786. *Researches on Acetylenic Compounds.   Part LII.*   The Prepar-
ation and Anomalous Absorption Spectra of Some* bicyclo[2 : 2 : 1]-
Heptane Derivatives.†

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Diels–Alder reactions between *cyclo*pentadiene and buta-2 : 3-dienoic
and but-2-ynoic acid give unsaturated *bicyclo*heptane derivatives which
show some unexpected spectroscopic properties. The structures of the
products have been established, and the effects of molecular simplification
upon these optical anomalies have been investigated.

THE abnormal ultraviolet absorption spectra of 2 : 5-dihydro-aceto- and -butyro-phenones
(maxima at unexpectedly long wavelengths and of reduced intensities), discovered by
Bowden and Jones,[1] have initiated discussions of the absorption spectra of *cyclo*hexa-1 : 4-
diene derivatives generally.[2,3,4] Diels–Alder reactions with but-2-ynoic and buta-2 : 3-
dienoic acid have now been studied in order to prepare a range of crystalline adducts in
which these effects could be further illustrated and elucidated.

Buta-2 : 3-dienoic acid combined with butadiene at 60°, but no pure component could
be isolated from the heterogeneous product.   With *cyclo*pentadiene, even at 20°, an adduct
was obtained for which the stereoisomeric structures (I) and (II), and structure (III),
required consideration.   The last was eliminated on spectroscopic grounds, and also by
preparing an authentic specimen of this structure from but-2-ynoic acid by a reaction
which proceeded only at 160°.

Direct application of Alder and Stein's rules [5] requires the formation of an adduct of
structure (I), but formation of the isomer (II) either directly or by epimerisation of isomer

1 Bowden and Jones, *J.*, 1946, 52.
2 Braude, Jones, Sondheimer, and Toogood, *J.*, 1949, 607.
3 Bartlett and Lewis, *J. Amer. Chem. Soc.*, 1950, **72**, 1005.
4 Cram and Steinberg, *ibid.*, 1951, **73**, 5691.
5 Alder and Stein, *Annalen*, 1934, **514**, 1; *Angew. Chem.*, 1937, **50**, 510.

(I) during the reaction is not entirely precluded. Hydrogenation of the adduct gave a liquid mixture of tetrahydro-derivatives from which one crystalline isomer was isolated in low (7%) yield, although the infrared spectra of the total hydrogenation product and of
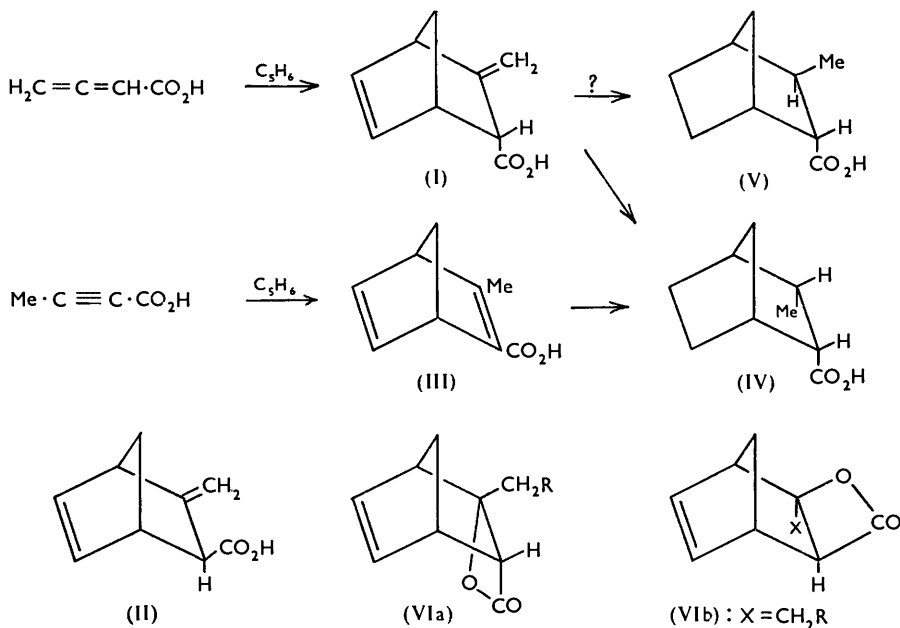
the solid, as solutions, were virtually identical. (Since *bicyclo*heptane derivatives show extraordinarily large melting-point depression coefficients, the low yield of crystallisable material does not imply that very large quantities of other compounds were present.) Alder and his collaborators [6] have prepared all four stereoisomeric 2-methyl*bicyclo*[2 : 2 : 1]-heptane-3-carboxylic acids, and our specimen proved to be identical with that formulated as (IV). Thus the buta-2 : 3-dienoic acid adduct must have structure (I), and, as would be expected, the acid (IV) predominates over the higher-melting isomer (V) in the hydrogenation product. Hydrogenation of acid (III) gave the same crystalline tetrahydro-derivative in 40% yield, a result which confirms the configuration (IV) assigned [6] to it.

Treatment of acid (I) with bromine in sodium hydrogen carbonate solution gave a bromo-lactone, while the corresponding simple lactone was obtained with 50% sulphuric acid. These showed carbonyl bands in the infrared region at 1790 and 1780 cm.$^{-1}$ respectively, which eliminates the structures (VI) expected on Markownikow addition to the exocylic methylene group; indeed, provided that careful intensity measurements were made (see below), these infrared spectra also indicated that the latter grouping was still present in the molecule and that the endocyclic double bond was not. Ozonolysis gave about 20% yields of formaldehyde from each lactone, which confirms this conclusion. Upon the simplest postulates this would in turn prove the structures (VII; R = Br or H) for the lactones and (I) for the original adduct; but, if possible Wagner–Meerwein rearrangements are admitted,[7] lactones (VII) and (VIII) (identical when R = H) might be obtained similarly from an adduct of structure (II).

The effects of alkalis on the acids (I) and (III) were next examined in the hope of equilibrating acids (I—III). While acid (I) was stable to alkali, the characteristic ultraviolet absorption maxima of the isomer (III) were gradually lost in 9N-potassium hydroxide at 118°, and a 30% yield of the acid (I) was obtained. This isomerisation, to a product in which formal conjugation is destroyed and hyperconjugation is diminished, is a remarkable

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[6] We are indebted to Professor K. Alder for kindly communicating to us his unpublished observations.

[7] See Berson and Swidler, *J. Amer. Chem. Soc.*, 1954, **76**, 4060, for a summary.

example of the predominance of Baeyer strain in such systems.[8] While the results are not entirely conclusive, it appears probable that in these experiments equilibrium between acids (I) and (II) was established, and that (II) was the less stable isomer and so was not formed in quantity. Although in saturated *bicyclo*heptane derivatives the *endo-* is normally less stable than the *exo-*form, introduction of an ethylenic linkage reduces steric crowding in the former and might also stabilise it through non-classical electronic interaction.

(I) →

(R = H or Br)

(VII)　　　　　　(VIII)
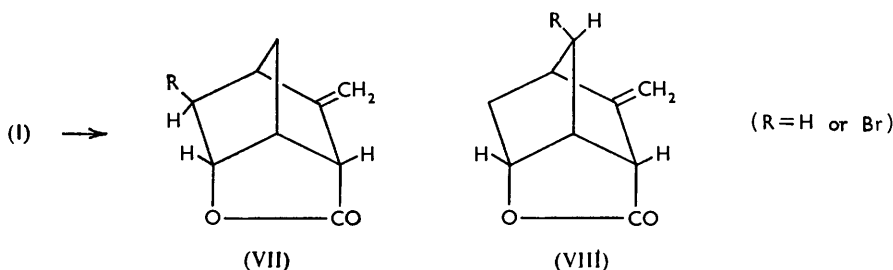
The adduct (I) could be esterified, and recovered by alkaline hydrolysis of the ester; the ester was also obtained directly from ethyl buta-2 : 3-dienoate and *cyclo*pentadiene, though in lower yield than when the free acid was used.[9] The ester of the adduct (III) rapidly became a glass when exposed to air at room temperature, whereas the ester of the isomer (I) is stable.

Ultraviolet absorption spectra reported below for the acids (I) and (III) were unexpected, and a number of compounds were therefore prepared in which the various structural peculiarities were introduced separately. Thus hydrogenation of (III) over platinum resulted in a diminution in uptake-rate after the absorption of 1 mol., and the conjugated acid (IX; R = Me), whose structure followed from its normal and unambiguous ultraviolet and infrared spectra, was readily isolated when uptake was interrupted. Treatment of *cyclo*pentadiene with propiolic acid at 0° as described by Alder *et al.*[10] gave adduct (X)—a striking contrast with the analogous but much slower reaction with but-2-ynoic acid. Unfortunately, semihydrogenation of (X) did not prove possible, even when palladium was used.

The ketone (XI) was prepared by heating but-3-yn-2-one with *cyclo*pentadiene as described by Petrov and Sopov.[11] It proved to be even more unstable than the esters of (III) and (X), and could not be regenerated from its semicarbazone. (It is therefore the only substance among the group discussed below which was not either crystalline itself or obtained by one very simple and mild reaction from a crystalline precursor.)

*cyclo*Hexa-1 : 3-diene did not react with but-2-ynoic acid even at 100°, but with propiolic acid it gave a 30% yield of the adduct (XII) at *ca.* 70°.

Butadiene reacted with but-2-ynoic and propiolic acid in benzene at 80° and 55° respectively, giving the adducts (XIII; R = Me) (4%) and (XIII; R = H) (8%); at 170° with propiolic acid the only product (34%) was benzoic acid. The dihydrobenzoic acid (XIII; R = H) was reported by Alder and Backendorf [12] as a product of the reaction between butadiene and acetylenedicarboxylic acid, but its structure was not then proved rigorously. The spectrographic results below clearly differentiate acids (XIII) from their aromatic analogues and, though abnormal, are consistent with these structures in view of the spectrum of the acid (III); they are quite inconsistent with the fully conjugated alternatives, which would imply absorption maxima near 3000 Å. On hydrogenation, acid (XIII; R = H) smoothly gave *cyclo*hexanecarboxylic acid.

Hydrogenation of acid (XIII; R = Me) over palladium gave the acid (XIV; R = Me).[13]

[8] Cf. Brown, Brewster, and Shechter, *J. Amer. Chem. Soc.*, 1954, **76**, 467.
[9] Cf. Holmes, *Org. Reactions*, 1948, **4**, 71.
[10] Alder and Stein, *Annalen*, 1936, **525**, 183.
[11] Petrov and Sopov, *J. Gen. Chem. U.S.S.R.*, 1953, **23**, 1085 (*Zhur. obshchei Khim.*, 1953, **23**, 1034).
[12] Alder and Backendorf, *Ber.*, 1938, **71**, 2199.
[13] Kay and Perkin, *J.*, 1905, **87**, 1066.

Penta-2 : 3-dienedioic acid (previously termed " glutinic acid " and formulated as pent-2-ynedioic acid) [14] reacted with *cyclo*pentadiene at 35°, giving a normal adduct (XVIII), the properties and conditions of formation of which confirm the revised structure [14] of the parent acid.

Structures (IX), (X), (XI), (XII), (XIII), (XIV), (XV), (XVII), (XVI), (XVIII), (XIX), (XX).
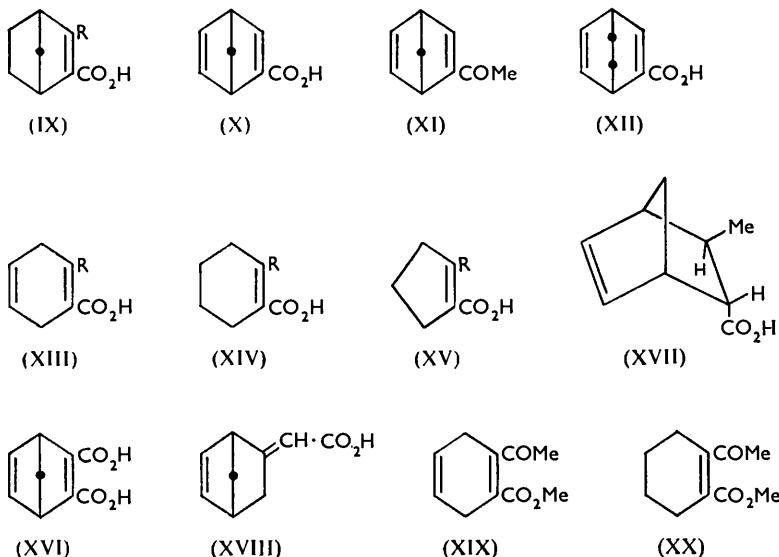
Ultraviolet Absorption Spectra.—The ultraviolet spectra, observed under comparable conditions, are shown in Figs. 1 and 2 and in the Table. Our data for acids (XIV; R = H) and (XV; R = Me) agree well with the results of Ungnade and Ortega [15] and Eglinton

Ultraviolet absorption spectra.

	R = H		R = Me		
	$\lambda_{max.}$ (Å)	$10^{-3}\varepsilon$	λ_{max} (Å)	$10^{-3}\varepsilon$	Δ_{Me} (Å)
(a) Acids.					
(XIV)	2170	10·3	2250	9·2	80
(XV)	2220	11·5	2320	11·1	100
(IX)	—	—	2340	8·1	—
(XIII)	(at 2015 Å, ε 6000)		(at 2045 Å, ε 6000)		~30
	2360	2·1	2360	2·55	0
(X, III)	(at 2000 Å, ε 11,000)		2030	8·7	>30
	2290	3·7	2310	3·8	20
	~2650	~1·5	2670	2·35	~0
(XII)	(at 2020 Å, ε 7800)				
	2240	7·8			
(b) Ketones.					
1-Acetyl*cyclo*hexene and its 2-Me deriv.[2]	2320	12·5	2490	6·9	170
1-Acetyl*cyclo*pentene and its 2-Me deriv.[20]	2390	13	2530	10	140
2 : 5-Dihydroacetophenone and its 6-Me deriv....	2450	4	2450	5	0
(XI)	(at 2000 Å, ε 6750)				
	2400	5·3			
	2760	1·75			
(c) Related compounds.					
(XVI)	(at 2000 Å, ε 13,000)				
	2470	5·15			
(XVIII)	2190	12			
(XIX)	(at 2150 Å, ε 3000)				
	2450	2·0			
(XX)	2200	6·0			

[14] Jons, Mansfield, and Whiting, *J.*, 1954, 3208.
[15] Ungnade and Ortega, *J. Amer. Chem. Soc.*, 1951, **73**, 1564.

and Whiting,[16] respectively. The position of $\lambda_{max.}$ now reported for *cyclo*pent-1-ene-carboxylic acid (XV; R = H), however, differs significantly from that reported earlier by Braude and Forbes.[17] Professor E. A. Braude, who very kindly provided the specimen used here, has also redetermined the absorption spectrum, and reports $\lambda_{max.}$ 2215 Å (ε 11,200), in excellent agreement with our results. For acid (XIV; R = Me), our data agree poorly with those reported, for a specimen of undisclosed physical constants and method of preparation, by Ungenade and Ortega,[15] but in view of the simplicity of our preparative method, and the good agreement with the other constants in the literature, we believe that our results are authentic.

FIG. 1. *Ultraviolet absorption of acids (in 95% ethanol) with β-hydrogen atoms (in formulæ XIII, XIV, and XV, R = H).*
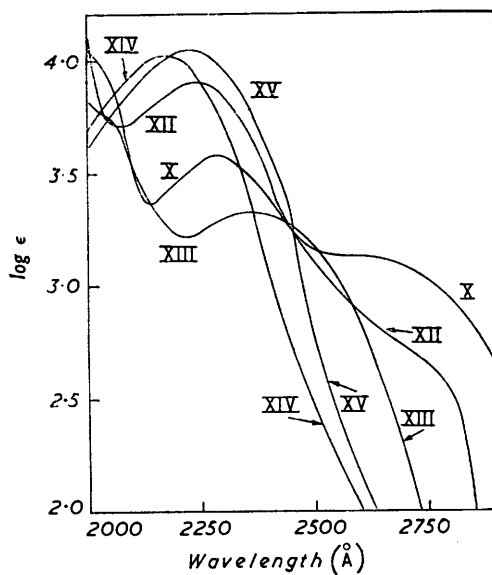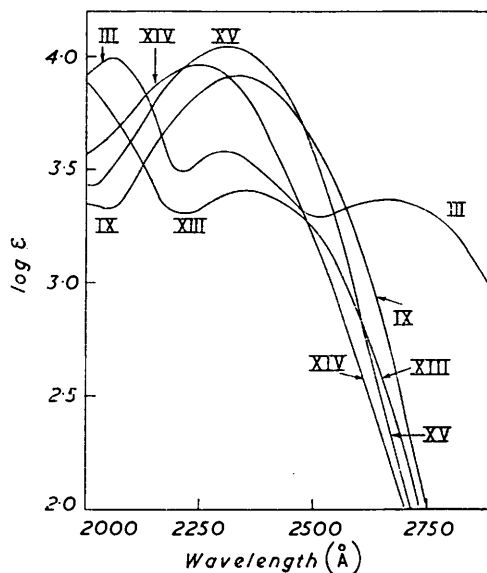
FIG. 2. *Ultraviolet absorption spectra of acids (in 95% ethanol) with β-methyl substituents (in formulæ IX, XIII, XIV, and XV, R = Me).*

The spectra of the monoethylenic reference compounds (XIV, XV, and IX; R = Me) illustrate neatly the effects of Baeyer strain. In a cyclic αβ-ethylenic acid a reduction in the angle α, consequent upon the closing of a ring and the introduction of strain, will increase the importance of canonical form *B* relatively to *A* (see Brown, Brewster, and Shechter[18]). In such a weakly polarised system the latter is of course the more important,
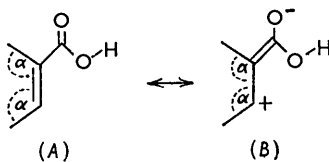
and the change is towards equality; it will therefore stabilise the excited state preferentially, and displace the absorption maximum bathochromically [19]—hence the observed ascending order for $\lambda_{max.}$ values. (A somewhat similar discussion of the spectra of αβ-ethylenic ketones has recently appeared.[20]) The values of $\Delta\lambda_{max.}$ for β-substitution of a methyl

[16] Eglinton and Whiting, *J.*, 1953, 3025.
[17] Braude and Forbes, *J.*, 1951, 1775.
[18] Brown, Brewster, and Shechter, *J. Amer. Chem. Soc.*, 1954, **76**, 467.
[19] Brooker, Keyes, Sprague, Van Dyke, Van Lare, Van Zandt, White, Cressman, and Dent, *ibid.*, 1951, **73**, 5332.
[20] Schubert and Sweeney, *ibid.*, 1955, **77**, 2297.

group are $+80$ and $+100$ Å in the *cyclo*hexene and *cyclo*pentene derivatives, respectively. The corresponding acyclic compounds, 3-methylbut-2-enoic (tiglic) and 2 : 3-dimethylbut-2-enoic acid, have $\lambda_{max.}$ 2125 and 2210 Å, respectively,[21] giving $\Delta\lambda_{max.}$ 85 Å.

Introduction of a second, unconjugated ethylenic linkage into structures of type (XIV), giving (XIII), profoundly changes the spectrum. Both *cyclo*hexa-1 : 4-diene derivatives (XIII) show bands at 2360 Å; but in view of their low intensities and the absence of the usual bathochromic effect of methyl substitution, there seems little reason to consider these bands as representing the normal electronic transitions of $\alpha\beta$-ethylenic acids, which occur at 2170 and 2250 Å in the reference *cyclo*hexenes. On the contrary, the 2170 and 2250 Å bands may more profitably be compared with the bands with maxima just below 2000 Å for (XIII), which show intensities of the right order of magnitude and some indication of a bathochromic shift on substitution of methyl for hydrogen. The two *bicyclo*heptadiene derivatives, (III) and (X), show more complex spectra. Here the case for assigning the short-wavelength bands to the normal electronic transition is stronger; and *two* distinct abnormal bands are observed, while the *bicyclo*octane derivative (XII) is intermediate between (X) and (XIII; R = H), as might be expected. Cristol and Snell[22] observed a remarkable photochemical reaction, in which the acid (XVI), which has an absorption spectrum similar to those of the monocarboxylic acids, is converted into a *tetracyclo*heptane derivative. In all probability one of the medium-intensity bands, at least, of the *bicyclo*heptadiene derivatives involves excitation to an electronic state in
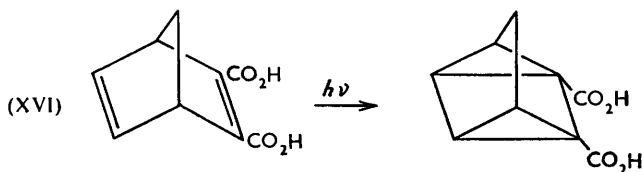
which the electrons of the non-conjugated bond are implicated.[3,4] From this the molecule passed into a *tetracyclo*heptane structure. It is possible that the simple *cyclo*hexa-1 : 4-dienes undergo a similar reaction, related to the abnormal bands at *ca.* 2400 Å. The ketone (XI) bears the same relationship to 2 : 5-dihydroacetophenone that acid (X) bears to the *cyclo*hexadiene-acid (XIII; R = H), and their ultraviolet spectra show an analogous relationship. The absence of a bathochromic shift on introduction of a β-methyl group into 2 : 5-dihydroacetophenone[2] parallels the observations above. In these ketones, also, the medium-intensity bands should therefore be ascribed[4] to abnormal transitions directly involving the non-conjugated bond, rather than to a displacement of the normal $\alpha\beta$-ethylenic ketone band through hyperconjugation; almost certainly examination of the 2000—2200 Å region would reveal a second absorption band in these cases, as in that of (XI).

The adduct (I) showed end-absorption at 2000—2200 Å appreciably more intense (ε 8000 at 2000 Å) than would be expected from the chromophores present, and even the adduct (XVII) prepared from *cyclo*pentadiene and crotonic acid absorbed much more strongly (ε_{2000} 5100) than *cyclo*hexene (ε_{2000} *ca.* 1000). Some non-classical interaction between adjacent unsaturated systems in a rigid molecule is probably general; complete saturation of the rings as in the dihydro-derivative of the lactone (VII; R = H), obtained by acid cyclisation of (XVII), naturally resulted in virtual transparency even near 2000 Å.
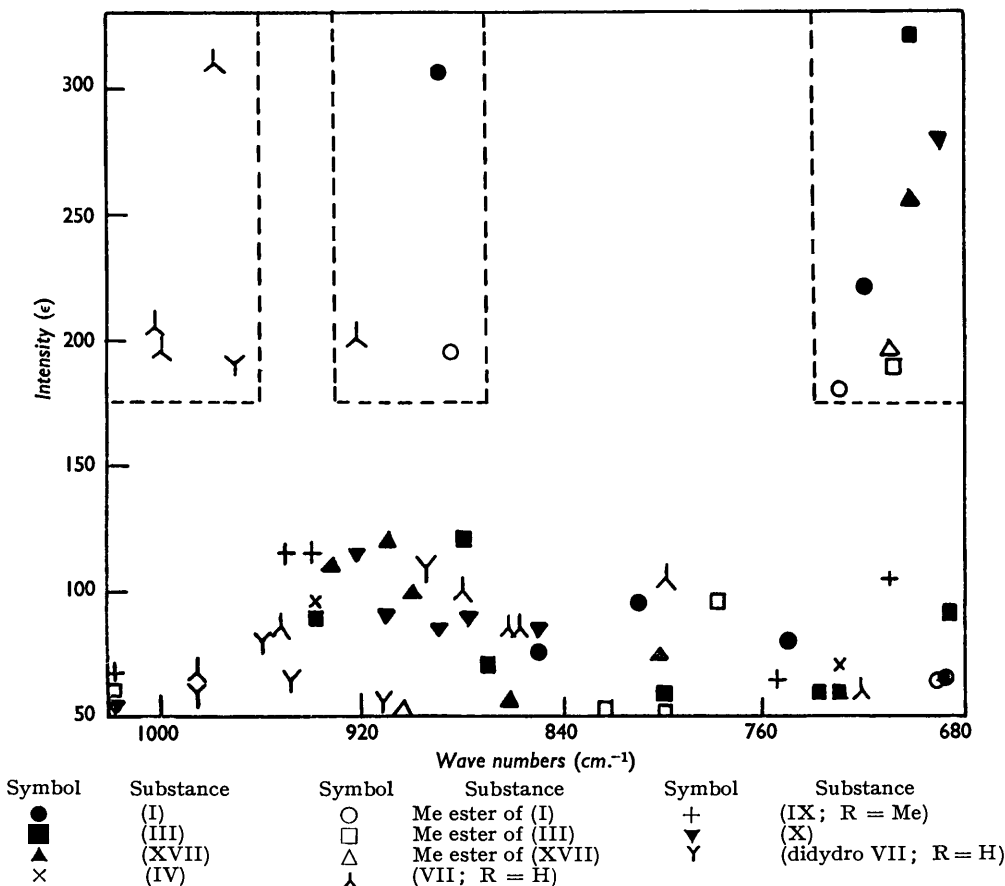
Infrared Absorption Spectra.—These also presented several points of interest. The di- and tri-cyclic compounds all have unusually rigid molecules, and this presumably explains the exceptional number of sharp, intense bands observed in the " fingerprint " region, *i.e.*, 660—1200 cm.$^{-1}$. In such molecules, any " skeletal " (*i.e.*, C–C deformation or stretching) vibration must be communicated to the polar groups, and will therefore cause a considerable change in dipole moment and thus correspond to an intense infrared

[21] Braude and Evans, *J.*, 1955, 3331.
[22] Cristol and Snell, *J. Amer. Chem. Soc.*, 1954, **76**, 5000.

band.[23] Similarly, any change in the intramolecular strains (*e.g.*, as a result of hydrogenating an ethylenic linkage) would be expected to affect the frequency of these skeletal modes. Thus, whereas it is usually possible to pick out olefinic C–H out-of-plane deformation bands by inspection, because they are so much more intense than the various C–C deformation bands, etc., and because they disappear on hydrogenation, this was impossible with the spectra of the compounds discussed above, even where those of the corresponding dihydro-derivatives were available for comparison. When, however, "apparent" molar extinction coefficients (*i.e.*, neglecting slit-width and false energy corrections, but allowing for base-line errors) were calculated, and the results plotted

FIG. 3. *Infrared maxima of* bicyclo*heptane derivatives* (*in* CS$_2$).

Symbol	Substance	Symbol	Substance	Symbol	Substance
●	(I)	○	Me ester of (I)	+	(IX; R = Me)
■	(III)	□	Me ester of (III)	▼	(X)
▲	(XVII)	△	Me ester of (XVII)	Υ	(didydro VII; R = H)
×	(IV)	⅄	(VII; R = H)		

(Fig. 3), it was at once possible to identify these bands by their appreciably (but not overwhelmingly) greater intensities. These maxima fall within the broken lines in Fig. 3.

All compounds believed on chemical grounds to possess the groupings *cis* HC═CH and/or H$_2$C═C< showed *one* band (for each) with ε >180 in the regions (680—740 and 870—930 cm.$^{-1}$, respectively) normal for these modes. Except for the tricyclic lactones (see below), none of the bands attributable to skeletal vibrations had ε >120. Thus, despite the approximate nature of the methods used for measuring intensities, the results (uncertain to perhaps ε ±20, with most of the sources of error acting similarly on all bands in a given region) were of real value. The overtone ethylenic C–H out-of-plane deformation bands at *ca.* 1790 cm.$^{-1}$ were, of course, superimposed in the spectra of the lactones (VII; R = H

[23] R. N. Jones, Nolin, and Roberts, *J. Amer. Chem. Soc.*, 1955, **77**, 6331.

and Br) on the intense carbonyl bands, and the $\diagdown$C=C$\diagdown$ stretching modes were barely distinguishable at *ca.* 1680 cm.$^{-1}$, an abnormal frequency not unexpected in view of the strained environment of the methylene group. The region below 1000 cm.$^{-1}$ was thus the only one available for structural confirmation of these lactones.

In the unbridged *cyclo*hexa-1 : 4-diene derivatives (XIII; R = Me and H), and the methyl ester of the latter, the *cis*-CH=CH– out-of-plane deformation mode was probably represented by the intense absorption below 670 cm.$^{-1}$ at the transmission limit of the available sodium chloride prism.

The tricyclic lactones (VII; R = H and Br) and some related tricyclic lactones [24] showed intense and sometimes complex absorption at 970—1000 cm.$^{-1}$. This might be confused with an ethylenic out-of-plane deformation band due to the grouping *trans*-CH=CH–, but not with analogous bands for *cis*-CH=CH– or $\diagdown$C=CH$_2$. In the compounds possessing the grouping H–C=C–CO$_2$R (R = H or Me) an intense band was observed at 750—775 cm.$^{-1}$, near bands in the very simple spectra of tiglic acid and its ethyl ester, which have the same partial structure. This is almost certainly attributable to the C–H out-of-plane deformation process, moved from the normal 800—840 cm.$^{-1}$ region by the effect of the carboxyl grouping.[25]

The C=O stretching bands (dimer) of the unbridged *cyclo*hexa-1 : 4-diene acids (XIII; R = Me and H) were split into well-resolved doublets at 1685 and 1669 cm.$^{-1}$, and 1687 and 1665 cm.$^{-1}$, respectively. In the bridged diene-acids one broad band was observed at *ca.* 1670 cm.$^{-1}$. With these reservations, bands in the 1600—1750 cm.$^{-1}$ region were normal and could be taken as confirming the various structures assigned.

Experimental

Acid fractions were normally isolated *via* saturated potassium hydrogen carbonate solution. Ultraviolet absorption spectra were determined in 95% EtOH by means of a Unicam SP 500 spectrophotometer; infrared spectra with a Perkin-Elmer Model 21 spectrophotometer; and m. p.s on a Kofler block.

3-*Methylene*bicyclo[2 : 2 : 1]*hept-5-ene-2-carboxylic Acid* (I).—A solution of buta-2 : 3-dienoic acid (2·0 g.) and *cyclo*pentadiene (4·3 g.) in ether (10 c.c.) was set aside at room temperature for 12 hr. Isolation of the acidic fraction and crystallisation from pentane gave the *adduct* (I) (3·0 g.), m. p. 69—70° (Found : C, 71·75; H, 6·55. C$_9$H$_{10}$O$_2$ requires C, 72·0; H, 6·7%). The *methyl* ester, prepared with diazomethane, had b. p. 100—105° (bath-temp.)/10 mm., $n_D^{14·5}$ 1·4950 (Found : C, 73·1; H, 7·1. C$_{10}$H$_{12}$O$_2$ requires C, 73·15; H, 7·35%).

Ethyl 3-*Methylene*bicyclo[2 : 2 : 1]*hept-5-ene-2-carboxylate.*—A solution of ethyl buta-2 : 3-dienoate (2·24 g.) and *cyclo*pentadiene (1·32 g.) in ether (5 c.c.) was heated under reflux for 2 hr. Evaporation and distillation of the residue gave recovered ethyl buta-2 : 3-dienoate (1·3 g.) and the *ethyl ester* (0·58 g.), b. p. 105—107°/21 mm., n_D^{18} 1·4832 (Found : C, 73·9; H, 7·85. C$_{11}$H$_{14}$O$_2$ requires C, 74·15; H, 7·9%). Hydrolysis with 10% aqueous potassium hydroxide (2 hr. at 90°) gave a 70% yield of the corresponding acid.

3-*Methylene*-6-*hydroxy*bicyclo[2 : 2 : 1]*heptane-2-carboxylic Lactone* (VII; R = H).—The above acid (I) (350 mg.) was shaken with sulphuric acid (10 c.c., 50%) for 3 hr. at 20°. Isolation of the neutral fraction and crystallisation from pentane gave the very volatile *lactone* (240 mg.), m. p. 49·5—50·5° (Found : C, 72·0; H, 6·7. C$_9$H$_{10}$O$_2$ requires C, 72·0; H, 7·0%). Ozonolysis of 260 mg. in acetic acid (40 c.c.) for 1 hr. gave formaldehyde, identified as its dimedone derivative (120 mg.), m. p. and mixed m. p. 187—190°.

5-*Bromo*-3-*methylene*-6-*hydroxy*bicyclo[2 : 2 : 1]*heptane-2-carboxylic Lactone* (VII; R = Br).— A solution of the acid (I) (200 mg.) in saturated sodium hydrogen carbonate (5 c.c.) was treated with bromine (210 mg.) in carbon tetrachloride (5 c.c.). Evaporation of the organic layer and crystallisation from benzene–light petroleum (b. p. 40—60°) gave the *bromo-lactone* (210 mg.), m. p. 77—78° (Found : 47·0; H, 4·15. C$_9$H$_9$O$_2$Br requires C, 47·2; H, 3·95%). Ozonolysis of 290 mg. as above gave the dimedone derivative (80 mg.) of formaldehyde.

3-*Methyl*bicyclo[2 : 2 : 1]*hepta-2 : 5-diene-2-carboxylic Acid* (III).—But-2-ynoic acid (5·0 g.) and di*cyclo*pentadiene (10·0 g.) were heated under reflux in nitrogen for 2·5 hr. The acid fraction

[24] Henbest and Nicholls, unpublished work.
[25] Freeman, *J. Amer. Chem. Soc.*, 1953, **75**, 1859; Allan, Meakins, and Whiting, *J.*, 1955, 1874.

was crystallised from water, giving the *acid* (III) (2·0 g.), m. p. 92° (Found : C, 72·0; H, 6·7. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%). The *methyl* ester, prepared using diazomethane, had b. p. 55° (bath-temp.)/0·05 mm., n_D^{20} 1·4962 (Found : C, 72·5; H, 7·45. $C_{10}H_{12}O_2$ requires C, 73·15; H, 7·35%).

When this acid (500 mg.) was heated with 9N-potassium hydroxide (50 c.c.) at 118° for 10 min., and the acid fraction was isolated, crystallisation from pentane gave the isomeric acid (I) (170 mg.), m. p. and mixed m. p. 69—70°.

Hydrogenation Experiments.—(a) The acid (I) (2·7 g.), pre-reduced platinic oxide (0·1 g.), and ethanol (30 c.c.) were shaken until absorption ceased (910 c.c. at 20°/752 mm.). Filtration and evaporation gave an oil which was dissolved in pentane and cooled to −70°; the solid was then separated by means of a pipette. After five crystallisations from pentane at −70° the solid obtained (*ca.* 700 mg.) melted constantly at 31—35°. It was dried, pressed on porous porcelain at 20°, and crystallised twice more from pentane, giving 180 mg. of acid (IV), m. p. 51—53°, raised to 54·5—55·5° on admixture with an authentic specimen (m. p. 57—58°).

(b) The acid (III) (1·00 g.) in ethyl acetate (40 c.c.) was shaken with pre-reduced platinic oxide (0·1 g.) in hydrogen, 324 c.c. being absorbed at 24·5°/753 mm. Filtration, evaporation of the solvent, distillation, and crystallisation from pentane at −70° gave the saturated acid (IV) (0·40 g.), m. p. 47—49°, raised to 54° on recrystallisation and undepressed on admixture with an authentic sample (Found : C, 70·3; H, 9·3. Calc. for $C_9H_{14}O_2$: C, 70·1; H, 9·15%).

(c) The acid (III) (500 mg.) in ethyl acetate (40 c.c.) was shaken in hydrogen with pre-reduced platinic oxide (50 mg.) until 84 c.c. had been absorbed at 23°/747 mm., whereafter the rate of uptake decreased. Evaporation, distillation, and crystallisation at −70° gave 3-*methyl*bicyclo-[2 : 2 : 1]*hept-2-ene-2-carboxylic acid* (IX) (130 mg.), m. p. 41—44° (Found : C, 71·05; H, 8·05. $C_9H_{12}O_2$ requires C, 71·0; H, 7·95%).

3-*Carboxymethylene*bicyclo[2 : 2 : 1]*hept-5-ene-2-carboxylic Acid* (XVIII).—*cyclo*Pentadiene (330 mg.) and penta-2 : 3-dienedioic acid (640 mg.) in ether (10 c.c.) were heated under reflux for 2 hr. Evaporation of the solvent and crystallisation from water gave the *adduct* (900 mg., 93%), m. p. 235—236° (Found : C, 61·8; H, 5·3. $C_{10}H_{10}O_4$ requires C, 61·85; H, 5·2%). The *dimethyl ester*, prepared by using diazomethane, had b. p. 95° (bath-temp.)/0·01 mm., n_D^{18} 1·5092 (Found : C, 64·35; H, 6·25. $C_{12}H_{14}O_4$ requires C, 64·85; H, 6·35%).

cyclo*Hexa-1 : 4-diene-1-carboxylic Acid* (XIII; R = H).—A mixture of propiolic acid (5·0 g.), butadiene (10 c.c.), quinol (0·1 g.), and benzene (10 c.c.) was heated in an autoclave to 55° for 15 min., then set aside at 20° for 60 hr. Isolation of the acidic fraction and crystallisation from water gave the acid (XIII; R = H) (0·72 g., 8%), m. p. 122°, strongly depressed on admixture with benzoic acid (Found : C, 67·9; H, 6·6. $C_7H_8O_2$ requires C, 67·75; H, 6·5%). Alder and Backendorf [12] give m. p. 123° for an acid believed to be (XIII; R = H). Catalytic hydrogenation (uptake 2 mols.) gave *cyclo*hexanecarboxylic acid, charactised as its amide, m. p. and mixed m. p. 184°.

2-*Methyl*cyclohexa-1 : 4-diene-1-carboxylic Acid* (XIII; R = Me).— A mixture of but-2-ynoic acid (7·4 g.), butadiene (16 c.c.), quinol (0·1 g.), and benzene (10 c.c.) was heated in an autoclave at 60—100° for 16 hr. Extraction with potassium hydrogen carbonate solution, acidification, and crystallisation of the precipitate from pentane gave the *adduct* (0·5 g., 4%), m. p. 132° (Found : C, 69·8; H, 7·4. $C_8H_{10}O_2$ requires C, 69·55; H, 7·3%). Continuous extraction of the aqueous filtrate with ether gave but-2-ynoic acid (5·2 g.).

2-*Methyl*cyclohex-1-ene-1-carboxylic Acid* (XIV; R = Me).—The above acid (87 mg.) in ethanol (20 c.c.) was shaken in hydrogen in the presence of 2% palladium–calcium carbonate until 16·0 c.c. were absorbed at 18°/750 mm. Filtration, evaporation, and crystallisation from water gave the acid (XIV; R = Me) (43 mg.), m. p. 87°. Kay and Perkin [13] give m. p. 87°.

2-*Acetyl*bicyclo[2 : 2 : 1]*hepta-2 : 5-diene* (XI).—But-3-yn-2-one (2·0 g.) and *cyclo*pentadiene (3·0 g.) were heated under reflux for 4 hr. Distillation gave the *adduct* (XI), b. p. 76° (bath-temp.)/0·1 mm., n_D^{23} 1·5070 (Found : C, 80·5; H, 6·95. $C_9H_{10}O$ requires C, 80·55; H, 7·5%). The lemon-yellow 2 : 4-*dinitrophenylhydrazone*, m. p. 133—134°, was crystallised from aqueous ethanol, and had $\lambda_{max.}$ 3650 Å (ε 20,500) (Found : N, 17·8. $C_{15}H_{14}O_4N_4$ requires N, 17·85%). The *semicarbazone* crystallised from aqueous ethanol, decomposed at 195°, and showed maxima at 2350 and 2840 Å (ε 10,000 and 15,700, respectively) (Found : C, 62·55; H, 6·7. $C_{10}H_{13}ON_3$ requires C, 62·8; H, 6·85%).

Petrov and Sopov [11] give b. p. 92°/20 mm., n_D^{20} 1·5098, for the ketone, in good agreement with the data given above; but for the 2 : 4-dinitrophenylhydrazone and semicarbazone they report m. p. 182·5—183·5° and 166—167°. They were unable to recrystallise the latter; and they noted (and explained) the polymerisation (dimerisation) of the parent ketone.

6 s

bicyclo[2 : 2 : 1]*Octa*-2 : 5-*diene*-2-*carboxylic Acid* (XII).—A mixture of propiolic acid (1·0 g.), *cyclo*hexa-1 : 3-diene (1·5 g.), and dioxan (5 c.c.) was heated under reflux for 12 hr. Isolation of the water-insoluble acidic fraction gave an oil which was extracted with boiling light petroleum (b. p. 60—80°) : the solid which separated was recrystallised from water, giving the *acid* (XII) (0·6 g.), m. p. 78—80° (Found : C, 71·7; H, 6·8. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%).

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