Molecular Spectra and Conformations of Conjugated Dienones

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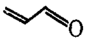
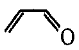
An extensive series of conjugated dienones has been studied using infrared, nmr, and uv spectroscopy. *all-trans*-Dienones have *s-trans*-diene units and exist as equilibrium mixtures of *s-cis*- and *s-trans*-enone conformers. β substitution leads to an entirely *s-cis*-enone unit while α substitution results in an *s-trans*-enone unit. α,β-*cis*-γ,δ-*trans*-Dienones have *s-trans*-diene and *s-cis*-enone units. Both *all-trans*- and *cis,trans*-dienones normally are planar-conjugated molecules. Highly substituted *all-trans*-dienones like 4,6-dimethylheptadienone (**16**) and β-ionone are almost certainly significantly out of planarity. α,β-*cis*-Dienones which have no stable planar conformation exist as the valence isomeric α-pyrans. α,β-*trans*-γ,δ-*cis*-Dienones exist as mixtures of *s-cis*- and *s-trans*-enone conformers both with *s-trans*-diene units and may deviate slightly from planarity. *cis*-δ-Phenyl groups are twisted out of the diene plane. 1-Phenyl dienones have *s-cis*-enone and *s-trans*-diene units. Small deviations from planarity, <25°, would not be revealed by our data.

As part of a thorough study of photoisomerization reactions of α-, β-, γ-, δ-unsaturated ketones,[2] we have pursued spectroscopic investigations as a means of identification and in an attempt to specify details of conformations. Aside from rigid steroidal dienones[3] and cyclohexadienones,[4] very little spectroscopic data on conjugated dienones have been reported in the literature. Numerous spectroscopic studies of the closely related α,β-unsaturated ketones have been published, and the important observations and structural conclusions are summarized below.

Rigid *s-trans*-enones (**1**) generally exhibit two bands in the 1600–1700-cm^{-1} region.[5,6] Rigid *s-cis*-enones (**2**) also exhibit two bands in this region, but, owing to stronger coupling of the C═O and C═C stretching vibrations,[7] their separation is greater than in the s-trans cases. The ratio of integrated absorption intensities $\epsilon_{CO}/\epsilon_{CC}$ varies from 0.6 to 3.5 for *s-cis*-enones and is greater than 6 for the s-trans compounds.[5-10] $\nu_{COs\text{-}cis} - \nu_{COs\text{-}trans}$ is approximately constant at +20–25 cm^{-1}.[5-10] Many conformationally flexible enones exhibit up to four absorption bands in the 1600–1700-cm^{-1} region, indicating the presence of both s-cis and s-trans conformers.[5,6,8-13] Noack and Jones have demonstrated by variable-temperature studies of *trans*-3-pentenone that the multiplicity of bands was not caused by Fermi resonance and that the s-trans conformer was more stable than the s-cis.[13]

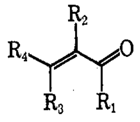


1

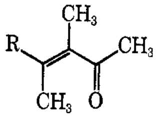


2

Conformational conclusions drawn from these studies can be summarized as follows.[13] The s-cis and s-trans conformers of **3** will exist in equilibrium when R$_2$ and R$_3$ = H and R$_1$ is less bulky than *tert*-butyl. If R$_3$ is alkyl or if R$_1$ = *tert*-butyl,[9] steric interactions destabilize the s-trans conformer to the extent that it is not detected. If R$_1$ and R$_2$ are alkyl, the s-cis conformer is destabilized, and only the s-trans is detected. When R$_1$, R$_2$, R$_3$, and R$_4$ are all alkyl groups, nonplanar conformations probably result. Several groups have remarked that such compounds exhibit abnormally broad C═C bands and attributed this fact to nonplanarity.[5,12] This conclusion finds support in the ^{13}C nmr studies of Marr and Stothers who showed that shielding of the carbonyl carbon was normally independent of conformation but that the carbonyl carbons of **5a** appeared at significantly lower field than usual.[14]



3



5a, R = CH$_3$
b, R = CH$_2$CH$_3$

Nmr spectroscopy has proven to be of great value in determining the stereochemistry of acyclic enones.[15] β-Methyl groups and hydrogens which are cis to the carbonyl group are significantly more deshielded than their trans counterparts.[12,15] Data on rigid enones[15] and the study of Kossanyi[12] show clearly that deshielding of the cis β substituent is associated with the presence of the s-cis conformation and is presumably caused by the long-range anisotropic effect of the carbonyl group. Faulk and Fry have shown that in "peralkyl" enones (**3**, R$_1$–R$_4$ = alkyl) the chemical shift difference between cis and trans β-methyl groups disappears, presumably owing to the twisting of the carbonyl out of the double-bond plane.[16] Ultraviolet spectra of enones have long been used in structure proof owing to the sensitivity of their π,π^* absorption

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(1) (a) NSF Trainee, 1965–1969; (b) Alfred P. Sloan Foundation Fellow, 1969–1971.

(2) A. F. Kluge and C. P. Lillya, *J. Org. Chem.*, **36**, 1988 (1971).

(3) (a) L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959, p 20, report uv data. (b) R. N. Jones, P. Humphries, and K. Dobriner, *J. Amer. Chem. Soc.*, **72**, 956 (1950), report ir data.

(4) *Cf.* E. C. Friederich, *J. Org. Chem.*, **33**, 413 (1968), who reports ir, nmr, and uv data.

(5) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

(6) R. Mecke and K. Noack, *Chem. Ber.*, **93**, 210 (1960).

(7) K. Noack, *Spectrochim. Acta*, **18**, 1625 (1962).

(8) R. Mecke and K. Noack, *ibid.*, **12**, 391 (1958).

(9) M. E. Kronenberg and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **84**, 17 (1965).

(10) W. P. Hayes and C. J. Timmons, *Spectrochim. Acta, Part A*, **24**, 323 (1968).

(11) C. J. Timmons, *et al.*, paper presented at the Fourth International Meeting of the European Molecular Spectroscopy Group, Bologna, Italy, 1959; *cf.* ref 5.

(12) J. Kossanyi, *Bull. Soc. Chim. Fr.*, 704 (1965).

(13) K. Noack and R. N. Jones, *Can. J. Chem.*, **39**, 2225 (1961).

(14) D. H. Marr and J. B. Stothers, *ibid.*, **43**, 596 (1965).

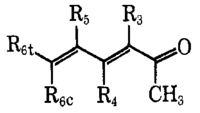
(15) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd ed., Pergamon Press, London, 1969, pp 91, 222–223.

(16) D. D. Faulk and A. Fry, *J. Org. Chem.*, **35**, 364 (1970).

maxima to structure.[17] Braude and Timmons[18] have interpreted the reduced absorption intensity of some enones which are hindered in their s-trans conformations in terms of nonplanarity. However, Mecke and Noack[6,8] have pointed out that this interpretation is inconsistent with ir evidence for the existence of a nearly planar s-cis conformation for some of these compounds. It now seems clear that the reduced absorption intensity is associated with preferred s-cis conformations[6,17] and that only severely hindered compounds such as **5a** and **5b** are nonplanar.

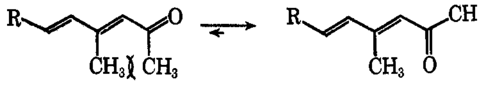
Infrared Spectra.—Carbonyl and carbon–carbon double-bond infrared stretching frequencies for a number of dienones are listed in Table I. Addition of a second conjugated double bond modifies the enone stretching frequencies relatively little, carbonyl frequencies being only 8–10 cm^{-1} lower in dienones than in enones.[19] Thus in analogy to enones we have interpreted bands above 1650 cm^{-1} as carbonyl bands and those at lower frequency as C=C bands. Compounds **17**, **18**, and **30** which have rigid *s-trans*-enone moieties exhibit single carbonyl absorptions at 1670, 1669, and 1660 cm^{-1}, respectively. Jones *et al.*,[19] found $\nu_{CO}(CS_2)$ 1663–1669 cm^{-1} for several rigid all-s-trans steroidal dienones.[20] The two carbonyl bands exhibited by 3-(*trans-β*-styryl)-2-cyclohexenone (**29**) are probably caused by Fermi resonance involving the overtone of the out-of-plane stretching frequency of the α-olefinic hydrogen as has been clearly demonstrated for a number of cyclohexenones.[21]

trans,trans-3,5-Heptadienone (**6**) gives a spectrum which is typical of many flexible *α,β-trans*-dienones. Its two carbonyl absorptions at 1690 and 1670 cm^{-1} are in the right regions for *s-cis-* and *s-trans*-enone conformers, respectively. The 3,5-deuterio derivative, **6**-*3,5*-d_2, also exhibits two carbonyl absorptions, ruling out Fermi resonance (*vide supra*) as a cause of band multiplicity.[21] A similar demonstration has been made in the case of *trans,trans*-cinnamylideneacetone (**22**) and **22**-*2*-*d*. In this case the three maxima in the carbonyl region by **22** are reduced to two upon α-deuteration (**22**-*2*-*d*). Thus, the infrared evidence shows clearly that flexible *α,β-trans*-dienones in which the α and β substituents, R_3 and R_4 in **45**, are hydrogen exist as mixtures of *s-trans-* and *s-cis*-enone conformers.[22] Typical carbonyl stretching frequencies seem to be $\nu_{CO}^{CCl_4}$(s-trans) 1660–1670 cm^{-1} and $\nu_{CO}^{CCl_4}$(s-cis) 1680–1690 cm^{-1}. The difference between ν_{CO}(s-cis) and ν_{CO}(s-trans) of 18–21 cm^{-1} is in good agreement with that observed for simple enones.



45

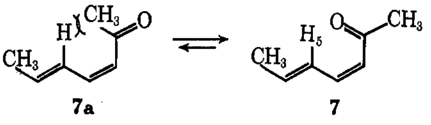
As in the case with enones, when R_4 = CH_3, the s-trans conformation is destabilized by a 1,3 methyl–methyl interaction[23] (**46**) and only the s-cis conformer (**47**) is detected. Thus, compounds **25** and **26** exhibit single carbonyl absorptions in the s-cis region.[24] When R_3 = CH_3 (**15**), only the s-trans conformer is detected with ν_{CO} 1665 cm^{-1}.



46 **47**

R = CH_3, C_6H_5

α,β-cis-Dienones would be expected to be unstable in their s-trans conformations (**7a**). In agreement with expectation, the *α,β-cis*-dienones **7**, **10**, **12**, **23**, and **27** all exhibit single carbonyl absorptions in the s-cis region.



7a **7**

These infrared data and the conformational conclusions based upon them are consistent in all details with those from simple enones. The additional double bond of the dienones clearly does not perturb the carbonyl stretching vibrations in any drastic way. In contrast to the carbonyl absorptions, the C=C absorptions do not seem to depend on molecular structure in a simple fashion and are of no real use in the deduction of conformation. In agreement with the above vinology principle, the carbonyl absorptions of the trienones **41**, **42**, **44**, and **45** mirror those of their dienone analogs. 6-Phenyl-3,5,7-octatrien-2-one (**43**) would be expected to exhibit separate carbonyl absorptions for its *s-cis-* and *s-trans*-enone conformers (*cf.* dienones **22** and **22**-*2*-*d*), but only one absorption at 1660 cm^{-1} corresponding to an s-trans conformer is observed.

Nmr Spectra.—Nmr data for a series of dienones, deduced by first-order analysis, are listed in Table II. Coupling constants and exact chemical shifts have not been specified for non-first-order spectra. In many cases assignments have been made unambiguously on the basis of specific deuterium labeling or signal multiplicity. These assignments have provided a sound basis for assignment of the remaining signals by process of elimination or by analogy. Details of important assignments are discussed below.

In general, the H_3 signal is the farthest upfield of all the olefinic hydrogen signals. Unambiguous assignment of the H_3 signal by means of specific deuterium labeling has been accomplished for **6** and **22**. Compound **6**-*2,5*-d_2 was prepared as shown in eq 1. Incorporation of deuterium at C_5, presumably during the Perkin condensation, was apparent from the nmr spectrum of the tricarbonyl iron complex of **6**-*3,5*-d_2.[25] The nmr spectrum of **6**-*3,5*-d_2 at 60 MHz reveals a greatly diminished upfield doublet which is partially merged with signals from H_{6c} and H_5 on its low-field side.[26]

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[17] *Cf.* A. I. Scott, "Interpretation of the Ultra-Violet Spectra of Natural Products, Pergamon Press, London, 1964, pp 57–63.

[18] E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 3766 (1955).

[19] (a) E. R. Blout, M. Fields, and R. Karplus, *J. Amer. Chem. Soc.*, **70**, 194 (1948); (b) R. N. Jones, P. Humphries, and K. Dobriner, *ibid.*, **72**, 956 (1950).

[20] Three compounds: two $\Delta^{4,6}$-3-ones and one $\Delta^{3,5}$-7-one.

[21] (a) K. Noack, *Spectrochim. Acta*, **18**, 697 (1962); (b) H. N. A. Al-Jallo and E. S. Waight, *J. Chem. Soc. B*, 73 (1966).

[22] Only **24** does not exhibit the expected doubling of the carbonyl absorption, and its carbonyl band is broad.

[23] The 1,3 methyl–methyl and 1,3 methyl–hydrogen interactions have been estimated as 7.6 and 1.6 kcal/mol, respectively, in 1,8-substituted naphthelene-type structures: J. Packer, J. Vaughan, and E. Wong, *J. Amer. Chem. Soc.*, **80**, 905 (1958).

[24] Compound **11** exhibits a principal maximum in the s-cis region at 1677 cm^{-1} but has several shoulders in the carbonyl region as well.

[25] C. P. Lillya and R. A. Sahatjian, *J. Organometal. Chem.*, in press.

[26] The spectrum of **6** has been discussed previously: N. A. Clinton and C. P. Lillya, *J. Amer. Chem. Soc.*, **92**, 3065 (1970).

TABLE I
INFRARED AND ULTRAVIOLET ABSORPTION OF DIENONES

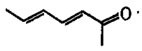
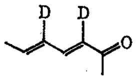
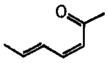
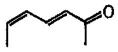
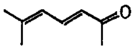
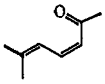
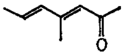
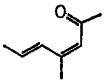
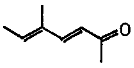
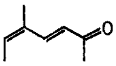
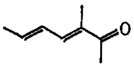
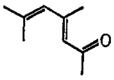
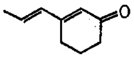
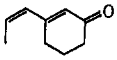
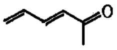
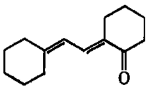
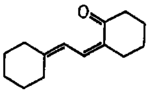
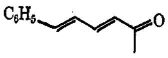
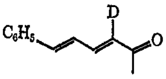
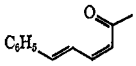
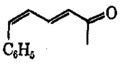
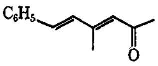
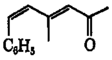
		Infrared[a]		Ultraviolet		
	Compound	ν_{CO} (cm^{-1})	ν_{CO} (cm^{-1})	λ_{max} (nm)	ϵ_{max}	Solvent
6		1690, 1670	1643, 1596	265	28,950	C_6H_{12}
		1685, 1665^b		270	28,500	EtOH^c
6-*3,5-d*$_2$		1685 (sh), 1667	1630, 1594, 1582			
7		1690	1634, 1580	273	13,960	C_6H_{12}
				279	10,400	95% EtOH
8		1691, 1673	1630, 1595	267	22,400	C_6H_{12}
				273 (sh)	20,900	
9		1685, 1667^b	1635, 1590^b	278	27,000	C_6H_{12}
				286	22,400	EtOH^d
10		1680^b	1625, 1574^b	286	22,700	C_6H_{12}
11		1710 (sh), 1677, 1670 (sh), 1650 (sh)	1634, 1585	272.5	22,800	C_6H_{12}
12		1680	1638, 1580	279	7,360	C_6H_{12}
13		1695 (sh), 1666^b	1622^b	267.5	28,300	C_6H_{12}
14		1686, 1670	1628, 1588	273.5	18,250	C_6H_{12}
				279 (sh)	17,860	
15		1665^b	1640, 1601^b	269	28,200	C_6H_{12}
16		1680^b	1632, 1595, 1580^b	276	10,000	C_6H_{12}
17		1670	1642, 1590	260	33,500	C_6H_{12}
18		1669	1631, 1608, 1581	265	21,800	C_6H_{12}
19				258	32,500	CH_3OH^e
20				310	22,500	EtOH^f
				297	25,300	Et_2O^g
21				305	15,200	EtOH^f
22		1693, 1676, 1657	1626, 1615, 1601, 1592	310	38,000	C_6H_{12}
				233	7,900	
				319	36,200	EtOH^h
22-*3-d*		1686, 1665	1621, 1605, 1589, 1582, 1570			
23		1685	1615, 1581, 1568	323.5	32,100	C_6H_{12}
				226	10,900	
24		1652^b	1609, 1583^b	299	12,600	C_6H_{12}
				225	12,600	
25		1681	1580	317	30,800	C_6H_{12}
				243	6,300	
				235	7,500	
				323	24,500	EtOH^i
				237	8,500	
26		1685	1600, 1590	296.5	9,830	C_6H_{12}
				236	11,200	

TABLE I (*Continued*)

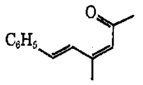
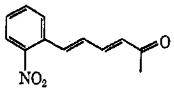
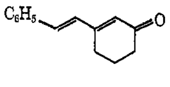
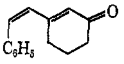
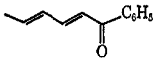
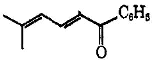
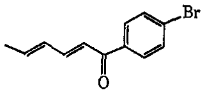
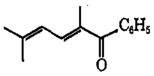
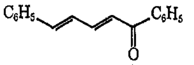
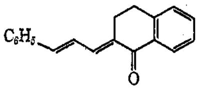
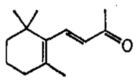
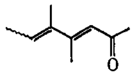
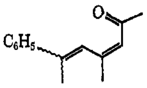
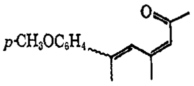
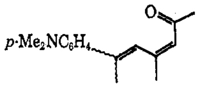
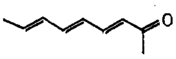
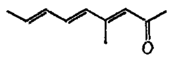
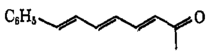
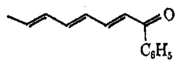
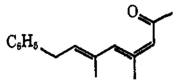
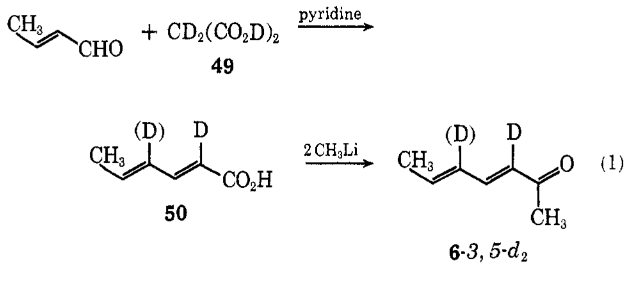
	Compound	Infrared[a]		Ultraviolet		
		ν_{CO} (cm^{-1})	ν_{CC} (cm^{-1})	λ_{max} (nm)	ϵ_{max}	Solvent
27		1675[b]	1615, 1580, 1570[b]	321	23,900	C_6H_{12}
28				292	23,000	C_6H_{12}
				220	9,570	
29		1675 (sh), 1665	1622, 1600, 1586	312	39,400	C_6H_{12}
				240	8,700	
				233	9,900	
				323	25,500	EtOH[j]
				235	11,250	
30		1660	1620, 1601, 1580	285	14,400	C_6H_{12}
				232	10,900	
31		1670	1635, 1601, 1595, 1585 (sh)	288	21,700	C_6H_{12}
				297	19,500	EtOH[h]
32		1665	1630, 1601 1587, 1577 (sh)	308	27,600	C_6H_{12}
				315	25,000	EtOH[q]
				219	9,500	
33		1668	1632, 1593	292	29,400	C_6H_{12}
				298	29,400	
				302.5	29,000	EtOH
56a				302	27,600	EtOH[r]
34		1663	1602, 1586	330	39,800	C_6H_{12}
				343	35,500	EtOH
				342	38,900	CH_3OH[k]
35		1668	1609, 1682	343	35,400	C_6H_{12}
				355	28,500	EtOH
36				295	10,700	EtOH[l]
37				281	14,400	EtOH[m]
38		1685[m]	1599	302.5	11,700	CH_3OH[n]
39		1685[m]	1600	292.5	10,900	CH_3OH[n]
40		1681[m]	1612	370	17,900	CH_3OH[n]
				268	12,900	
41		1681 (sh), 1663[b]	1640, 1611, 1580[b]	308	40,300	n-C_6H_{14}[o]
				297	41,000	
42		1672[b]	1640, 1596, 1570[b]	320	29,200	C_6H_{12}
				307	35,300	
43		1660[k]	1605, 1595, 1580, 1570[k]	342	49,000	Et_2O[p]
44		1664	1601, 1576	336 (sh)	24,100	C_6H_{12}
				325	24,900	
				264	10,900	
				247	11,450	
				238	12,200	
				232	11,600	
				340	36,600	EtOH[o]
				268	10,270	
45		1683	1598	341.5	17,900	CH_3OH[n]

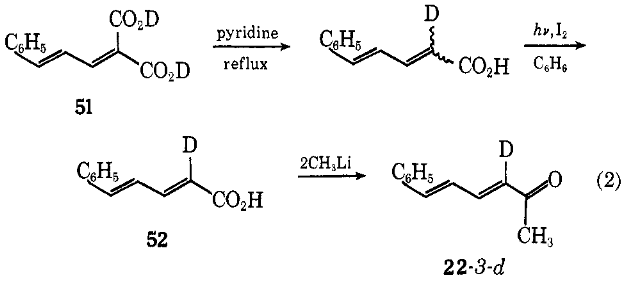
TABLE I (*Footnotes*)

[a] Ambient temperature, all spectra in carbon tetrachloride solution unless otherwise specified. [b] Neat liquid between sodium chloride disks. [c] S. Heilbron, E. R. H. Jones, and R. W. Richardson, *J. Chem. Soc.*, 287 (1949). [d] G. Martin, *Ann. Chim.* (*Paris*), **4**, 541 (1959). [e] R. F. Heck, *J. Amer. Chem. Soc.*, **85**, 3383 (1963). [f] I. T. Harrison and B. Lythgoe, *J. Chem. Soc.*, 837 (1958). [g] K. Dimroth, *Chem. Ber.*, **71**, 1346 (1938). [h] R. Kuhn and H. A. Staab, *ibid.*, **87**, 262 (1954). [i] C. H. Eugster, C. Garbers, and P. Karrer, *Helv. Chim. Acta*, **35**, 1179 (1952). [j] J. M. Conia and U. O'Leary, *C. R. Acad. Sci.*, Ser. B, **249**, 1002 (1959). [k] J. F. Thomas and G. Branch, *J. Amer. Chem. Soc.*, **75**, 4793 (1953). [l] Y. R. Naves, *Helv. Chim. Acta*, **31**, 893 (1948). [m] J. Royer and J. Dreux, *Tetrahedron Lett.*, 5589 (1968). [n] G. Kobrich and D. Wunder, *Justus Liebigs Ann. Chem.*, **654**, 131 (1962). [o] M. Kröner, *Chem. Ber.*, **100**, 3172 (1967). A preparation of ours exhibited the same spectrum but with low ϵ values (*ca.* 27,000). The cause of this discrepancy is under investigation. [p] D. J. Zepka, Ph.D. Thesis, University of Massachusetts, 1969. [q] J.-P. Montillier and J. Dreux, *Bull. Soc. Chim. Fr.*, 3638 (1969). [r] A. Duperrier and J. Dreux, *Tetrahedron Lett.*, 3127 (1970).



49 **50** **6**-*3,5-d*$_2$

At 100 MHz the H_3 doublet of **6** is fully resolved, and double resonance experiments show clearly that H_3 is coupled to H_4 which appears downfield at τ 2.93. Preparation of **22**-*3-d* was accomplished as shown in eq 2. The nmr spectrum of **22**-*3-d* was similar to that of **22** in all major respects except that the upfield doublet at τ 3.85 was almost completely absent. Assignment of the upfield olefinic signal to H_3 also finds support from assignments based on spin–spin coupling patterns. The one-hydrogen singlets in the olefinic region exhibited by **17**, **25**, **26**, **29**, and **30** must be due to H_3. The H_3 signal in **16** can be assigned on the basis of allylic coupling with the 4-methyl group. Finally the 5-methyl compounds **13** and **14** exhibit two widely spaced olefinic doublets which can be assigned with confidence to H_3 and H_4 by analogy.



51 **52** **22**-*3-d*

Assignment of the H_3 signal makes possible determination of the vicinal coupling constant J_{34} and allows unambiguous assignment of configuration about the α,β (3,4) double bond.[27] Compounds **6**, **8**, **9**, **12–14**, **22**, **24**, and **31–33** with J_{34} = 15–16 Hz clearly have α,β-trans configurations while **10** and **23** with J_{34} = 12 Hz have α,β-cis configurations.

The H_4 signal is the lowest field olefinic signal in α,β-*trans*-dienones and is well resolved in the spectra of the aliphatic compounds. The assignment has been made unambiguously for **6** on the basis of deuterium labeling and double resonance (*vide supra*). Spin–spin splitting patterns make assignment of H_4 clear in **9**, **13**, **14**, and **15**. As is the case with enones,[12,15] some of the deshielding of H_4 is attributable to the anisotropic effect of the carbonyl group when the enone unit is in the s-cis conformation. Thus, **6** and **13**, which infrared spectroscopy reveals as mixtures of *s-cis-* and *s-trans-*enone conformers, exhibit H_4 signals at τ 2.93 and 2.91, while **15**, which infrared shows to be entirely s-trans, exhibits an H_4 signal at *ca.* 0.15 ppm to higher field. A further effect on the chemical shift of H_4 is the deshielding by 0.3–0.4 ppm associated with the presence of a methyl group in the 6c position (**8**, **9**, **14**, and **32**). Among the possible causes of the deshielding are the direct field and van der Waals effects[23] of the methyl group.[28] Methyl groups in the 4 position are strongly deshielded in agreement with enone data[12,15] and with our conclusions based on infrared evidence that these compounds (**11**, **16**, **25**, and **26**) have *s-cis*-enone units.

In α,β-*cis*-dienones H_4, no longer affected by carbonyl anisotropy, appears at higher field; and it is H_5, dramatically deshielded by the carbonyl group, which appears at lowest field. In **7** and **23** quartets at τ 2.48 and 1.86 respectively (J_{45} = 12, J_{56c} = 15 Hz) are assigned to H_5 because of the large trans vicinal coupling.[27] The H_4 signal should be a near triplet with both J_{34} (cis) and J_{45} = ~12 Hz. The doublet for H_5 in **10** was assigned on the basis of its broadening owing to allylic coupling with the 6-methyls. In **12** only H_5 can give a doublet (τ 2.41), and in **27** the doublet at τ 1.64 is assigned to H_5 rather than H_{6c} by analogy.[29] The large downfield shift of H_5 which occurs when the configuration of the α,β bond is changed from trans to cis is consistent only with planar α,β-*cis*-dienones possessing *s-cis*-enone and *s-trans*-diene conformations (see **7**). Strong deshielding of H_5 owing to carbonyl anisotropy is predicted in conformation **7** by the Pople model.[30–32] An analogous effect in the dienone tagatone (**53**, see Table II) has been described by Bishop and Musher,[34] and similar deshielding in an α,β-*cis*-dienoic ester has also been described.[35] The s-cis conformation of the enone unit in the α,β-*cis*-dienones is in full accord with their infrared carbonyl stretching frequencies.

The nmr spectra also provide definitive information about diene conformation which is not available from infrared spectra. From the value of J_{45} = 10–12 Hz in **6–10**, **15**, **23**, **24**, and **32**, it is clear that their diene units

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(27) *Cf.* A. A. Bothner-By, *Advan. Magn. Resonance* **1**, 207 (1965).

(28) Reference 15, p 71.

(29) This leaves a doublet at τ 3.20 to be assigned as H_{6c} in agreement with the τ 3.1 shift of H_{6c} in the closely analogous compound **25**.

(30) Reference 15, p 88.

(31) J. A. Pople, *J. Chem. Phys.*, **37**, 60 (1962).

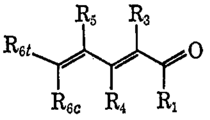
(32) Deshielding of H_5 does not seem consistent with the shielding model constructed by Karabatsos, *et al.*,[33] using the carbonyl anisotropies of ApSimon, *et al.* In contrast the relative shielding of H_3 with respect to the other olefin hydrogens seems in accord with the Karabatsos model but not with that of Pople. In fact Jackman and Sternhell[15] have observed that no single model for carbonyl shielding accounts adequately for all the available data.

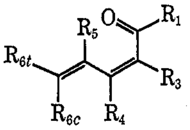
(33) G. J. Karabatsos, G. D. Sonnichsen, N. Hsi, and D. J. Fenoglio, *J. Amer. Chem. Soc.*, **89**, 5067 (1967).

(34) E. O. Bishop and J. I. Musher, *Mol. Phys.*, **6**, 621 (1963).

(35) G. Englert, *Z. Anal. Chem.*, **181**, 447 (1961).

TABLE II
NMR SPECTRA OF DIENONES[a]


I

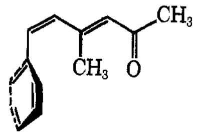

II

Compound		Chemical shifts in τ units[c] and signal multiplicity[d]						
No.	Structure[b]	R_1	R_3	R_4	R_5	R_{6c}	R_{6t}	Coupling constants,[e] Hz
6	I, $R_{1,6t} = CH_3$	7.82 s	4.00 d	2.93 o	∼3.9 m	∼3.9 m	8.18 d	$J_{34} = 15, J_{45} = 10, J_{6c6t} = 4.5$
6-*3,5-d*	I, $R_{1,6t} = CH_3$; $R_{3,5} = D$	7.85 s	. . .	∼3.0 b	. . .	∼3.9 m	8.18 d	$J_{6c6t} = 6$
7	II, $R_{1,6t} = CH_3$	7.85 s	∼4.05	∼3.6	2.48 q	∼3.85	8.17 d	$J_{45} = 12, J_{56c} = 15, J_{6c6t} = 7$
8	I, $R_{1,6c} = CH_3$	7.82 s	∼4	2.64 q	∼4	8.12 d	∼4	$J_{34} = 16, J_{45} = 10.5, J_{6c6t} = 5.5$
9	I, $R_{1,6c,6t} = CH_3$	7.80 s	4.05 d	2.60 q	4.05 d	8.10 s	8.10 s	$J_{34} = 15, J_{45} = 11$
10	II, $R_{1,6c,6t} = CH_3$	7.89 s	4.20 d	3.45 t	2.81 d, b	8.12 s[f]	8.18 b[f]	$J_{34} = 12, J_{45} = 12, J_{56c} \leq 1$[g]
11	I, $R_{1,4,6t} = CH_3$	7.88 s	∼3.9	7.83 s	∼3.9	∼3.9	8.17 d	$J_{6c6t} = 5$
12	II, $R_{1,4,6t} = CH_3$	7.90 s	4.10 s, b	8.07 s, b	2.41 d, b	3.88 o	8.17 d, b	$J_{56c} = 15, J_{6c6t} = 4.5$
13	I, $R_{1,5,6t} = CH_3$	7.83 s	4.03 d	2.91 d	8.26 s, b	4.06 q, b	8.22 d	$J_{34} = 16, J_{6c6t} = 6$
14	I, $R_{1,5,6c} = CH_3$	7.78 s	3.96 d	2.47 d	8.17 s, b	8.13 d	4.2 q, b	$J_{34} = 16, J_{6c6t} \sim 6$
15	I, $R_{1,3,6t} = CH_3$	7.78 s	8.19 s	3.08 d	∼3.7 m	∼3.9 m	8.11 d	$J_{45} = 10$
16	I, $R_{1,4,6c,6t} = CH_3$	7.90 s	4.30 s, b	7.87 d	4.03 s, b	8.17 s	8.17 s	$J_{34} \sim 1$[g]
17	I, $R_{1,4} = (CH_2)_3$; $R_{6t} = CH_3$[h]	7.5–8.1 m	4.30 s	7.5–8.1 m	3.95 m	3.95 m	8.16 d	$J_{6c6t} = 5$
18	I, $R_{1,4} = (CH_2)_3$, $R_{6c} = CH_3$[h]	7.3–8.1 m	∼4.2	7.3–8.1 m	∼4.2	8.14 d	∼4.2	$J_{6c6t} = 5$
22	I, $R_1 = CH_3$; $R_{6t} = C_6H_5$	7.82 s	3.85 d	∼2.7	∼3.1	∼3.1	2.6 m	$J_{34} = 15$
22-*3-d*	I, $R_1 = CH_3$; $R_{6t} = C_6H_5$; $R_3 = D$	7.80 s	. . .	∼2.7	∼3.1	∼3.1	2.6 m	
23	II, $R_1 = CH_3$; $R_{6t} = C_6H_5$	7.84 s	4.05 d	3.55 t	1.86 q	3.29 d	2.7 m	$J_{34} = 12, J_{45} = 12, J_{56c} = 15$
24	I, $R_1 = CH_3$; $R_{6c} = C_6H_5$	7.82 s	3.87 d	∼2.7	3.68 t	2.61 s	3.08 d	$J_{34} = 16, J_{45} = 11, J_{56t} = 11$
25	I, $R_{1,4} = CH_3$; $R_{6t} = C_6H_5$	7.87 s	3.85 s, b	7.70 d	3.35 d	3.1 d	2.7 m	$J_{34} = 1.5$,[g] $J_{56c} = 16$
26	I, $R_{1,4} = CH_3$; $R_{6c} = C_6H_5$	7.98 s	3.87 s, b	7.94 s, b	3.95 d	2.8 s	3.46 d	$J_{56t} = 12$
27	II, $R_{1,4} = CH_3$; $R_{6t} = C_6H_5$	7.92 s	3.95 s, b	8.04 d	1.64 d	3.20 d	2.7 m	$J_{34} = 1$,[g] $J_{56c} = 16$
29	I, $R_{1,4} = (CH_2)_3$[i] $R_{6t} = C_6H_5$	7.3–8.1 m	4.02 s	7.3–8.1 m	3.12 s	3.12 s	2.65 m	
30	I, $R_{1-4} = (CH_2)_3$; $R_{6c} = C_6H_5$	7.3–8.1 m	4.10 s	7.3–8.3 m	3.73 d	2.78 s	3.31 d	$J_{56t} = 12$
31	I, $R_1 = C_6H_5$; $R_{6t} = CH_3$	2.1–2.9 m	3.18 d	∼2.7	3.9 m	3.9 m	2.13 t[j]	$J_{34} = 15$
32	I, $R_1 = C_6H_5$; $R_{6c,6t} = CH_3$[l]	2.2–3.0 m	3.23 d	2.39	3.96 d[k]	8.12 b	8.12 b	$J_{34} = 15, J_{45} = 12, J_{Allylic} \backsim 1$[g–k]
56a	I, $R_1 = C_6H_5$; $R_{3,6c,6t} = CH_3$[m]	2.3–2.7 m	7.99	3.02	3.77	8.12	8.33	$J_{45} = 11, J_{34} = 1.4$,[g] $J_{56} = 1.3$[g]
56b	I, $R_1 = C_6H_5$; $R_{5,6c,6t} = CH_3$[m]	2.0–2.3 2.4–2.8 m	3.15 d	2.04 d	8.08 s	8.17 s	8.17 s	$J_{34} = 15$
33	I, $R_1 = p\text{-}BrC_6H_4$; $R_{6t} = CH_3$	2.25–2.55 m	3.29 d	2.68 q	∼3.8 m	∼3.8 m	8.10 d	$J_{34} = 15, J_{6c6t} = 5, J_{45} \backsim 10$
53	II, $R_1 = i\text{-Bu}$; $R_4 = CH_3$[n]		3.93 s, b		2.06 o	5.57 m	5.34 m	$J_{56c} = 10.9, J_{56t} = 17.7, J_{36c} = 1.5, J_{6c6t} = 1.3$

[a] As *ca.* 10% solutions in carbon tetrachloride unless otherwise noted. [b] Only substituents other than ^1H are listed. [c] Chemical shifts relative to internal tetramethylsilane. [d] s = singlet, d = doublet, t = triplet, q = quartet, o = octet, m = multiplet, b = broadened. [e] Coupling constants are based on first-order analysis and should be reliable within ±1 Hz in most cases. [f] Assignment of 6-methyls is based on the expectation that *cis*-allylic coupling with H_5 will be larger than *trans*-allylic coupling; *cf.* ref 15, pp 316–324. [g] Allylic coupling constant. [h] In deuteriochloroform. [i] D. E. Kuhn, Ph.D. Thesis, University of Massachusetts, 1969. [j] The unusual triplet multiplicity is probably caused by virtual coupling effects; *cf.* ref 26. [k] Each peak of the H_5 doublet appears as a symmetrical pentuplet with a line separation of *ca.* 1 Hz. This requires that H_5 be nearly equally coupled to both the *cis-* and *trans*-methyl hydrogens. [l] An essentially identical spectrum is reported in footnote *m*. [m] J.-P. Montillier and J. Dreux, *Bull. Soc. Chim. Fr.*, 3638 (1969). [n] Parameters based on complete analysis of a spectrum of the neat dienone at 29.914 MHz (ref 34).

are in the expected[36] s-trans conformation.[37] Typical vicinal coupling across the essential single bond of *s-cis*-dienes is only 5–7 Hz.[37b,38] The large J_{45} values suggest that the *s-trans*-diene units of both α,β-*cis*- and α,β-*trans*-dienones do not deviate very much from planarity.[37b]

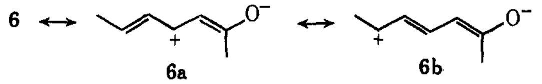
Conformations of 6-phenyl substituents can also be deduced from the nmr data. Compounds **22**, **23**, **25**, **27**, and **29**, which bear a phenyl group in the 6*t* position, all exhibit the complex multiplet of a conjugated phenyl group.[39] In contrast, **24**, **26**, and **30**, which bear a phenyl group in the more crowded 6*c* positon, all exhibit sharp singlets characteristic of unconjugated phenyl groups.[39] Therefore, in the γ,δ-cis compounds the δ-phenyl group is twisted out of the dienone plane, owing to steric interactions. The pronounced upfield shift of the 4-methyl group (0.28 ppm) on going from **25** to its γ,δ-cis isomer **26** can be attributed to long-range shielding by the out-of-plane phenyl group (**26a**).



26a

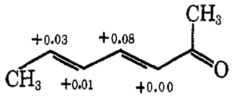
The value of J_{34} = 11 Hz in **24** shows that at least in this case the diene unit remains close to planarity.

Nmr chemical shifts should be particularly characteristic of the electronic structure of the dienones. For example, **15** exists exclusively as an *s-trans*-enone; yet H_4, though no longer deshielded by an *s-cis*-carbonyl, appears far downfield at τ 3.08. This suggests that for *trans,trans*-dienones carbonyl anisotropic effects on chemical shifts are small with respect to charge distribution effects. The deshielding of H_4 can be rationalized in terms of contributions of structures such as **6a** to the dienone resonance hybrid. Both resonance theory and HMO theory predict the alternation of charge along the diene chain which seems to be reflected in the relative chemical shifts of H_3, H_4, and H_5 for cyclic dienones[4,37b] and our compounds. For both types of dienones H_6 has about the same chemical shift as H_5 in apparent contradiction to the expected electron deficiency at C_6. However, hydrogens on the termini of dienes probably are intrinsically more shielded than the internal olefinic hydrogens. *trans,trans*-2,4-Hexadiene in CCl_4 exhibits multiplets at τ 4.4 and 4.05 for the terminal (2,5) hydrogens and internal (3,4) hydrogens, respectively. Using these as standard values for an "unperturbed" diene and treating H_{3-5} as internal hydrogens and H_{6c} as a terminal hydrogen, we have calculated $\Delta\tau$ values for **6** which represent the downfield shifts experienced by the olefinic hydrogens owing to conjugation of the diene with a carbonyl group.[40] Sorensen's equation (3), developed for polyenylic cations,[41] can then be used to compute a rough estimate of the "excess positive charge density" at each carbon (Δq). The calculation assumes that carbonyl anisotropic effects are relatively small and that the olefinic carbons of *trans,trans*-2,4-hexadiene bear no net charge. The results in formula **54** show the expected charge alternation. CNDO/2 calculations of Bertelli and Andrews[42] on *all-s-trans*-2,4,6-heptatrienal (**55**) over carbons 2–5 in the same sense though excess negative charge at C_2 and C_4 is predicted.[43] The calculated charges on the hydrogen atoms themselves, however, show a totally different pattern with excess positive charge decreasing in the order 2 > 4 > 5 > 3.[42]

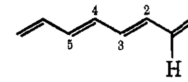


6a **6b**

$$\Delta q = 14.7\Delta\tau \qquad (3)$$



54



55

The nmr data, as a whole, point clearly to planar or nearly planar conjugated dienones and agree in all details with deductions based on infrared spectroscopy. Further, the nmr data require that the diene units have s-trans conformations and that 6*c*-phenyl groups be twisted out of the diene plane.

Ultraviolet Spectra.—Wavelength maxima and intensities for π,π^* absorptions of the dienones are recorded in Table I. The π,π^* assignment is clear from the intensity of these absorptions and the bathochromic shift of the maxima caused by an increase in solvent polarity.[44] Data for n,π^* absorptions are collected in Table III. Assignment of these bands is based on their characteristic low intensities and the hypsochromic shift of the absorption maximum for **6** as solvent polarity is increased.[45a]

The uv data are in good qualitative accord with conformational deductions based on infrared and nmr spectroscopy. The π,π^* maxima of all-trans aliphatic dienones **6**, **9**, **13**, **15**, and **17** in cyclohexane range from 265 to 278 nm (ϵ 27,000–33,500) in good agreement with data on analogous rigid steroidal dienones[46] which must be nearly planar. *trans,trans*-Dienones with *s-cis*-enone moieties exhibit reduced π,π^* absorption intensities as would be expected on the basis of enone

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(36) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, pp 21–22.

(37) (a) A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.*, **87**, 3445, 3451 (1965); (b) A. A. Bothner-By and E. Moser, *ibid.*, **90**, 2347 (1968).

(38) This is true in the specific case of conjugated cyclohexadienones as well.[4, 37b]

(39) See ref 25 for a discussion of this effect.

(40) For H_{3-5} $\Delta\tau_i = 4.05 - \tau_{H_i}$ (dienone), and $\Delta\tau_{6c} = 4.4 - \tau_{6c}$ (dienone).

(41) T. S. Sorensen, *J. Amer. Chem. Soc.*, **87**, 5075 (1965).

(42) D. J. Bertelli and T. G. Andrews, Jr., *ibid.*, **91**, 5280 (1969).

(43) The trienal is chosen for comparison rather than the more closely related *trans*-2,4-pentadienal, because the latter lacks a terminal substituent which seems to play an important role in affecting the calculated charge on the carbons of the terminal double bond. Compare the compounds above and methyl vinyl ketone with 3-penten-2-one in ref 41.

(44) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1964, p 207.

(45) Reference 44: (a) pp 186–187; (b) p 389.

(46) $\Delta^{3,5}$-7-ones give $\lambda_{max}^{EtOH\ or\ CHCl_3}$ 277–280 (24,400–28,000) and $\Delta^{4,6}$-3-ones give $\lambda_{max}^{EtOH\ or\ Et_2O}$ 273–284 (26,300–33,900). *Cf.* ref 17, pp 407–409. Roughly 11 nm must be subtracted from the ethanol values to allow direct comparison with our cyclohexane values.

TABLE III
n,π^* ABSORPTION MAXIMA FOR DIENONES

Compound	λ_{max}	ϵ_{max}	Solvent
trans-2,4-Pentadienal	325	51	95% EtOH[a]
6	335	65	C_6H_{12}
	330	84	Et_2O
	b		MeOH
7	330	90	Et_2O
8	335	82	Et_2O
15	320	93	Et_2O
17	320	126	Et_2O
	343	57	
	358	48	
	377	29	
18	338	63	Et_2O

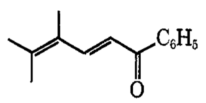
[a] E. L. Pippen and M. Nanaka, *J. Org. Chem.*, **23**, 1580 (1958). [b] Not observable.

data.[6,17] Thus ϵ_{max} values for **11** and **20** are 22,800 and 22,000–25,000, respectively.

Comparison of cinnamylideneacetone (**22**) with its *s-cis*-4-methyl derivative **25** reveals a drop in ϵ_{max} from 38,000 to 30,800, and the trienones **41** and **42** are related in a similar fashion. In every case the shift of the enone conformational equilibrium to all-s-cis is accompanied by a bathochromic shift of λ_{max} which is in accord with planar s-cis conformations. A change in structure from trans,trans to α,β-cis reduces the intensity of the π,π^* absorption as expected[6,17] and is accompanied by a bathochromic shift of up to 13.5 nm (**22** *vs.* **23**). This shift, like the infrared and nmr data, is in accord with conformations which do not deviate significantly from planarity.

Isomerization of *all-trans*-dienones which bear a phenyl substituent in the 6*t* position to the γ,δ-cis compounds is accompanied by large hypsochromic shifts and reduction of π,π^* absorption intensity (**24**, **26**, **30**). These shifts confirm that 6*c* phenyl groups are twisted out of conjugation as deduced by nmr spectroscopy. The case of γ,δ-cis aliphatic dienones is not so clear. Trans → cis isomerization of the γ,δ double bond (**6** → **8**, **13** → **14**, and **17** → **18**) is accompanied by a bathochromic shift of the π,π^* maximum (**8** and **14** exhibit two maxima of similar intensity) and a pronounced diminution of absorption intensity. Use of the $\epsilon^\theta/\epsilon^0 = \cos^2\theta$ relationship,[47] where θ is the angle of deviation from planarity about an essential single bond, gives values for of 28, 37, and 36° for **8**, **14**, and **18**, respectively. However, sterically induced nonplanarity does not offer an entirely consistent explanation of these spectral changes. Normally a hypsochromic shift of the absorption maximum accompanies twisting about an essential single bond,[45b] not the bathochromic shift seen here. If the twisting is the result of steric interaction between the 6*c*-methyl and the 4 substituent, it ought to be much more pronounced in **18**, where it is the result of a 1,3 methyl–methylene interaction, than it is in **8** and **14**, where it is the result of a 1,3 methyl–hydrogen interaction.[23] Yet this does not appear to be the case (*vide supra*). The vicinal coupling constant across the essential single bond of the diene unit in **8** is 10.5 Hz, seemingly inconsistent with the large distortion[37b] from planarity estimated from absorption intensities. Finally, **9** with a 6*c*-methyl group has "normal" π,π^* absorption intensity. Thus, the source of the low absorption intensities in the γ,δ-cis compounds is not completely clear, and it seems probable that **8** and **14** do not deviate from planarity by an angle so large as that derived from the Braude equation.[47]

The highly substituted dienone **16** should have no stable planar conformation for its diene unit.[48] In fact, Dreux, *et al.*, have suggested that it is nonplanar on the basis of its weak uv absorption, λ_{max}^{EtOH} 286 nm (ϵ 16,200).[49] Our glpc purified **16** exhibits an even lower value, $\epsilon_{max}^{C_6H_{12}}$ 10,000, which supports the nonplanar structure. β-Ionone (**36**) is almost certainly nonplanar as well.[48] Duperrier and Dreux[49b] also suggest that dienone **56b** is nonplanar on the basis of its λ_{max}^{EtOH} 301 nm but give no value for ϵ_{max}. The low absorption intensities for the highly substituted α,β-*cis*-dienones **37–40** (compare **23**) also suggest nonplanar structures.



56b

Allinger, *et al.*,[50] have calculated ultraviolet spectra for *all-s-trans*-dienones in the vapor phase. They obtain two π,π^* maxima with a 6–35-nm separation but report that the plotted spectra exhibit only one merged maximum. The vapor-phase spectrum of **6** exhibits two maxima of nearly equal intensity at 253 and 244 nm with hints of other structure in the form of inflections on either sides of the main absorption. While these may be the two maxima predicted by Allinger, *et al.*,[50] their *ca.* 1500-cm^{-1} separation also allows interpretation in terms of vibrational structure. They could also arise as a consequence of coexisting *s-cis-* and *s-trans*-enone conformers exhibiting different maxima. The calculations predict that very similar 5–6-nm bathochromic shifts will be caused by α-, β-, γ-, or δ-methyl substitution. Our data for 3,5-heptadienone (**6**) and its monomethyl derivatives reveal 4-, 7.5-, 2.5-, and 13-nm bathochromic shifts for α-, β-, γ-, and δ-methyl substitution, respectively (*cf.* **6**, **15**, **11**, **13**, and **9**). The large shift associated with β substitution may arise from the preference for the *s-cis*-enone conformation. The large δ-methyl effect is supported by the 20-nm shift caused by introducing a δ-methyl into **31** (compare **32**) and is not predicted by the calculations.[51] Agreement between the calculated and observed maxima for the few compounds for which data exist (**6**, **9**, and **19**) is poor.

Conformation of Phenone Derivatives.—Deduction of conformation is a more subtle problem in the case of the phenone derivatives **31–34** than it is for the other dienones. All the phenone derivatives exhibit a single carbonyl stretching frequency in the infrared suggesting conformational homogeneity. For structures

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[47] H. B. Klevens and J. R. Platt, *J. Amer. Chem. Soc.*, **71**, 1714 (1949); E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

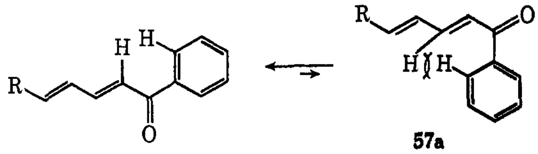
[48] F. Johnson, *Chem. Rev.*, **68**, 375 (1968).

[49] (a) P. Roullier, D. Gagnaire, and J. Dreux, *Bull. Soc. Chim. Fr.*, 168 (1966); (b) A. Duperrier and J. Dreux, *Tetrahedron Lett.*, 3127 (1970).

[50] N. L. Allinger, T. W. Stuart, and J. C. Tai, *J. Amer. Chem. Soc.*, **90**, 2809 (1968).

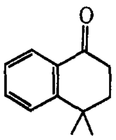
[51] The observed pattern of substituent effects is also not consistent with changes in π-electron density only during the $\pi \rightarrow \pi^*$ transition which can be obtained from Salem's π change densities for 3,5-hexadienone (**19**): A. Devaquet and L. Salem, *ibid.*, **91**, 3793 (1969).

which approach planarity the s-cis conformation (**57**) should be preferred owing to steric destabilization of



57 **57a**

the s-trans conformation (**57a**). Compound **58**, a rigid *s-trans*-phenone, exhibits $\nu_{CO}/(CCl_4)$ 1688 cm^{-1}.[52]

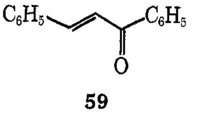


58

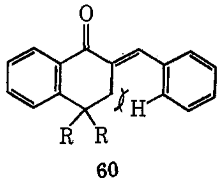
Substraction of 8 cm^{-1} to simulate the effect of a second conjugated double bond[19] gives a value of 1660 cm^{-1} for an s-trans model. The crotonylidene derivatives **31**–**33** do exhibit carbonyl stretching at higher frequencies, 1665–1670 cm^{-1}, in agreement with s-cis conformations, but the difference is small. No deduction can be drawn from comparison of **34** and **35**.

Nmr evidence is more compelling. For aliphatic dienones the chemical shift of H_3 is conformation dependent varying from τ 4.30 and 4.2 for rigid s-trans compounds **17** and **18** to *ca.* τ 3.9 for **11** which is entirely s-cis. In **31**–**33** H_3 appears much farther downfield and over the small range of τ 3.18–3.29. Using τ 3.9 and 4.25 as base values for H_3 in s-cis and s-trans conformers, respectively, we have estimated the chemical shift of H_3 in **31**–**33** by introducing corrections for the inductive effect of β-phenyl *vs.* β-methyl and for the long-range anisotropic effect of the phenyl group.[53] The values τ 3.9 for s-trans and τ 3.3 for s-cis show that the s-cis conformation is in much closer agreement with the average observed value of τ 3.23. A consequence of the s-cis conformational preference should be a downfield shift of the H_4 signal owing to anisotropy of the carbonyl group. Such a shift of 0.2–0.25 ppm occurs on going from aliphatic dienones to phenone derivatives (**6** and **13** *vs.* **31** and **33**). This is also true when a 6c-methyl is present (**8**, **9**, and **14** *vs.* **32**).

Comparison of the uv absorption of **34** and its s-cis analog **35** reveals a decrease in absorption intensity in the latter. Hassner and Cromwell[54] interpreted a similar, but more pronounced, difference between *trans*-chalcone (**59**) and two s-cis analogs (**60**) in terms of an s-trans conformation for **59**. We feel that a significant portion of the low absorption intensities of **35**, **60a**, and **60b** can be attributed to nonplanarity arising from 1,3 hydrogen–methylene and phenyl–methylene interactions.[23] The reduced intensity of the uv absorption of *cis*-1-phenylpropene relative to that of its trans isomer[55] illustrates the operation of just such an effect. It is worth noting that the carbonyl stretching frequencies reported for **59**, **60a**, and **60b** in CCl_4, 1667, 1666, and 1673 cm^{-1}, respectively,[54] do not support a change in enone conformation.



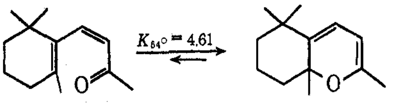
59



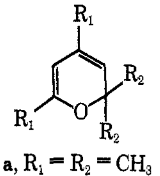
60

a, R = H
b, R = CH_3

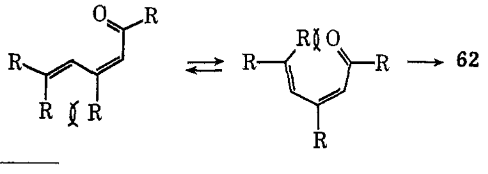
Dienone–Pyran Equilibria.—α,β-*cis*-Dienones can also exist as valence isomeric α-pyrans. The only reported example of a compound which exists as an equilibrium mixture is *cis*-β-ionone (**61**).[56] Interconversion of **61a** and **61b** is so facile as to prevent their separation. 2,2,4,6-Tetraalkyl-α-pyrans (**62**) have been prepared by treatment of α-pyrones with 2 equiv of a Grignard reagent and appear to exist exclusively in the pyran form.[57] Thus, the compounds do not form 2,4-dinitrophenylhydrazone derivatives; their uv spectra are similar to those of *s-cis*-dienes;[58] and catalytic hydrogenation of **62b**[59] gives a tetrahydropyran. In contrast, the aliphatic α,β-*cis*-dienones **7**, **10**, **12**, **21**, and **53**, which do not have the above substitution pattern, exist in the dienone form. Evidence for this is their intense uv absorption and the presence of an nmr signal for the uniquely deshielded H_5. These compounds can all adopt stable planar dienone conformations (see Table I). Owing to steric interactions *cis*-β-ionone (**61a**) and the 4,6,6-trialkyldienones corresponding to general structure **62** have no available stable planar



61a **61b**



62 a, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = n$-Bu



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[52] We thank Mr. Michael McLaughlin for the gift of a sample of this compound.

[53] Details are given in the Experimental Section.

[54] (a) A. Hassner and N. H. Cromwell, *J. Amer. Chem. Soc.*, **80**, 893 (1958). (b) In the solid state chalcone and its *p*-methoxy derivative are s-cis: D. Rabinovitch and G. M. J. Schmidt, *J. Chem. Soc. B*, 6, 11 (1970).

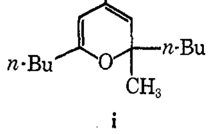
[55] C. G. Overberger, D. Tanner, and E. M. Pearce, *J. Amer. Chem. Soc.*, **80**, 4566 (1958): *cis*-1-Phenylpropene, λ_{max} 242 (13,000) and 280 (320); trans-, λ_{max} 249 (17,000) and 283 (1000) (no solvent given).

[56] E. N. Marvell, G. Caple, T. A. Gosink, and G. Zimmer, *ibid.*, **88**, 619 (1966).

[57] R. Gompper and O. Christman, *Chem. Ber.*, **94**, 1784 (1961).

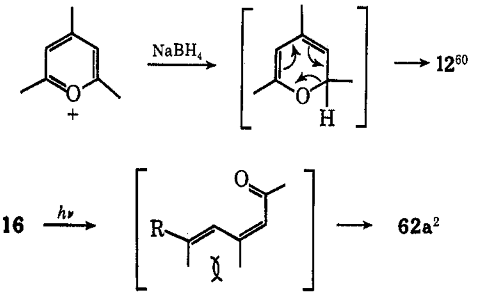
[58] For **61b** λ_{max} (CH_3OH) 208 (3230) and 253 (7000).

[59] The method of synthesis and structural evidence[57] are also consistent with a mixture of **61b** and i.

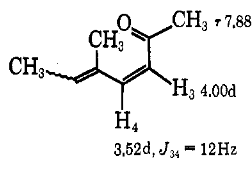


i

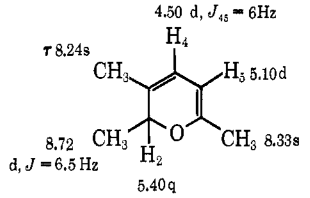
conformations and therefore prefer their pyran forms (**61b** and **62**). Because interconversion is rapid the method of synthesis does not determine the valence isomer obtained. Thus



It is steric destabilization of the dienone valence isomer, not the specific 4,6,6-trisubstitution pattern, which is essential for the existence of pyran. Thus, irradiation of **13** produces **14** and a second fraction which has been identified as an equilibrium mixture of **63a** and **63b**.[2,61] Compounds **63** were isolated as a single



63a



63b

glpc fraction which exhibited uv maxima at 284 nm (ε 3900) and 211 nm (ε 2300). The nmr spectrum in $CDCl_3$ (see **63b**) was consistent with the pyran structure and in agreement with other α-pyran spectra reported in the literature.[56,62,63] In addition weaker signals corresponding to nonintergral numbers of hydrogens were observed and assigned as shown in **63a**. Comparison of the integral of the dienone H_3, H_4, and H_6 (assumed to occur near H_3 and H_4) signals with that of all other olefinic hydrogens leads to an estimate of 13% dienone content. In agreement with the argument above, 2,3,4,6-tetramethyl-α-pyran contains no dienone valence isomer (benzene solution)[63] while simple dienals do not close to pyrans.[64]

Replacement of a 6-alkyl group with a substituent capable of extending the conjugated π system understandably leads to greater preference for the open dienone valence isomer. Thus Köbrich and Wunder[65] have shown that the highly hindered 4,6-dimethyl-6-phenyldienone **38** exists primarily as a dienone and that this is probably also the case when the conjugating 6 substituent is *p*-anisyl (**39**), *p*-(dimethylamino)phenyl (**40**), and *trans*-β-styryl (**45**). Whether a significant amount of the pyran valence isomer is present in these cases is under investigation.

Dreux and his coworkers have studied pyrans under conditions which place them in equilibrium with *trans*-dienones and have recently observed that many of the same factors pointed out above control the α-pyran ⇄ *trans*-dienone equilibrium.[49b]

Summary.—Analysis of ir, uv, and nmr data has led to a set of self-consistent deductions about the conformations of conjugated dienones. Except for highly substituted compounds which are nonplanar or tautomerize to α-pyrans, evidence is in favor of conformations which are close enough to planarity to be labeled meaningfully as s-cis or s-trans. Deviations from planarity of less than 25°, however, will not be revealed by our data.

Experimental Section

General and Spectra.—Infrared spectra of CCl_4 solutions or thin films were recorded on a Beckman IR-10 instrument and were calibrated with the 1601-cm^{-1} polystyrene band. Absolute positions of absorption maxima are estimated to be accurate within ±5 cm^{-1}, and relative positions of any two carbonyl maxima can be estimated within ±3 cm^{-1}. Nmr samples were prepared as *ca.* 10% solutions in carbon tetrachloride. Spectra were recorded at a probe temperature of 39 ± 2° and were calibrated relative to internal tetramethylsilane. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory directed by Mr. Charles Meade. Compound **35** was prepared as reported in the literature,[66] mp 137–139° (lit.[66] 132–134°). Condensation of *O*-nitrocinnamaldehyde and acetyl methyl diethyl phosphonate anion gave **28**, mp 73–74° (lit.[67] 73.5°).

Perdeuteriomalonic Acid (49). From Carbon Suboxide.—Approximately 3 g of carbon suboxide[68] was obtained from 84 g of diacetyltartaric anhydride. The carbon suboxide was contained in a vacuum trap in a Dry Ice–acetone bath. To the trap were added 15 ml of dry tetrahydrofuran and 4 ml of D_2O. The trap was sealed and left in an ice bath for 20 hr. The tetrahydrofuran was removed on a rotary evaporator. The trap was then attached to a vacuum pump to remove the remaining volatiles. There remained in the flask 1.85 g of perdeuteriomalonic acid as white crystals.

Exchange Method.—Malonic acid (11 g, 0.105 mol) and 3 g of D_2O (0.15 mol) were added to a 300-ml, round-bottom flask. The mixture was allowed to stand for 30 min. The water was then removed on a vacuum pump (0.05 mm). This procedure was repeated five times. The isotopic purity of the product was not assayed.

***trans,trans*-Sorbic-*2,4*-d_2 Acid (50).**—To a 200-ml, round-bottom flask equipped with a reflux condenser were added 6.315 g of perdeuteriomalonic acid (58.5 mmol), 4.1 g of crotonaldehyde (58.5 mmol), and 10 ml of anhydrous pyridine. The flask was set in an oil bath at 80–85°. Gas evolution was monitored with a mineral oil bubbler. The flask was removed from the oil bath after 3 hr. The contents of the flask as transferred to a 50-ml erlenmeyer flask and cooled in an ice bath. An ice-cold solution of 3 ml of concentrated sulfuric acid in 6 ml of water was added to the flask. The precipitate was collected by filtration. The filtrate was cooled in an ice bath, and an additional crop of crystals was collected. The precipitate was dissolved in 50 ml of boiling water. The flask was left at 5° in a cold room overnight. Subsequent filtration and drying gave 1.442 g of sorbic-*2*-*d* acid (21.8%) as long white needles, mp 133–134° (reported[69] for perprotio compound, mp 134°). In a second run a yield of 31.4% was obtained. The isotopic purity was not assayed.

***trans,trans*-3,5-Heptadienone-*3,5*-d_2** (6-*3,5*-d_2).—To a 100-ml, three-neck, round-bottom flask equipped with nitrogen inlet tube, reflux condenser, magnetic stirring bar, and a rubber stopple were added 1.442 g of sorbic-*2*-*d* acid (12.7 mmol) and 50 ml of dry ether. A 2.3 *M* solution of methyllithium in ether (12.6 ml, 25.3 mmol) was added with a syringe. A precipitate formed upon the addition of the methyllithium, and this precipitate did

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[61] Experimental details are given in ref 2.

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[66] W. Herzog and J. Kreidel, *Chem. Ber.*, **55**, 3394 (1922).

[67] L. Diehl and A. Einhorn, *ibid.*, **18**, 2327 (1885).

[68] C. D. Hurd and F. D. Pilgrim, *J. Amer. Chem. Soc.*, **55**, 757 (1933).

[69] C. F. H. Allen and J. Van Allan, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 783.

not disappear after complete addition. The contents of the flask were heated at reflux for 30 min. Water (10 ml) was added slowly at first, then rapidly. The mixture was transferred to a separatory funnel and shaken, and the aqueous layer was discarded. The ether layer was washed with three additional 10-ml portions of water. The ether layer was dried for 1 hr (Na_2SO_4). Subsequent filtration and removal of the ether on a rotary evaporator at reduced pressure left a yellow oil. This oil was filtered through 20 g of alumina with 35 ml of benzene. Removal of the solvent on a rotary evaporator left 0.7135 g of *all-trans*-3,5-heptadienone-*3,5-d_2* as a yellow oil (50.7%). Further purification was effected by distillation on a micromolecular still at 45-50° (30 mm). A sample of the product was analyzed by glpc, and it had the same retention time as the perprotio compound (on a 20 ft × 0.25 in. 5% FFAP on Anakrom AB column): ir (CCl_4) 2230 (C—D), 1685, 1667 (C═O), 1630, 1594, 1582 (C═C), 972 cm^{-1} (trans CH═CH).

trans,trans-**5-Phenyl-2,4-pentadienoic-*2-d* Acid (52).**—To a 100-ml, round-bottom flask were added 2.80 g of *trans*-cinnamalmalonic acid, 25 ml of anhydrous tetrahydrofuran, 1 ml of D_2O, and one drop of a 2.58 *M* solution of methyllithium in ether. The liquid was evaporated under a stream of nitrogen. The flask was placed for 2 hr on a rotary evaporator attached to a vacuum pump (0.05 mm). This exchange procedure, without the addition of methyllithium, was repeated two additional times to give *trans*-cinnamylidenemalonic acid-*O,O-d_2* (**51**).

The flask was then fitted with a reflux condenser leading to a mineral oil bubbler. To the flask were added 20 ml of anhydrous pyridine and two drops of D_2O. The contents of the flask were heated at reflux for 3 hr, then allowed to cool to room temperature, and poured into 200 ml of ether. The ether solution was extracted with three 50-ml portions of 6 *N* hydrochloric acid. The ether layer was then shaken with 100 ml of 5% potassium hydroxide solution and was discarded. The aqueous layer was washed with 50 ml of ether, separated, and acidified with concentrated hydrochloric acid. The resulting suspension was extracted with two 50-ml portions of ether. The combined ether layers were dried for 1 hr (Na_2SO_4). Subsequent decantation and removal of ether on a rotary evaporator at reduced pressure left a yellow solid. This solid was taken into 200 ml of hot benzene, and the solution was added to a 200-ml, round-bottom flask equipped with a reflux condenser and containing 0.2 g of iodine. The contents of the flask as heated at reflux and irradiated with a 250-W sun lamp for 30 min. The benzene was removed on a steam bath. The remaining solid was washed with two 30-ml portions of a saturated potassium iodide solution and was collected on a Büchner funnel. The collected solid was recrystallized five times from 25-ml portions of benzene to yield 0.672 g of *trans,trans*-5-phenyl-2,4-pentadienoic-*2-d* acid as off-white plates, mp 167.5-170°. The reported melting point of the perprotio compound is 165-166°.[70] The combined mother liquors from the benzene recrystallizations were shaken with three 30-ml portions of a saturated solution of potassium iodide. The benzene was removed on a steam bath, and the residue was recrystallized from 20 ml of benzene to give an additional 0.435 g of product. The total yield was 1.307 g (58%). The application of this same decarboxylation procedure to perprotiocinnamalmalonic acid resulted in a 46% yield of *trans,trans*-5-phenyl-2,4-pentadienoic acid, mp 169-170°.

trans,trans-**6-Phenyl-3,5-hexadienone-*3-d* (22-*3-d*).**—*trans,trans*-5-Phenyl-2,4-pentadienoic-*2d* acid was treated with 2 equiv of methyllithium in diethyl ether using a procedure identical with that described for preparation of **6**-*3,5-d_2* (*vide supra*). The product was obtained as white crystals: mp 68-68.5°; ir (CCl_4) 2250 (C—D), 975, 967 cm^{-1} (trans CH═CH).

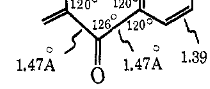
all-trans-**3,5,7-Nonatrienone (41).**—*all-trans*-2,4,6-Octatrienoic acid[71] (2.24 g, 16.2 mmol) was treated with 2 equiv of methyllithium in diethyl ether using the procedure described for preparation of **6**-*3,5-d_2* (*vide supra*) to give 0.87 g (39%) of a yellow oil: ir (CCl_4) 992 cm^{-1} (trans CH═CH); uv max (C_6H_{12}) 310 nm (ϵ 27,000), 299 (27,300) (lit.; Table II); nmr (CCl_4) τ 8.22 (d, 3, J = 5 Hz, CH_3CH═), 7.85 (s, 3, CH_3CO–), 4.3-3.4 (complex, 5, olefin hydrogens), 2.94 (q, 1, $J_{4,3}$ = 16 Hz, $J_{4,5}$ = 10 Hz, 4-hydrogen).

(*E,E,E*)-4-Methyl-3,5,7-nonatrienone (42).—(*E,E,E*)-3-Methyl-2,4,6-octatrienoic acid[72] was prepared by the method described by Kuhn and Hoffer[73] for the high-melting isomer, giving white needles, mp 164-165° (lit.[73] mp 160-161°). This acid (1.85 g, 12.2 mmol) was treated with 2 equiv of methyllithium using the procedure described for preparation of **6**-*3,5-d_2* (*vide supra*) to give 1.38 g (75%) of a yellow oil: ir (CCl_4) 978, 957 cm^{-1} (trans CH═CH); nmr (CCl_4) τ 8.20 (d, 3, J = Hz, CH_3CH═), 7.82 (s, 3, CH_3CO), 7.75 (s, 3, 4-methyl), 4.5-3.1 (complex, 5, olefin hydrogens).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.38; O, 10.65. Found: C, 80.01; H, 9.45.

all-trans-**1-Phenyl-2,4,6-octatrienone (44).**—To a 250-ml, red-tinted, round-bottom flask equipped with a reflux condenser and containing a few boiling stones were added 6 g (15.8 mmol) of benzoylmethylenetriphenylphosphorane, 5 g of sorbaldehyde, and 70 ml of dry benzene. The solution was heated at reflux for 24 hr. The benzene was removed on a rotary evaporator at reduced pressure leaving a slushy, brown solid which was then washed with three 25-ml portions of ether. The remaining solid (triphenylphosphine oxide) was discarded. The ether was removed on a rotary evaporator at reduced pressure leaving a brown solid. This solid was washed with three 50-ml portions of hot Skellysolve B. The combined washings were cooled in an ice bath, and the resulting precipitate was collected by filtration. This gave 1.8 g of an orange-yellow powder, which upon sublimation (100°, 1 mm) gave 1.5 g of yellow crystals, mp 88-94°. The sublimate was filtered through 50 g of alumina with approximately 100 ml of benzene-Skellysolve B (1:1). Solvent was removed on a steam bath, and the resulting solid was recrystallized from two 30-ml portions of Skellysolve B to give 0.4 (12.6%) of *all-trans*-1-phenyl-2,4,6-octatrienone, mp 97-97.5° (lit.[74] mp 94-95°), ir (CCl_4) 1000 cm^{-1} (trans CH═CH).

Estimation of the Chemical Shift of H_3 in Phenone Derivatives.—The estimation was made for planar s-cis and s-trans conformers by starting with chemical shifts for H_3 in pure *s-cis*- (**11**) and *s-trans*- (**17** and **18**) methyl dienones. These values were corrected for the effect of replacing the methyl group with an "in-plane" phenyl group. Long-range phenyl anisotropic effects were estimated from Jackman and Sternhell's version of the Bovey-Johnson shielding diagram.[75a] The distance between H_3 and the center of the benzene ring was estimated on the basis of the following parameters.[76] The distance was 4.0 Å in the s-cis conformer and 4.9 Å in the s-trans conformer. The inductive effect of β-phenyl *vs.* β-methyl was estimated starting with the chemical shift difference between the methyl groups of propane and ethylbenzene, 0.3 ppm.[75] This value must be reduced by the deshielding which the methyl of ethylbenzene experiences from phenyl anisotropy since we have estimated this separately. Reference to the Bovey-Johnson diagram[75a] suggests that this effect should be *ca.* 0.2 ppm. Therefore the inductive effect of β-phenyl should cause a *ca.* 0.1 ppm downfield shift of H_3. Calculations are summarized below.



	τ(s-trans)	τ(s-cis)
Base value for CH_3 derivative	4.25	3.9
Inductive effect of β-phenyl	−0.1	−0.1
Anistropic effect of phenyl	−0.25	−0.5
Chemical shift of H_3 in phenyl derivative	3.9	3.3

Registry No.—**6**, 18402-90-9; **6**-*3,5-d_2*, 29178-91-4; **7**, 4857-17-4; **8**, 4173-40-4; **9**, 16647-04-4; **10**, 29178-96-9; **11**, 29178-97-0; **12**, 29178-98-1; **13**, 29178-99-2; **14**, 29179-00-8; **15**, 29179-01-9; **16**, 29179-02-0; **17**, 29179-03-1; **18**, 29179-04-2; **19**, 20432-46-6; **20**, 29179-11-1; **21**, 29179-12-2; **22**, 29179-13-3; **22**-*3-d*,

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Photoisomerization Products of Conjugated Dienones

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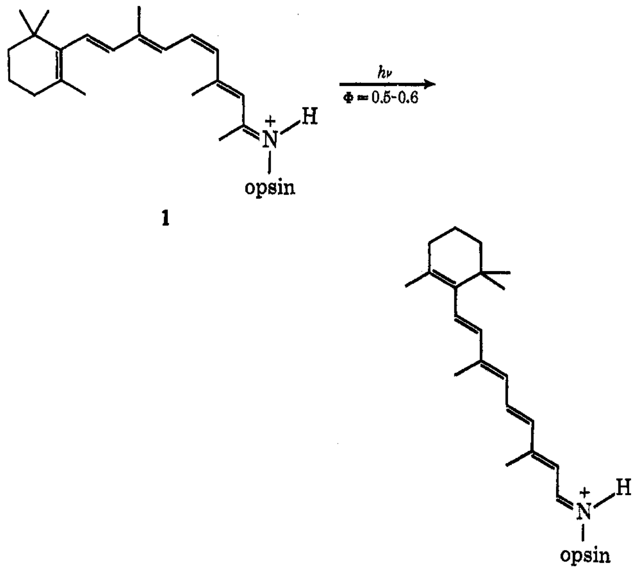
Irradiation of dilute (10^{-2}–10^{-4} *M*) diethyl ether solutions of conjugated dienones rapidly produces photostationary-state mixtures of the all-trans, cis,trans, and trans,cis isomers. Exceptions are 4-methyl-3,5-heptadienone (**21**), which undergoes isomerization only about its α,β double bond, and the 1-aryldienones **44**, **46**, and **47**, which seem to undergo only γ,δ photoisomerization. α-Pyran formation occurred on irradiation of 4,6-dimethyl-3,5-heptadienone (**24**) and 5-methyl-3,5-heptadienone (**27**) as the result of ring closure of the respective α,β-*cis*-dienones in what are possibly dark reactions. Failure to detect any cis,cis photoisomers has been tentatively attributed to their rapid conversion to α,β-cis-γ,δ-trans isomers *via* the valence isomeric α-pyrans in the dark.

The initial chemical event in vision is a remarkably specific cis to trans photoisomerization of the 11 double bond of the visual pigment rhodopsin (**1**).[2] This isomerization, which triggers but does not constitute in itself the visual process, occurs in an 11-*cis*-retinal unit which is bound to the protein opsin *via* a protonated Schiff base linkage and fits snugly into the protein surface. The specificity of 11 isomerization could be an electronic property of the protonated retinylidene imine chromophore or might arise because alternative isomerizations are geometrically prohibited by the fit with the protein surface. Photoisomerization of *all-trans*-retinal itself (**2**) has been variously reported to give a mixture of isomers in which all-trans predominates[3] and to give the 13-cis isomer specifically.[4,4a] In a program designed to investigate the properties of excited states which are electronically similar to those of rhodopsin and retinal, we have examined the relatively simple dienones which have two isomerizable double bonds and a carbonyl group in conjugation.



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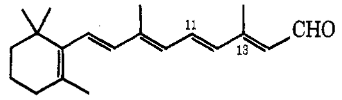

2

In contrast to the extensive studies of cross-conjugated dienones,[5] investigations of the photochemistry of conjugated dienones have been relatively rare. Early reports showed that conjugated dienones bearing aromatic groups gave photodimers both in solution and solid phases.[6,7] Irradiation of some steroidal dienones resulted in formation of cyclobutane-type dimers.[8] *trans*-β-Ionone (**3**) gave pyran **4**[9-11] and smaller amounts of the unconjugated dienone **5**.[12] In an

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(1) (a) NSF Cooperative Fellow, 1965–1969; (b) Alfred P. Sloan Foundation Fellow, 1969–1971.

(2) For a summary of knowledge of the molecular basis of vision, see E. W. Abrahamson and S. E. Ostroy, *Progr. Biophys. Mol. Biol.*, **17**, 179 (1967); C. B. D. Bridges, *Compr. Biochem.*, **27**, 31 (1967); G. Wald, *Science* **162**, 230 (1968).

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