not been recorded owing to irreproducibility. Separation of the products was effected by column chromatography, followed by preparative thin-layer chromatography, on silica gel with benzene as eluent. The required product always had the highest R_f value. Some unchanged ketone was recovered in all cases, together with considerable amounts of intractable resinous materials. The dibenzylidene and dicinnamylidene derivatives of the 5-, 6-, and 7-membered ring ketones were prepared as described above (1) and had the melting points shown below. 2,5-Dibenzylidenecyclopentanone, pale-yellow needles (methanol), m.p. 189°. 2,6-Dibenzylidenecyclohexanone, yellow plates (methanol), m.p. 118–119°. 2,7-Dibenzylidenecycloheptanone, pale-yellow needles (methanol), m.p. 107°. 2,5-Dicinnamylidenecyclopentanone, yellow needles (trichloroethylene), m.p. 232–233°. 2,6-Dicinnamylidenecyclohexanone, yellow microcrystals (trichloroethylene), m.p. 181–182°. 2,7-Dicinnamylidenecycloheptanone, yellow microcrystals (trichloroethylene), m.p. 209°. 2,5-Dibenzylidenecyclopent-3-enone (15), lemon-yellow needles (trichloroethylene), m.p. 157°.

2,8-Dibenzylidenecyclooctanone (1)

A strong solution of potassium hydroxide (2 ml) in 1:1 methanol/water was added to a solution of cyclooctanone (3 g) together with excess freshly distilled benzaldehyde in a small volume of methanol. The mixture was warmed and then left to stand 1 h. On addition of water a yellow oil was deposited. This was separated from the solution and dissolved in the minimum volume of methanol. On cooling, white plate-like crystals of 2,8-dibenzylidenecyclooctanone were precipitated (1.75 g) which, on recrystallization from more methanol, had m.p. 111°. 2,4-Dinitrophenylhydrazone – deep red crystals from ethanol, m.p. 193–194°.

Anal. Calcd. for $C_{22}H_{22}O$ (mol.wt., 302): C, 87.40; H, 7.28; Found (mol.wt., 315): C, 87.49; H, 7.50.

2,9-Dibenzylidenecyclononanone was prepared by the general method described above for **1**, but the mixture was refluxed for 3 h, extracted with ether, dried, and chromatographed (benzene on silica gel). Recrystallization of the product from methanol gave white needles, m.p. 80°. 2,4-Dinitrophenylhydrazone – red crystals from ethanol, m.p. 154–155°.

Anal. Calcd. for $C_{23}H_{24}O$: C, 87.34; H, 7.59. Found: C, 87.13; H, 7.69.

2,10-Dibenzylidenecyclodecanone was also prepared as described for **1**. Recrystallization of the precipitated oil from pentane gave white plates, m.p. 108°.

Anal. Calcd. for $C_{24}H_{26}O$ (mol.wt., 330): C, 87.28; H, 7.88. Found (mol.wt., 340): C, 87.25; H, 7.82.

2-(α-Hydroxybenzyl) Cyclopentadecanone was obtained from the attempted preparation of the dibenzylidene derivative as described above for **1**. Recrystallization of the product from methanol gave white needles, m.p. 138°.

Anal. Calcd. for $C_{22}H_{34}O_2$: C, 80.00; H, 10.30. Found: C, 80.80; H, 10.45.

The infrared spectrum showed strong bands at 3360 and 1705 cm^{-1} attributable to the OH and CO stretching vibrations respectively, but no C=C stretching frequency was observable.

The ^{1}H nuclear magnetic resonance spectrum showed a doublet at $\tau = 7.15$, superimposed upon a triplet; a double doublet at $\tau = 5.28$; a multiplet centered on $\tau = 7.65$; a multiplet centered on $\tau = 8.75$ and a multiplet centered on $\tau = 2.70$. On deuteration the doublet at $\tau = 7.15$ disappears and the double doublet at $\tau = 5.28$ is resolved into one doublet. The integrated areas are in accord with the assigned structure.

2,8-Dicinnamylidenecyclooctanone (2)

Excess freshly distilled cinnamaldehyde, containing a little dissolved cyclooctanone, was added slowly, with stirring, to a solution of cyclooctanone (1 g) in methanol containing 1 ml of a strong solution of potassium hydroxide in 1:1 methanol/water solution. The mixture was allowed to stand for 4 h, any precipitated cinnamic acid filtered off, and the filtrate extracted with ether. Chromatography of the residue remaining after evaporation of the ether, using benzene on silica gel, yielded several products, that having the highest R_f being collected. Recrystallization from methanol of the solid obtained after removal of benzene gave yellow needles, m.p. 133°. 2,4-Dinitrophenylhydrazone – red crystals from ethanol, m.p. 145°.

Anal. Calcd. for $C_{26}H_{26}O$: C, 88.14; H, 7.35. Found: C, 88.00; H, 7.37.

2,9-Dicinnamylidenecyclononanone was prepared as described above for **2**, the mixture being allowed to stand for 8 h. Recrystallization of the product from methanol gave pale-yellow needles, m.p. 147°. 2,4-Dinitrophenylhydrazone – red crystals from methanol, m.p. 140°.

Anal. Calcd. for $C_{27}H_{28}O$: C, 88.04; H, 7.66. Found: C, 88.30; H, 7.67.

2,5-Dicinnamylidenecyclopent-3-enone

This compound was prepared by the method described by Chapman and Pasto (15) for the dibenzylidene compound, using 2,5-dicinnamylidenecyclopentanone as starting material. The product was obtained as fine orange needles which, on recrystallization from trichloroethylene, had m.p. 228°. 2,4-Dinitrophenylhydrazone – black crystals from ethanol, m.p. 252°.

Anal. Calcd. for $C_{23}H_{18}O$: C, 89.52; H, 5.81. Found: C, 89.18; H, 6.00.

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