447. *Absorption Spectra of Ketones. Part IV.* The Steric Requirements for Spectroscopic Interaction between a Carbonyl Group and a βγ-Double Bond.*

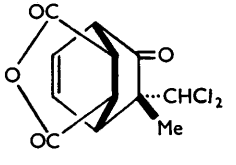
By R. C. Cookson and N. S. Wariyar.

Some *bicyclo*[2 : 2 : 2]oct-5-en-2-ones have been synthesised by the Diels–Alder reaction. The structure has been determined of a tetracarboxylic acid produced by treatment with acid of the adduct of anethole with two mols. of maleic anhydride.

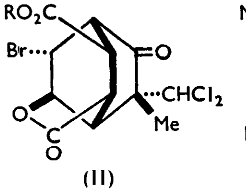
Examination of the absorption spectra of these and other ketones suggests that the carbonyl band near 290 mμ is abnormally intense only when the *p*-orbitals of $C_{(1)}$ and $C_{(3)}$ in the system, $\overset{1}{\mathrm{C}}\mathrm{O}-\overset{2}{\mathrm{C}}-\overset{3}{\mathrm{C}}=\overset{4}{\mathrm{C}}$, point at one another. The intensity of the band is increased by substitution on the olefinic double bond.

Open-chain βγ-unsaturated ketones and α-phenyl-ketones have been known for several years to show an unusually intense absorption band in their ultraviolet spectra at about 290 mμ.[1-5] We have examined the effect of the structure of the ketones on the absorption band to find out what steric and electronic factors determine the intensity. But before the absorption spectra are discussed the preparation of some *bicyclo*[2 : 2 : 2]octenones, needed for the investigation, will be described.

Although 6-dichloromethyl-6-methyl*cyclo*hexa-2 : 4-dien-1-one did not react with maleic anhydride in boiling benzene, the Diels–Alder adduct (I) was formed in good yield at 190°.



(I)



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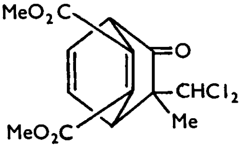
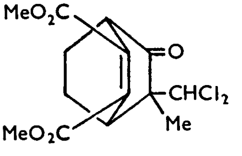


(III)



(IV)

Bromination of the derived dicarboxylic acid to a bromo-lactone acid (II; R = H) confirms that the anhydride group in the adduct (I) is *cis* to the olefinic double bond. [Minimisation of compression in the transition state for addition would probably lead to the configuration of the methyl group shown in (I), but there is no experimental verification of

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* Part III, *J.*, 1955, 1651.

[1] Biquard, *Bull. Soc. chim. France*, 1941, **8**, 55.

[2] Kumler, Strait, and Alpen, *J. Amer. Chem. Soc.*, 1950, **72**, 1463.

[3] *Idem, ibid.*, p. 4558.

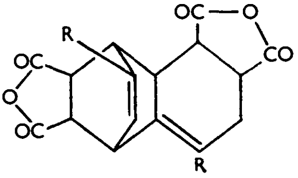
[4] Shapiro, *J. Org. Chem.*, 1949, **14**, 837.

[5] Braude and Timmons, *J.*, 1953, 3144.

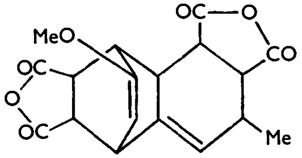
this.] The dienone added dimethyl acetylenedicarboxylate to give the diunsaturated compound (III), which rapidly took up one mol. of hydrogen over platinum, yielding the mono-unsaturated ester (IV).

Hukki[6] has shown that the adduct of *p*-methyl*iso*propenylbenzene with two mols. of maleic anhydride has the structure (V; R = Me), and Alder and Schmitz-Josten[7] more recently that the corresponding adduct from styrene itself has the structure (V; R = H). There can be little doubt that other products from the Wagner–Jauregg reaction, including that from anethole,[8] have analogous structures. Bruckner and Kovács[9] have in fact been able to interpret the known chemistry of the anethole adduct in terms of (VI).

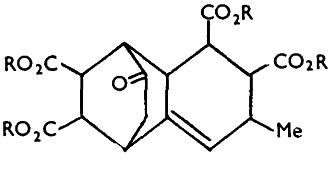
Hydrolysis of the adduct (VI) yields an acid, easily converted into a dianhydride and characterised by the tetramethyl ester (VII; R = Me). On long boiling with acid the original adduct (VI), like the derived keto-acid or its derivatives (VII), forms an isomeric keto-acid, characterised by a distinct tetramethyl ester. Since the isomerised acid no longer forms an anhydride, Buckner and Kovács[9] suggested that it might be a stereoisomer of (VII) in which both pairs of carboxyl groups are *trans*. Their conclusion about the stereochemistry of the carboxyl groups is probably justified, but it seemed to us that a migration of the double bond might also be involved in the isomerisation. Conjugation of the double bond with either of the carboxyl groups was ruled out by the resistance to formation of an anhydride and by the infrared spectrum of the tetramethyl ester which showed no strong absorption in the double-bond stretching region at frequencies lower than 1730 cm.$^{-1}$ (in CS$_2$). The ultraviolet absorption of the substance (discussed later) suggested that the double bond had moved to the tetrasubstituted position (see VIII).



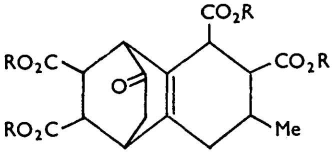
(V)



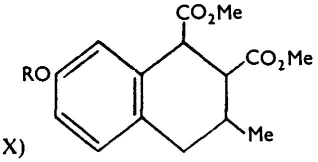
(VI)



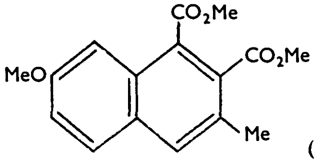
(VII)



(VIII)



(IX)



(X)

Structure (VIII) was vindicated by the behaviour of the tetramethyl ester on pyrolysis. At 200° dimethyl fumarate split off, leaving a phenol, isolated as the methyl ether. This product of pyrolysis was identified as the tetralin derivative (IX; R = Me) by its typical absorption spectrum and by dehydrogenation to a (methoxy)methylnaphthalenedicarboxylic

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[6] Hukki, *Acta Chem. Scand.*, 1951, **5**, 31.

[7] Alder and Schmitz-Josten, *Annalen*, 1955, **595**, 1.

[8] Bruckner, *Ber.*, 1942, **75**, 2034.

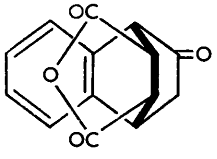
[9] Bruckner and Kovács, *J. Org. Chem.*, 1948, **13**, 641; 1949, **14**, 65; Bruckner, Kovács, and Huhn, *ibid.*, 1951, **16**, 1481.

ester, which was shown to be (X) by comparison with an authentic sample made from the known anhydride.[8,9]

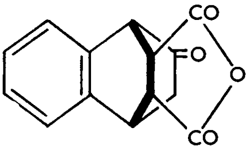
The Diels–Alder dissociation to dimethyl fumarate and the phenol (IX; R = H) shows that the original carbon skeleton of (VI) is not changed during the isomerisation. The position of the double bond in the isomeric ester explains why that ester dissociates to a phenol under conditions that do not affect the original ester (VII). When the adduct (VI) decomposes it regenerates anethole and maleic anhydride, without formation of a tetralin derivative.[9]

Takeda and his colleagues [10] have isolated the two possible adducts of β-naphthol with maleic anhydride. Their assignment [11] of the *exo*-configuration * (XI) to the more abundant isomer and the *endo*-configuration (XII) to the less abundant one was based on the higher dipole moment of the latter. Chemical proof of the correctness of the assignment has now been found in the reduction of the *endo*-diacid (XIII; R = H) by potassium borohydride, followed by very mild treatment with acid, to a lactone-acid (XV; R = H) which with diazomethane gave a lactone-ester (XV; R = Me) characterised as a γ-lactone by the band in its infrared spectrum at 1776 cm.$^{-1}$ (in $CHCl_3$). The lactone-ester (XV) was also formed by reduction of the *endo*-diester (XIII; R = Me) with sodium borohydride: addition of hydride from the less hindered, *exo*, side of the carbonyl group is evidently immediately followed by addition of the resulting alkoxide to the ester carbonyl group and reaction is completed by loss of methoxide ion. Under the same conditions the *exo*-diester was reduced to a stable hydroxy-diester (XIV).

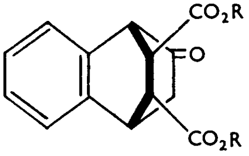
We now return to consideration of the ultraviolet absorption spectra. From the figures quoted in Tables 1, 2, and 3 it seems that nearly all βγ-unsaturated ketones, where the carbonyl group is not part of a ring, have an abnormally intense absorption band with its maximum at about 290 mμ, a similar position to that of the normal $n \longrightarrow \pi$ transition in saturated ketones.



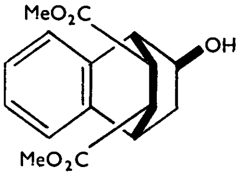
(XI)



(XII)



(XIII)



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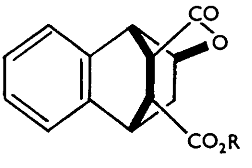

(XV)

The conformational freedom of these ketones makes it difficult to distinguish steric from other factors which might control the intensity of their absorption, but the intensity of absorption of the cyclic ketones, the conformations of which are known much more precisely and in some cases are geometrically fixed, seems to depend mainly on two factors, one steric and one electronic.

The steric factor in the system, $\overset{1}{C}O{-}\overset{2}{C}{-}\overset{3}{C}{=}\overset{4}{C}$, is such that no ketone shows an abnormally high extinction coefficient unless the *p*-orbitals of $C_{(1)}$ and $C_{(3)}$ are directed approximately

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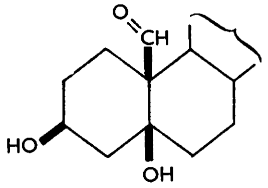
* In this paper *endo* and *exo* are used in the sense that *o*-phenylene is considered as the bridging group; that is, substituents on the same side of the *cyclo*hexane ring as the benzene ring are *exo*, those on the other side are *endo*.

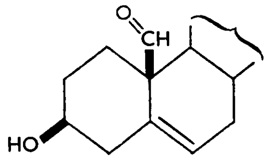
[10] Takeda and Kitahonoki, *J. Pharm. Soc. Jap.*, 1951, **71**, 860; 1953, **73**, 206, 280.

[11] Takeda, Nagakura, and Kitahonoki, *Pharm. Bull. Jap.*, 1953, **1**, 135.

towards one another.* So the *cyclo*pentenones (Table 5), having the carbonyl group and the olefinic double bond in approximately the same plane, show no spectroscopic interaction. 2-Phenyl*cyclo*hexanone (No. 24), where the equatorial conformation of the phenyl group [12] ensures that the geometrical condition for interaction cannot be satisfied, has a normal extinction coefficient; whereas 2 : 2-diphenyl*cyclo*hexanone (No. 26), where one phenyl group must be axial, so allowing the condition to be satisfied when the conformation about the C–Ph bond is suitable, does show increased extinction. [A rather similar geometrical arrangement holds in dianhydrodihydrostrophanthidin (partial formula XVII) (No. 58), which shows markedly stronger absorption than monoanhydrodihydrostrophanthidin (XVI) (No. 57).]

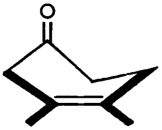


(XVI)



(XVII)

But the most revealing contrast is between β-tetralone (No. 38) and the *cyclo*hexenones with tetrasubstituted double bonds (Nos. 34—37) on the one hand, and the corresponding bridged-ring ketones (Nos. 47—52) on the other hand. The first group of ketones shows normal carbonyl absorption ($\varepsilon = 20$—80) while the second shows strong interaction ($\varepsilon = 300$—500). The most obvious difference between the two classes is that the unbridged ketones probably exist mainly in the distorted chair conformation (XVIII),[13] whereas the bridged ones must adopt a distorted boat conformation (XIX) : in the chair conformation the orbitals are skew to one another, in the boat their axes intersect.



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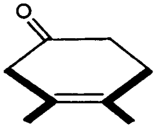
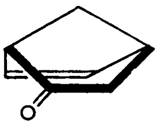
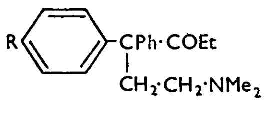


(XIX)



(XX)



(XXI)

Although the large increase in extinction coefficient of *bicyclo*[2 : 2 : 1]heptenone † (XX) (No. 56) compared with the *bicyclo*[2 : 2 : 2]octenones (Nos. 44—46) with disubstituted double bonds probably reflects the slightly closer approach of the π-orbitals in the former, it may be partly due to increased strain. Similar geometrical factors presumably cause the transannular addition reactions of *bicyclo*[2 : 2 : 1]heptadiene,[14] which are not shown by *bicyclo*[2 : 2 : 2]octadiene.[15]

Amongst the 3-alkylidene*cyclo*hexanones (Table 7) the two methylated cholest-5-en-3-ones (Nos. 39 and 40) show no interaction, while the 9β-ergosta-7-en-11-ones (Nos. 41 and 42) do exhibit significant interaction. The probable adoption of a distorted-chair conformation by ring A of the former pair and of a distorted boat by ring C of the latter seems inadequate, in itself, to account for the difference. The flattening of ring A caused by

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* From the available data we cannot give an exact definition of the geometry required for maximum interaction, but we would expect one condition to be that the atomic *p*-orbitals of $C_{(1)}$ and of $C_{(3)}$ should be in the same plane as $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$.

† The spectrum was measured by Mr. C. Sandris in Dr. G. Ourisson's Laboratory (Strasbourg) on a sample of the ketone (XX), generously given by Professor N. J. Toivonen (Helsinki). We are most grateful to Dr. Ourisson and Professor Toivonen for their kindness in suggesting our publication of their results.

[12] Alpen and Kumler, *J. Amer. Chem. Soc.*, 1950, **72**, 5745.

[13] Cf. Barton, Cookson, Klyne, and Shoppee, *Chem. and Ind.*, 1954, 21.

[14] Winstein and Shatavsky, *ibid.*, 1956, 56.

[15] Hine, Brown, Zalkow, Gardner, and Hine, *J. Amer. Chem. Soc.*, 1955, **77**, 594.

TABLE 1. *Open-chain βγ-unsaturated ketones.*

No.	Compound	Max. (mμ)	ε	Solvent	Ref.
1	4-Methylpent-4-en-2-one	290	80	IO	A
2	4-Hydroxyhept-5-en-3-one	281	300	Et	5
		290			
3	3-Hydroxy-3 : 5-dimethylhex-4-en-2-one	281	230	Et	5

TABLE 2. *α-Phenyl-ketones.*

4	Phenylacetaldehyde	*ca.* 300 [a]	100	Et	2
5	Phenylacetone	284 [a]	130	Et	1
		288 [a, b]	145	Et	2
		288 [a]	130	CH	1
6	1-Phenylbutan-2-one	284 [a]	130	Et	1
		288 [a]	130	CH	1
7	3-Phenylbutan-2-one	296 [a, b]	150	Et	2
		287			
8	3-Methyl-3-phenylbutan-2-one	296 [a, b]	160	Et	2
9	3-Methyl-3-phenylpentan-2-one	295 [a, b]	330	Et	B
10	4-Methyl-4-phenylhexan-3-one	296 [a, b]	260	Et	B
11	1-Ethylthio-3-phenylacetone	302	350	Et	C
12	1-Ethylsulphonyl-3-phenylacetone	286	150	Et	C
13	4-Benzyl-6-dimethylamino-4-phenylheptan-3-one hydrochloride	288 [a]	200	W	4
14	1 : 3-Diphenylacetone	294 [a, b]	220	He	3

TABLE 3. *αα-Diphenyl-ketones.*

15	1 : 1-Diphenylbutan-2-one	295 [a, b]	250	He	3
16	3 : 3-Diphenylbutan-2-one	298 [a, b]	410	He	3
17	4-Diethylamino-1 : 1-diphenylbutan-2-one hydrochloride	287	280	Et	D
18	4-Methoxy-3 : 3-diphenylbutan-2-one	290	210	Et	D
19	6-Dimethylamino-4 : 4-diphenylheptan-3-one hydrochloride	295	460	Et	2
		293 [a]	470	W	4
20	7-Dimethylamino-4 : 4-diphenylheptan-3-one hydrochloride	297 [a]	620	Et	2
21	6-Dimethylamino-4-phenyl-4-*p*-tolylheptan-3-one hydrochloride	289 [a]	790	W	4
22	6-Dimethylamino-4-*p*-methoxyphenyl-4-phenylheptan-3-one hydrochloride	291 [a]	1350	W	4

TABLE 4. *α-Phenyl- and α-vinyl-cyclanones.*

23	2-Phenyl*cyclo*pentanone	292 [e]	50	Et	E
24	2-Phenyl*cyclo*hexanone	290	40	He	3
		290 [a]	17	Et	F
25	4 : 5-Dimethyl-2-phenyl*cyclo*hexanone	290 [e]	30	Et	F
26	2 : 2-Diphenyl*cyclo*hexanone	298	125	Et	G
27	6-Phenyl*cyclo*hex-3-enone	293 [a]	130	Et	F
28	3 : 4-Dimethyl-6-phenyl*cyclo*hex-3-enone	295 [a]	170	Et	F
29	Methyl 3β-acetoxy-19-oxo-olean-12-en-28-oate	290	50	Et	H
		290	41	Et	I

Notes to Tables: [a] Read from small-scale graph. [b] Shows fine structure: main peak quoted. [c] Point of inflection. [d] Kindly given by Professor D. H. R. Barton, F.R.S., and Dr. D. Locke (unpublished data). [e] Reacts with solvent.

Solvents: Et = ethanol, He = *n*-hexane, CH = *cyclo*hexane, CHe = *cyclo*hexene, Cl = chloroform, IO = *iso*octane, W = water, T = toluene.

References: A, Gray, Rasmussen, and Tunnicliff, *J. Amer. Chem. Soc.*, 1947, **69**, 1630. B, Cram and Knight, *ibid.*, 1952, **74**, 5835. C, Fehnel and Resnick, *J. Org. Chem.*, 1955, **20**, 996. D, Wilson and Kyi, *J.*, 1952, 1321. E, Mislow and Hamermesh, *J. Amer. Chem. Soc.*, 1955, **77**, 1590; Mislow and Lazarus, *ibid.*, p. 6383. F, Wildman and Wildman, *J. Org. Chem.*, 1952, **17**, 581. G, Bennet and Burger, *J. Amer. Chem. Soc.*, 1953, **75**, 84. H, Ruzicka, Grob, Egli, and Jeger, *Helv. Chim. Acta*, 1943, **26**, 1218. I, This paper. J, McBee, Smith, and Ungnade, *J. Amer. Chem. Soc.*, 1955, **77**, 559. K, Dorfman, *Chem. Rev.*, 1953, **53**, 105. L, Birch, *J.*, 1946, 593. M, Birch, Murray, and Smith, *J.*, 1951, 1945. N, Cocker and Hornsby, *J.*, 1947, 1157. O, Birch, *J.*, 1950, 367. P, Wilds and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 5366. Q, Shealy and Dodson, *J. Org. Chem.*, 1951, **16**, 1427. R, Bladon, Henbest, Jones, Lovell, Wood, Woods, Elks, Evans, Hathaway, Oughton, and Thomas, *J.*, 1953, 2921; Burke, Turnbull, and Wilson, *ibid.*, p. 3237; Heusler and Wettstein, *Helv. Chim. Acta*, 1953, **36**, 398. S, Beaton, Spring, Stevenson, and Stewart, *Chem. and Ind.*, 1955, 35. T, Conroy and Firestone, *J. Amer. Chem. Soc.*, 1953, **75**, 2530. U, Burnell and Taylor, *J.*, 1955, 2054. V, Elderfield and Rothen, *J. Biol. Chem.*, 1934, **106**, 71. W, Braude and Timmons, *J.*, 1955, 3766. X, Meinwald, Emerman, Yang, and Büchi, *J. Amer. Chem. Soc.*, 1955, **77**, 4401. Y, Asahina, Ishidate, and Tukamoto, *Ber.*, 1936, **69**, 355. Z, Nasini, *Gazzetta*, 1883, **13**, 120. α, Francesconi, *R. Accad. naz. Lincei*, 1903, V, **12**, ii, 204. β, *Idem, ibid.*, p. 267.

TABLE 5. cyclo*Pent-3-enones.*

No.	Compound	Max. (mμ)	ε	Solvent	Ref.
30	2 : 2 : 3 : 4 : 5 : 5-Hexachloro*cyclo*pent-3-enone	318	15	He	J
31	3β-Acetoxyandrosta-5 : 14-dien-17-one	285	50	Et	K
32	Indan-2-one	293—313 [c]	*ca.* 10	Et	1
		293—316 [c]	*ca.* 10	CH	1

TABLE 6. cyclo*Hex-3-enones.*

33	3-Methyl*cyclo*hex-3-en-1-one	280	19	Et	L
34	2-Oxo-$\Delta^{9:10}$-octalin	281	38	Et	M
35	ψ-Santonin	290	35	Et	N
		290	41	Et	I
36	17β-Hydroxynorandrost-5(10)-en-3-one	272—294 [c]	51	Et	O
		282—289	36	Et	P
37	3β-Methoxy-5β-methyl-19-norcholest-9(10)-en-6-one	286	37	Et	Q
38	2-Tetralone	321	18	Et	I
		294	89		
		327	32	CH	1
		320	32		
		316	45		
		291	68		

TABLE 7. 3-*Alkylidene*cyclo*hexanones.*

39	4 : 4-Dimethylcholest-5-en-3-one [d]	293—294	38	Et	I
40	2 :2 : 4 : 4-Tetramethylcholest-5-en-3-one [d]	299—300	30	Et	I
41	3β- Acetoxy-9β-ergosta-7 : 22-dien-11-one	295	120	Et	R
42	3β-Acetoxy-5α-hydroxy-9β-ergosta-7 : 22-dien-11-one	293	190	Et	R
43	12-Oxotaraxeryl acetate	285	50	Cl	S

TABLE 8. bicyclo[2 : 2 : 2]*Octenones.*

44	7-Dichloromethyl-7-methyl-8-oxo*bicyclo*[2 : 2 : 2]oct-5-ene-2 : 3-dicarboxylic anhydride (I)	300—303	81	Cl	I
45	Dimethyl 7-dichloromethyl-7-methyl-8-oxo*bicyclo*[2 : 2 : 2]-oct-5-ene-2 : 3-dicarboxylate	302	84	Et	I
46	8-Allyl-1 : 8-dimethyl-7-oxo*bicyclo*[2 : 2 : 2]oct-5-ene-2 : 3-dicarboxylic anhydride	300	64	?	T
47	Tetracarboxylic acid (VIII; R = H)	296	350	Et	I
48	Tetramethyl ester (VIII; R = Me)	297	300	Et	I
49	1 : 2 : 3 : 4-Tetrahydro-9-oxo-1 : 4-ethanonaphthalene-7 : 8-*endo*dicarboxylic anhydride (XII)	299 [b]	340	Cl	I
		(294 [b]	340	Et) [e]	I
50	Dimethyl 1 : 2 : 3 : 4-tetrahydro-9-oxo-1 : 4-ethanonaphthalene-2 : 3-*endo*-dicarboxylate (XIII; R = Me)	294—295 [b]	505	Et	I
			485	Cl	I
51	*exo*-Anhydride (XI)	297 [b]	305	Cl	I
		(296 [b]	380	Et) [e]	I
52	*exo*-Ester (isomer of No. 50)	296 [b]	450	Et	I
		296 [b]	405	Cl	I
		298 [b]	345	He	I
53	Hydrate of diketone (XXIII)	310	170	W	U
54	Dimethyl 7-dichloromethyl-7-methyl-8-oxo*bicyclo*[2 : 2 : 2]-octa-2 : 5-diene-2 : 3-dicarboxylate (III)	298—305 [c]	290	Et	I
55	Dimethyl 5-dichloromethyl-5-methyl-6-oxo*bicyclo*[2 : 2 : 2]-oct-2-ene-2 : 3-dicarboxylate (IV)	300—305	290	Et	I

TABLE 9. *Miscellaneous.*

56	*bicyclo*[2 : 2 : 1]-Hept-5-en-2-one (XX)	295	315	Et	*
57	Anhydrodihydrostrophanthidin	303	25	Et	V
58	Dianhydrodihydrostrophanthidin	303	125	Et	V
59	*tert.*-Butyl 2-methyl*cyclo*hex-2-enyl ketone	290 [c]	45	Et	W
60	*cyclo*Hepta-3 : 5-dienone	290	560	Et	X
61	Santonide	300	1000	Et	19
62	Parasantonide (XXII; X = O)	300	1170	Et	19
63	Bromo-lactone ester (II; R = Me)	296	47	Et	I
64	Acetone	279	16·5	CH	I
		279	15·5	CHe	I

repulsion between axial methyl groups in the cholestenones (Nos. 39 and 40) may eliminate interaction in these cases.

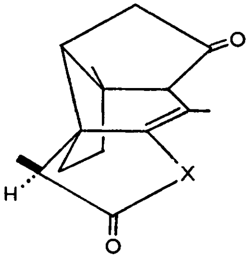
The electronic factor appears to be such that, in ketones with the same mutual orientation of the olefinic and the carbonyl group, electron release to the olefinic double bond increases the extinction coefficient. Thus the *bicyclo*[2 : 2 : 2]octenones with a tetrasubstituted double bond (Nos. 47 and 48) show much more interaction than those with a disubstituted double bond (Nos. 44—46). That some interaction occurs even in the latter ketones is shown by the fall in extinction coefficient brought about by conversion of the adduct (I) (No. 44) into the bromo-lactone (II; R = Me) (No. 63). In amidone hydrochloride (XXI; R = H) and its two analogues (XXI; R = Me and OMe) the *para*-substituent in the phenyl group would be expected to affect only slightly the conformation of the molecule in solution, so that variation in the intensity of the carbonyl band must be mainly due to differences in electronic distribution. There is a singificant increase in extinction coefficient in the series (XXI; R = H, Me, OMe) (Nos. 19, 21, and 22).*

The epimeric santonides (Nos. 61 and 62) remain the outstanding examples of this kind of spectroscopic interaction. The structure of parasantonide has been revealed as (XXII; X = O) through the extraordinary insight of Woodward,[16] who, with Kovach, pointed out that the unusual optical properties of the santonides must be associated with the particular relation of the enol lactone to the carbonyl group. Examination of a model of parasantonide (XXII; X = O) does indeed show that the electronic and steric factors are exceptionally favourable to the sort of interaction now under discussion.

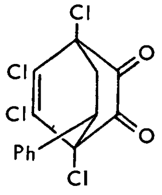
Substitution of electron-attracting and conjugating substituents on the double bond of *bicyclo*[2 : 2 : 2]octenone also causes an increase in ε (Nos. 53—55). The nature and configuration of substituents on the bridge have some influence on the intensity, but not on the wavelength, of the carbonyl band (Nos. 47—52).

The absorption of acetone (No. 64) in *cyclo*hexene is almost the same as in *cyclo*hexane, no doubt because of the improbability of the sufficiently close approach of a molecule of acetone to one of *cyclo*hexene in the necessary arrangements for interaction.

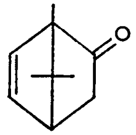
There are two alternative assignments of the transition responsible for most of the increase in intensity of the 290 mμ band in the ketones showing strong interaction, which would be consistent with the stereospecificity of the interaction : the absorption might be mainly from charge transfer[17] across space from the olefinic double bond to the carbonyl group, or it might be due to the normal $n \longrightarrow \pi$ transition of the isolated carbonyl group,[18]



(XXII)



(XXIII)



(XXIV)

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* Some contribution to the absorption of the carbonyl band of the ether (XXI; R = OMe) (No. 22) comes from the end-absorption of the *p*-methoxyphenyl chromophore. A very approximate correction for the overlapping of the two bands, by subtraction of the absorption of methanolic *p*-methoxytoluene at 291 mμ from the maximum absorption of the compound (XXI; R = OMe), gives an estimate of ε = 1150 for the contribution of the carbonyl band.

[16] Woodward and Kovach, *J. Amer. Chem. Soc.*, 1950, **72**, 1009; Woodward and Yates, *Chem. and Ind.*, 1954, 1391.

[17] Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811 and previous papers; Nagakura and Tanaka, *J. Chem. Phys.*, 1954, **22**, 236; Nagakura, *ibid.*, 1955, **23**, 1441; see also Simonetta and Winstein, *J. Amer. Chem. Soc.*, 1954, **76**, 18.

[18] McMurry, *J. Chem. Phys.*, 1941, **9**, 231.

influenced by the adjacent π-electrons (or, of course, a combination of both transitions of equal energy). The insensitivity of the wavelength of the maximum to substitution on the double bond tells against the first alternative, and the known sensitivity of $n \longrightarrow \pi$ transitions to polar environments [19] inclines us to accept the second.

TABLE 10.

Compound	$[\alpha]_D$	Solvent	Ref.
3-Phenylbutan-2-one	+918°	T	E
2-Phenyl*cyclo*pentanone	+4440	T	E
Dehydrocamphor (XXIV)	−735	Et	Y
Santonide	+693	Et	Z
	+754	Cl	Z
Parasantonide (XXII; X = O)	+892	Cl	Z
Parasantonide imide (XXII; X = NH)	+1135	Et	α
Parasantonide acetimide (XXII; X = NAc)	+697	Et	α
Parasantonide oximide (XXII; X = N·OH)	+999	Et	β

The maxima of phenylacetone (No. 5) and of 1-phenylbutan-2-one (No. 6), both of which indicate moderate interaction, are shifted to slightly shorter wavelengths by change from *cyclo*hexane to ethanol as solvent. The β-naphthol adduct (No. 52) shows a similar shift in passing from *n*-hexane to ethanol solution. Such a shift is characteristic of $n \longrightarrow \pi$ transitions in general,[20] and of the normal carbonyl band in particular.[21]

In conclusion we draw attention to the high optical activity (and rotatory dispersion) * of most asymmetric ketones that show the intense carbonyl band (Table 10). For parasantonide the same transition is undoubtedly involved in the 300 mμ absorption band in the ultraviolet spectrum and in the optically asymmetric band that has its centre at the same wavelength,[22] and it is suggestive that the value of $[\alpha]_D$ for derivatives of parasantonide (Table 10) seems to follow the electron-releasing capacity of X in formula (XXII).

EXPERIMENTAL

Addition of Maleic Anhydride to 6-*Dichloromethyl*-6-*methyl*cyclo*hexa*-2 : 4-*dien*-1-*one*.—The dienone, made from *o*-cresol according to von Auwers and Hessenland,[23] boiled at 125—130°/20—25 mm. and melted at 32—33°. The absorption spectrum of our sample (in EtOH, $\lambda_{max.}$ 303 mμ, ε 4000) differed widely from that reported by Dauben, Hance, and Hayes [24] ($\lambda_{max.}$ 299 mμ, ε 19,000). The lower figure for ε seems more likely to be correct since it approximates to values found for other *cyclo*hexa-2 : 4-dien-1-ones,[25] which uniformly have $\varepsilon_{max.}$ about 4000—6000.

The dienone (2·88 g.) and maleic anhydride (3·9 g.) were heated under nitrogen at 190—200° for 1 hr. The hard mass that resulted was extracted with boiling, dry ether (50 c.c.), which on cooling deposited 7-*dichloromethyl*-7-*methyl*-8-*oxo*bicyclo[2 : 2 : 2]*oct*-5-*ene*-2 : 3-*dicarboxylic anhydride* (I), m. p. 190—191°, raised to 193—194° by recrystallisation from dry ether containing a trace of acetic anhydride (yield 1·6 g.) (Found: C, 49·5; H, 3·7; Cl, 24·5. $C_{12}H_{10}O_4Cl_2$ requires C, 49·8; H, 3·5; Cl, 24·6%).

When a solution of the anhydride in boiling water was concentrated and cooled, the *diacid* crystallised in high yield (Found: C, 47·2; H, 3·7; Cl, 22·6. $C_{12}H_{12}O_5Cl_2$ requires C, 46·9; H, 3·9; Cl, 23·1%). The *dimethyl ester*, prepared with diazomethane, melted at 102—103° after recrystallisation from methanol (Found: C, 50·3; H, 4·7; Cl, 21·2. $C_{14}H_{16}O_5Cl_2$ requires C, 50·15; H, 4·8; Cl, 21·2%).

7-*Bromo*-5-*dichloromethyl*-8-*hydroxy*-5-*methyl*-6-*oxo*-2 : 3-*dicarboxylic* 2-*Acid* 3—8-*Lactone* (II;

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* Parasantonide has [α] −35,000° at 275 mμ and +32,000 at 321 mμ.[22]

[19] Goodman and Shull, *J. Chem. Phys.*, 1954, **22**, 1138.

[20] McConnell, *ibid.*, 1952, **20**, 700.

[21] Rice, *Proc. Roy. Soc.*, 1914, *A*, **91**, 76; *J. Amer. Chem. Soc.*, 1920, **42**, 727.

[22] Mitchell and Schwarzwald, *J.*, 1939, 889.

[23] Von Auwers and Hessenland, *Ber.*, 1908, **41**, 1805.

[24] Dauben, Hance, and Hayes, *J. Amer. Chem. Soc.*, 1955, **77**, 4609.

[25] Amongst others: Wessely and Sinwell, *Monatsh.*, 1950, **81**, 1055; Wessely and Koltan, *ibid.*, 1953, **84**, 291; especially la Lau, *J.*, 1953, 3217.

R = H).—Saturated bromine water was dropped into a solution of the preceding diacid (0·5 g.) in water (100 c.c.) containing sodium hydrogen carbonate (1·5 g.) until the solution became yellow. After acidification with acetic acid white crystals (0·8 g.) of the *bromo-lactone acid* appeared; they had m. p. 257—260° (decomp.), raised to 262—263° by two recrystallisations from methanol (Found: C, 37·5; H, 2·9; Cl + Br, 39·3. $C_{12}H_{11}O_5Cl_2Br$ requires C, 37·4; H, 2·85; 2Cl + Br, 39·1%).

The *bromo-lactone methyl ester* (II; R = Me), made with diazomethane, crystallised from methanol in needles, m. p. 255—256° (Found: C, 39·3; H, 3·2; Cl + Br, 37·9. $C_{13}H_{13}O_5Cl_2Br$ requires C, 39·0; H, 3·25; 2Cl + Br, 37·75%).

*Addition of Methyl Acetylenedicarboxylate to 6-Dichloromethyl-6-methyl*cyclo*hexa-2 : 4-dien-1-one.*—A mixture of the dienone (1·91 g.) and ester (3·0 g.) was heated under nitrogen at 190° for 1 hr. A solution of the product in hot methanol (20 c.c.) deposited crystals (2·3 g.), m. p. 89—90°, on cooling. Recrystallised twice from methanol the adduct, *dimethyl 7-dichloromethyl-7-methyl-8-oxo*bicyclo*[2 : 2 : 2]octa-2 : 5-diene-2 : 3-dicarboxylate* (III), melted at 95—96° (Found: C, 50·35; H, 4·0; Cl, 21·5. $C_{14}H_{14}O_5Cl_2$ requires C, 50·5; H, 4·2; Cl, 21·3%). Light absorption max. in EtOH: 218 and 298—305 mμ (ε 4090 and 290).

A solution of the adduct (1·0 g.) in ethanol (80 c.c.) containing Adams catalyst (0·15 g.) was shaken under hydrogen. After 1 mol. of hydrogen had been taken up at atmospheric pressure, absorption almost stopped. When the platinum had been removed and the solution concentrated, crystals melting at 80—81° were formed. After recrystallisation from methanol the dihydro-adduct (the bicyclo*oct-2-ene ester*) (IV) melted at 82—83° (Found: C, 50·35; H, 5·1. $C_{14}H_{16}O_5Cl_2$ requires C, 50·15; H, 4·8%), and had ε 5550 at 210 mμ.

Reaction of Maleic Anhydride with Anethole.—A more reproducible and more easily controlled reaction occurred in ethyl acetate solution than in the absence of solvent, as described by Bruckner and Kovács.[9] Anethole (10 g.), maleic anhydride (16·7 g.), dimethylaniline (0·3 c.c.), and ethyl acetate (20 c.c.) were boiled under reflux for 5 hr. Needles (9·1 g.) of the di-adduct (VI), m. p. 241—242°, crystallised from the cooled solution. This product was normally used directly for further transformations but could be recrystallised from acetone, and then melted at 247—249° (Found: C, 62·6; H, 4·6. Calc. for $C_{18}H_{16}O_7$: C, 62·8; H, 4·7%).

The adduct was converted as described by Bruckner and Kovács [9] into: the "A"-trimethyl ester, m. p. 179—180°; "B"-tetramethyl ester (VII; R = Me), m. p. 208—210°; the keto-tetracarboxylic acid (VIII; R = H), m. p. 260—262°; and the keto-ester (VIII; R = Me), m. p. 154—155°.

Pyrolysis of the Keto-Ester.—The keto-ester (VIII; R = Me) (0·50 g.) was heated at 200—210° for 24 hr. in a sublimation tube filled with nitrogen. The crystalline sublimate (91 mg.), melting at 97—99°, recrystallised from methanol, to give dimethyl fumarate, m. p. and mixed m. p. 102—103° (Found: C, 49·9; H, 5·5. Calc. for $C_6H_8O_4$: C, 50·0; H, 5·6%).

The residue in the sublimation tube was extracted with boiling methanol (10 c.c.), leaving an insoluble solid that consisted almost entirely of the unchanged keto-ester (VIII; R = Me). The methanol extract was treated with excess of diazomethane in ether. After evaporation of solvents under reduced pressure the residue was chromatographed on silica gel. Benzene eluted *dimethyl 1 : 2 : 3 : 4-tetrahydro-7-methoxy-3-methylnaphthalene-1 : 2-dicarboxylate* (IX), m. p. 71—72°, unchanged by recrystallisation from ether (Found: C, 66·0; H, 7·1. $C_{16}H_{20}O_5$ requires C, 65·7; H, 6·9%). Light absorption: $\lambda_{max.}$ 282 mμ (ε 2550).

Preparation of Dimethyl 7-Methoxy-3-methylnaphthalene-1 : 2-dicarboxylate.—(*a*) A mixture of sulphur (0·35 g.) and the adduct (VI) (1·0 g.) was heated for 15 min. at 230—235°, cooled, and extracted with boiling ethyl acetate. Yellow needles of the aromatic anhydride [9] separated from the cooled solution and melted at 215—217° after sublimation and two recrystallisations. The anhydride was dissolved in boiling methanol, and excess of diazomethane in ether was added to the cooled solution. When most of the solvents had been evaporated the *dimethyl ester* (X) separated, melting at 115—116° after crystallisation from methanol (Found: C, 66·3; H, 5·8. $C_{16}H_{16}O_5$ requires C, 66·7; H, 5·6%).

(*b*) The tetrahydro-compound (IX) (70 mg.) and sulphur (30 mg.) were heated at 230—235° for 15 min. Extraction with hot ethyl acetate and cooling gave needles melting at 115—116°, even after having been mixed with the naphthalene (X) made by method (*a*). The ultraviolet absorption curves of the two samples were identical: $\lambda_{max.}$ 270—274 and 348—350 mμ (ε 5500 and 2600).

Addition of Maleic Anhydride to β-Naphthol.—β-Naphthol (10 g.) and maleic anhydride (6·8 g.) were heated at 210—220° (gentle boiling) for ¾ hr. The crystals (8·6 g.) that separated from a slowly cooled solution of the product in the minimum quantity of hot ethyl acetate (about 50 c.c.) melted at 155—165°, after sintering at 145°. Three recrystallisations from ethyl acetate gave pure 1 : 2 : 3 : 4-tetrahydro-9-oxo-1 : 4-ethanonaphthalene-2 : 3-*exo*dicarboxylic anhydride (XI) (1·5 g.), m. p. 193—194°.

Fractional crystallisation from the mother-liquors from ethyl acetate yielded the *endo*-anhydride (XII) (0·4 g.), m. p. 192—193°. A mixture of the two stereoisomers melted at 152—155°.

Crystallisation of the separate anhydrides from water led to the two dicarboxylic acids, converted into the two dimethyl esters by diazomethane in methanol–ether : *exo*-ester, m. p. 96—97° (from methanol) ; *endo*-ester, m. p. 112—113° (from methanol). Of several methods of separating the *endo*- and *exo*-isomers that were tried much the best took advantage of the greater solubility of the *endo*- than of the *exo*-diacid in ether.

Reduction of the exo-*Diester.*—When sodium borohydride (0·5 g.) was gradually added to a solution of the *exo*-diester (0·70 g.) in methanol (10 c.c.), a vigorous reaction took place. After 2 hr. the mixture was diluted with water and extracted with chloroform. The oil (0·51 g.) that remained after evaporation of the chloroform layer crystallised from ethanol (m. p. 118—120°). Recrystallisation from ethanol gave needles of *dimethyl* 1 : 2 : 3 : 4-*tetrahydro*-9-*endo*-*hydroxy*-1 : 4-*ethanonaphthalene*-7 : 8-exo-*dicarboxylate* (XIV), m. p. 128° (Found : C, 66·3; H, 6·2. $C_{16}H_{18}O_5$ requires C, 66·2; H, 6·2%).

Reduction of the endo-*Diester.*—The *endo*-ester (0·75 g.) was treated in the same way as the *exo*-ester, to produce *methyl* 2-endo-*carboxy*-1 : 2 : 3 : 4-*tetrahydro*-9-endo-*hydroxy*-1 : 4-*ethanonaphthalene*-3-endo-*carboxylate* 2→9-*lactone* (XV; R = Me), m. p. 128—129°, depressed to 95—97° when the sample was mixed with the product of reduction of the *exo*-ester (Found : C, 69·75; H, 5·4. $C_{15}H_{14}O_4$ requires C, 69·75; H, 5·5%).

Reduction of the endo-*Diacid.*—Potassium borohydride (2·0 g.) was gradually added to a solution of the *endo*-diacid (1·0 g.) in aqueous methanol. Two hours later the resulting solution was just acidified with acetic acid. After removal of the solid that separated the filtrate was heated with a few drops of concentrated hydrochloric acid. Needle-shaped crystals (0·3 g.) appeared in the solution as it cooled. Recrystallised from aqueous methanol, the *lactone*-3-*acid* (XV; R = H) melted at 198—200° (Found : C, 68·9; H, 5·0. $C_{14}H_{12}O_4$ requires C, 68·85; H, 4·9%).

Diazomethane in ether–methanol converted this lactone-acid into a lactone-ester, melting at 128° after recrystallisation from methanol, that did not depress the m. p. of the lactone-ester got by reduction of the *endo*-diester with sodium borohydride.

bicyclo[1 : 2 : 2]Hept-6-en-4-one, prepared in Professor N. J. Toivonen's laboratory,[26] was purified through the semicarbazone, m. p. 207—208°, then distilled in nitrogen, and finally purified by fractional fusion under nitrogen. It had m. p. 24—25°, b. p. 61·8°/16·5 mm.

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[26] Toivonen and Kaila, *Suomen Kem.*, 1955, **28**, *B*, 91.