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UNSATURATED MACROCYCLIC CARBONYL BRIDGE COMPOUNDS

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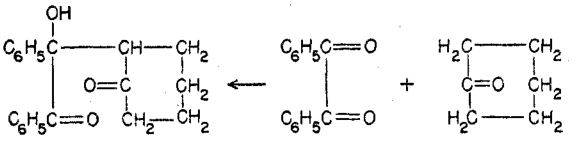
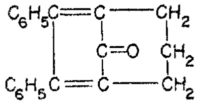
More than twenty years ago (1) the first unsuccessful attempt was made to prepare a carbonyl bridge compound containing a double bond at the bridgehead. A *bis* aldol-like condensation between benzil and cyclohexanone to give I could not be realized, even though benzil does condense twice with suitable open-chain ketones; instead, the 1:1 addition product (II) was obtained. Since that time this reaction has been shown to be general (2).

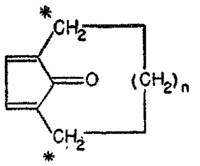


II



I

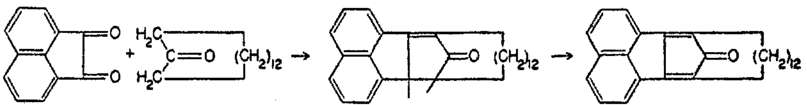
A structure such as I is unlikely because of the strain which would be introduced in its formation by the distortion of bond angles and/or distances; no substances with this unusual arrangement have yet been described. Such a structure also violates Bredt's rule (3–5) in the form in which it is commonly expressed. However, it is now known that the rule, which was based on a study of small ring systems, is not applicable to macrocyclic rings (5, 7, 8). The nonformation of the substance I may be attributed to the inability of the reactive groups to come within bond-forming distance of each other. A sufficiently long chain should be able to connect the atoms in such a way as to obviate that difficulty; from a study of models it was evident that such a bridged ring structure would be free from strain if one ring were sufficiently large. According to Prelog (6), the lower limit for the formation of bicyclic compounds having a double bond at a bridgehead is an 11-membered ring, in which case the sum of the bridge members equals nine (S = 9). Ignoring the spatial requirement of the carbonyl group, the lowest member of the series of cyclanones that should form a structure of type I would be cyclononanone. An additional factor, however, must be considered. It is an inherent property of the ethylenic bond that its substituent atoms must lie approximately in the same plane as the double bond itself. Thus, the C* in III must lie in the plane of the dienone ring. The aliphatic ring then must be sufficiently large to accommodate the oxygen atom without excessive steric hindrance.



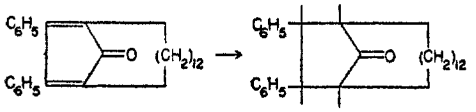
III

Examination of models shows this limit to be in the region of cyclotetradecanone or cyclopentadecanone. This is in agreement with views on the conformation of cyclic ketones—that the oxygen atom lies roughly inside the ring in the range C_{10} to C_{12}. These conclusions were tested by reactions of acenaphthenequinone and benzil with cyclononanone, cyclodecanone, cyclotetradecanone, cyclopentadecanone, and civetone according to a procedure previously described (2). Only in the case of the latter three ketones was condensation to a cyclopentadienone of the general type of I achieved.

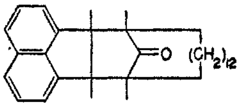
Acenaphthenequinone and cyclopentadecanone in methanol, with potassium hydroxide as a catalyst, at room temperature, give the carbinol, IV. The carbinol is dehydrated by boiling with acetic acid to give V. If the original reaction mixture is refluxed, a molecule of water is lost, and the doubly unsaturated ketone (V) is obtained directly. The red color of this compound is a characteristic property of cyclic cross-conjugated systems (2).



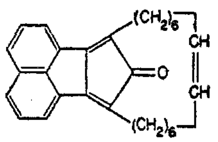
IV V



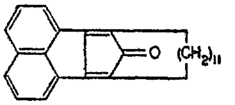
VI VII



VIII



IX

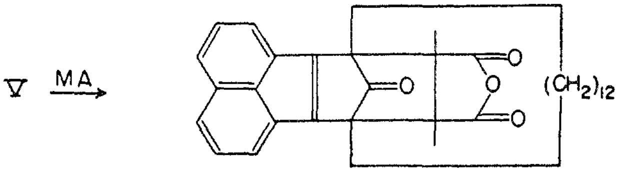


X

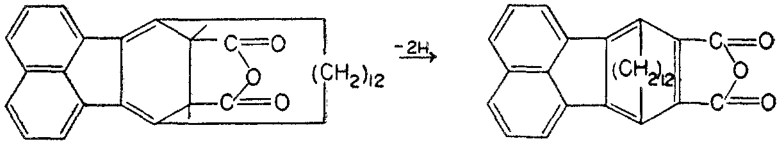
Cyclotetradecanone gives the analog (X) in low yield, while civetone gives the triply unsaturated ketone (IX). Benzil and cyclopentadecanone give VI. The cyclopentadienones, V, IX, and X, crystallize from alcohols in red needles, but when crystallized from ligroin the crystals are light yellow; VI separates from either solvent as red crystals. The red color is similar to that of other cyclopentadienones. Molecular weight determinations in benzene show that they are monomeric. Grignard analysis of these dienones show one addition, indicating the presence of a carbonyl group, which is confirmed by infrared analysis. They do not form dinitrophenylhydrazones, probably because of spatial considerations. Quantitative catalytic reduction of V and VI shows two double bonds in each.

and gives the tetrahydro derivatives, VIII and VII, respectively. In view of these facts, and from a comparison of the ultraviolet absorption spectra, to be discussed later, the structures V, VI, IX, and X are assigned to these products.

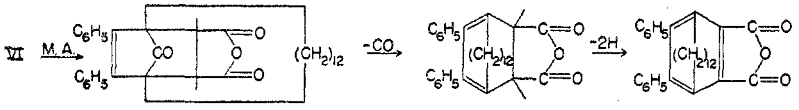
The ketones, V and VI, are essentially coplanar; therefore, the diene system should be quite open to dienophilic reagents. That this is indeed the case is demonstrated by the ready addition of maleic anhydride. The ketone, V, and the anhydride give the addition product, XI, at room temperature; this, in analogy to similarly constituted compounds, is readily decarbonylated to XII, which, in turn, may be dehydrogenated to the aromatic 7,10-endododecanofluoranthene-8,9-dicarboxylic anhydride (XIII). This anhydride was obtained directly from V and acetylenedicarboxylic acid. In an analogous series of reactions, the cyclic ketone, VI, reacts with maleic anhydride to give an endocarbonyl compound, XIV, which is decarbonylated to the anhydride, XV; the latter, in turn, is dehydrogenated to the anhydride of 17,18-dicarboxy-15,16-diphenylbicyclo-[12.2.2]octadeca-14,16,17-triene (XVI).



XI

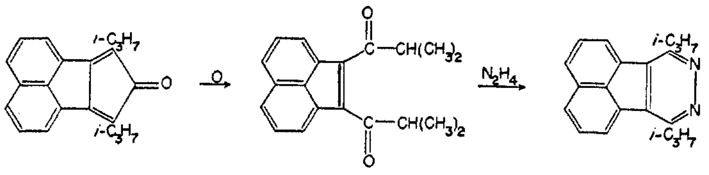


XII XIII



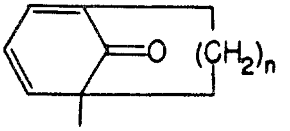
XIV XV XVI

The ultraviolet absorption spectrum of the cyclic ketone, V, changed rapidly on standing. In order to determine the nature of this change, a simpler model compound, XVII, was studied. This substance was irradiated with a 275-watt General Electric sunlamp in isoöctane solution, during which time air was introduced. The initially red solution became bright yellow at the completion of reaction, and yellow crystals separated in practically a quantitative yield. The product was 1,2-diisobutyrylacenaphthylene (XVIII). On Grignard analysis it showed two additions and no active hydrogen, and it readily formed 7,10-diisopropyl-8,9-diazafluoranthene (XIX) upon treatment with hydrazine, a reaction typical of 1,4-diketones.

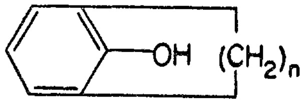


XVII XVIII XIX

In an attempt to effect this oxidation by means other than with molecular oxygen, peracetic acid was employed. The product in this case proved to be an α-pyrone (XX) instead of the unsaturated 1,4-diketone. This result is quite similar to that of Dilthey (9), who oxidized acecyclone with peracetic acid and obtained an α-pyrone. This difference in the products may be attributed to the nature of the oxidizing agent. Oxygen, a symmetrical diradical, adds to the ends of the double bonds, with subsequent elimination of carbon monoxide, whereas peracetic acid first adds to the carbonyl, the intermediate then decomposing *via* an ionic mechanism.

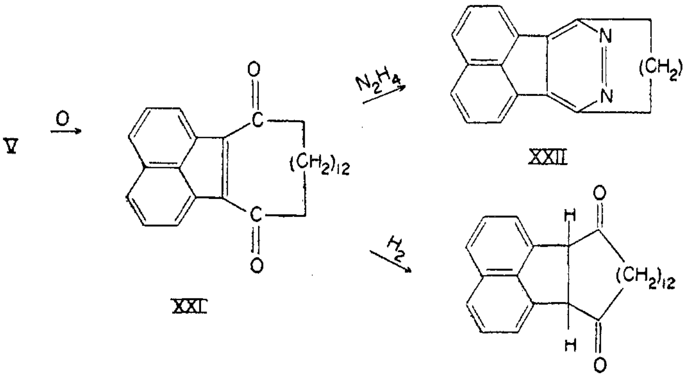


XXV



XXVI

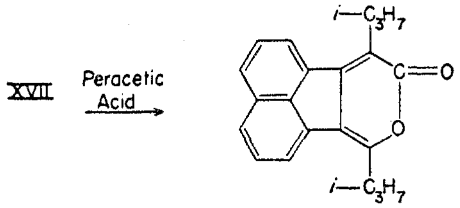
An analogous series of reactions was carried out on V. This latter compound was subjected to aerial oxidation to give XXI, which reacted readily with hydrazine to give XXII. Catalytic reduction of XXI gave the saturated 1,4-diketone (XXIII). In an attempt to produce a furan from the latter, the starting material was recovered.



XXI XXII XXIII

The physical and chemical properties of all these compounds are very similar to those of their open-chain analogs (20), especially in regard to their ultraviolet absorption spectra, which are discussed below. The large polymethylene bridge does not confer special properties on the molecule. However, although the dienones contain a crossed conjugated system, it has not, up to the present, been found possible to bring about a Michael addition reaction (18, 19) by addition of cyanoacetamide, *p*-toluenesulfinic acid, or ethyl malonate using alcoholic solutions and an alkaline catalyst. This may be attributed to the two substituents on the carbon atom in the *beta* position relative to the carbonyl group.

The substances described in this paper constitute a new class of compounds; they have two double bonds at a bridgehead which are not part of an aromatic system, and which, in addition, are conjugated with a carbonyl group. Prelog (6), who investigated the chemistry of the related *meta*-bridged polymethylene benzene derivatives (XXV, XXVI), found that such compounds are possible only with a bridge of at least five methylene groups. Fawcett (5) states that there have been no experimental reports of the ring size required for two bridgehead double bonds which are not part of an aromatic ring.



XX

The geometry of the five-membered ring ketones (III) (see above) is somewhat different from that of the *meta*-bridged benzene compounds, the former requiring longer polymethylene chains. Experimentally, it has been found that when cyclotetradecanone is used ($n = 11$) the yield of product falls to about 5%. This appears to be the smallest-sized ketone which can be used to form a polymethylene bridged cyclopentadienone.

DISCUSSION OF THE ULTRAVIOLET ABSORPTION SPECTRA

Ultraviolet absorption curves of all of the compounds were determined in methanol or isoöctane at a concentration of 1:50,000 except dibenzalacetone which was run at 1:100,000. Table I contains the summarized data.

Figure 1. Compounds IV and 2,5-di-*n*-propyl-3,4-(1,8-naphthylen)-2-cyclopenten-4-ol-1-one are similar, in respect to their conjugated systems, to 1-naphthalacetone (4). However, the three maxima of 1-naphthalacetone (224, 251, 334 mμ) are split and displaced slightly toward longer wavelengths in the cyclic ketones (228, 262, 341 mμ), probably due to the additional α,β-substituents on the double bonds. In the spectra of V and 2,5-di-*n*-hexyl-3,4-(1,8-naphthylen)-cyclopentadienone (10), the 262 mμ bond of IV is shifted to 278 mμ with a large increase in intensity in keeping with the increased conjugation.

Figure 2. Compounds VI and 2,5-diethyl-3,4-diphenylcyclopentadienone (20) (XXVII) differ from V and XVII in that the phenyl groups are not fused, and their effect on the spectrum should be approximately that of an additional double bond (12, 13). A comparison of the spectra of VI and XXVII (see Table I) shows little difference from one another, but when compared with dibenzalacetone, an apparently analogous compound, a striking difference is noted. The long-wavelength band in XXVII has a λ_{max} 295 ($\log \epsilon$ 3.96), and the short-wavelength band has a λ_{max} 255 ($\log \epsilon$ 4.33), whereas the corresponding bands in dibenzalacetone occur at λ_{max} 318 ($\log \epsilon$ 4.49) and λ_{max} 228 ($\log \epsilon$ 42.0). This difference in absorption spectra between dibenzalacetone and XXVII is attributed to the nonplanarity of the phenyl groups in the cyclopentadienones (16, 17).

TABLE I

ULTRAVIOLET ABSORPTION DATA

SUBSTANCE	λ_{max}	Log ϵ	SUBSTANCE	λ_{max}	Log ϵ
IV[a]	228	4.43	Naphthalacetone (11)	224	4.53
	262	4.02		251	4.22
	343	4.09		334	4.09
V[b]	278	4.60	2,5-Diethyl-3,4-diphenylcyclopentadienone[b] (2)	255	4.33
	365	3.87		295	3.96
VI[b]	254	4.38	2,5-Di-*n*-hexyl-3,4-(1,8-naphthylen)-cyclopentadienone[b] (10)	278	4.58
	297	4.00		365	3.87
				278	4.19
VIII[c]	292	3.90		350	3.86
XVIII[a]	238	4.40	Fluoranthene[a] (10)	235	4.6
	270	3.81		288	4.5
	338	4.16		322	3.7
	365	3.94		342	3.8
				358	3.8
XXI[a]	235	4.38			
	270	3.82	Acenaphthene[a]	290	3.73
	338	4.10			
	365	3.96	2,5-Di-*n*-propyl-3,4-(1,8-naphthylen)-2-cyclopenten-4-ol-1-one	228	4.40
XXII[b]	238	4.54		262	4.03
	293	3.6		341	4.04
	320	3.9			
	352	4.7	Dibenzalacetone[b]	228	4.20
	368	4.0		318	4.49
XXIII[b]	290	3.88			

[a] *Solvent:* Methanol, [b] Isoöctane, [c] Dioxane.

Figure 3. The spectra of the monoketone (VIII) and the diketone (XXIII)

are compared with acenaphthene. The similarity of the curves indicates the presence of an acenaphthene residue in both VIII and XXIII. Infrared analysis shows the presence of a carbonyl group. Grignard analysis shows two additions for XXIII and one active hydrogen for VIII, which probably arises from an easily enolizable α-hydrogen. These properties are in agreement with those predicted for the assumed structure. From the mode of formation of VIII and XXIII (*i.e.*, catalytic reduction), it is concluded that the hydrogen atoms of the cyclopentanone ring are in a *cis* configuration to each other.

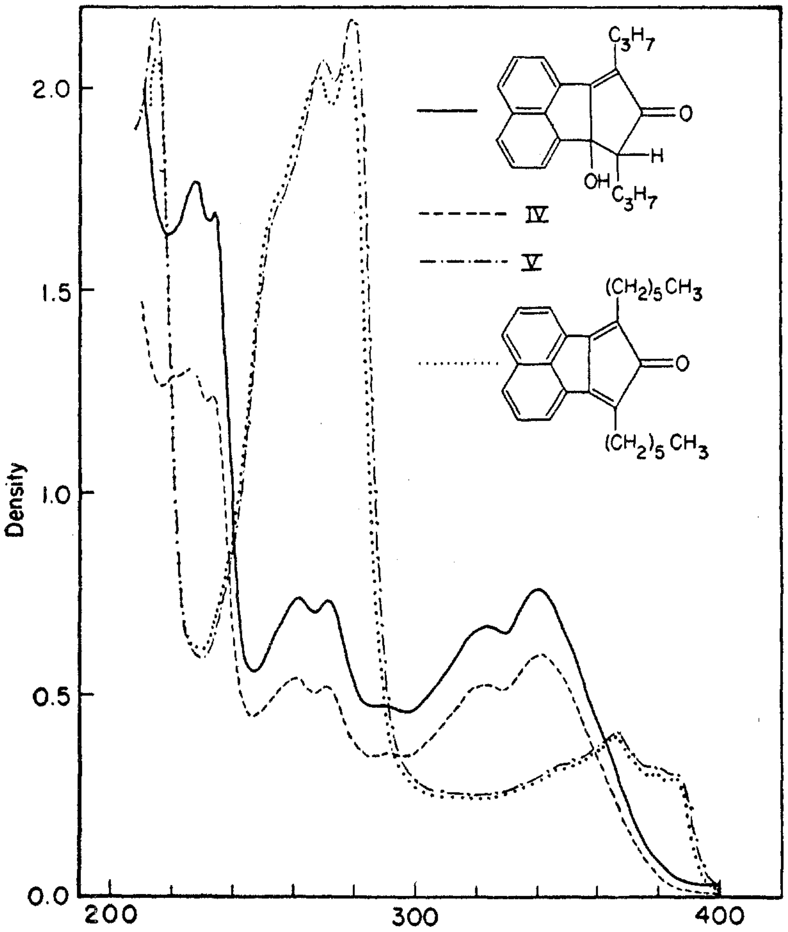


Fig. I

Figure 4. The spectra of the diketones (XVIII and XXI) are, as expected, essentially identical and resemble somewhat that of acenaphthylene (14) itself. There is, however, a general broadening of the absorption bands and a loss of fine structure typical of the conjugation effect. Consideration of the geometric re-

quirements of the molecule indicates that the carbonyl groups must be in a *cis* relation to one another.

Badger, *et al.* (15) have compared and contrasted the absorption spectra of several polynuclear heterocyclic aromatic compounds with those of their carbocyclic analogs. The chief differences seem to be that (a) the group III absorption bands of the azahydrocarbons are much more intense than those of the hydrocarbons; (b) there is a loss of fine structure in replacing the CH group by an N group; (c) the absorption of the azahydrocarbons often begins at longer wavelengths than that of their hydrocarbon analogs. The spectrum of XXII is compared with that of fluoranthene in Figure 5. The chief points of interest in this curve are that the fine structure in the azahydrocarbons is largely retained, and the group II absorption bands (270–290 mμ) have disappeared.

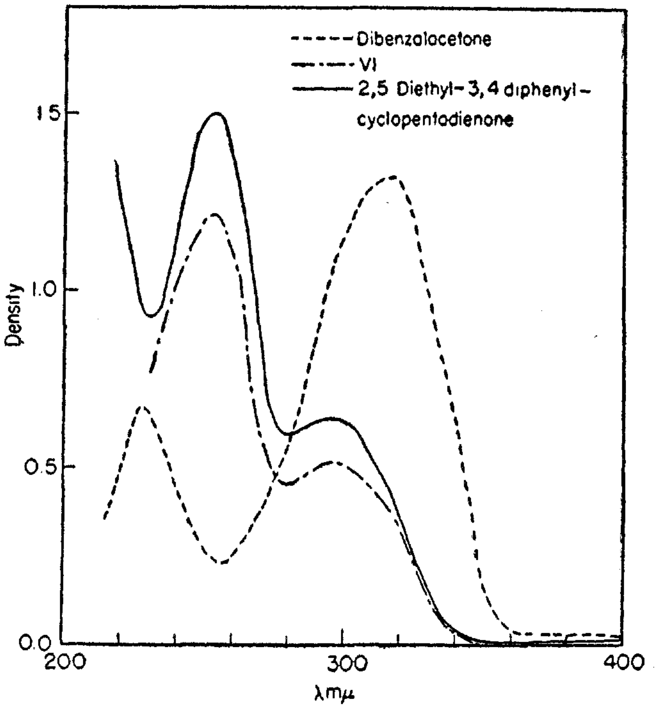


Fig. 2

EXPERIMENTAL

The dienones. The carbinols were obtained by the general procedure, as illustrated by the preparation of 6b-hydroxy-6b,7,8-19-tetradecahydro-7,20-methanocyclohexadeca[*1*,*2*-*a*]-acenaphthen-21-one (IV). A mixture of 9.1 g. of acenaphthenequinone, 12 g. of cyclopentadecanone, 100 ml. of methanol, and 10 ml. of 20% methanolic potassium hydroxide was stirred vigorously at room temperature until solution was complete (1½ hours). The reaction mixture was then poured into water, extracted twice with benzene, and the solvent was removed. The residue was taken up in 25 ml. of benzene, treated with Norit, and an equal volume of ligroin (b.p. 90–120°) was added. On chilling, 15.5 g. of nearly white crystals separated. The analytical results of this and succeeding compounds are collected in Table II. If the mixture was allowed to reflux during the addition reaction, dehydration took place to give the doubly unsaturated ketone (V). Three other procedures were used for dehydrating the carbinol (1). A mixture of 5 g. of the carbinol, 15 ml. of acetic anhydride, and a drop of concentrated sulfuric acid was warmed to 70° for five minutes, and cooled; the crystals were removed and dried. The solid was recrystallized from butanol; the yield of 8–19-dodecahydro-7,20-methanocyclohexadeca[*1*,*2*-*a*]acenaphthylen-21-one (V) was 4.3 g.; m.p. 170–171° (2). A mixture of 15.5 g. of the carbinol and 40 ml. of glacial acetic acid was refluxed for ten minutes and allowed to stand overnight. The yield was 14 g., m.p. 169–171° (3). A mixture of 2 g. of the carbinol, 12 ml. of methanol, and a drop of concentrated sulfuric acid was refluxed for ten minutes; on cooling to room temperature, 1.7 g. of product, m.p. 169–171°, separated.

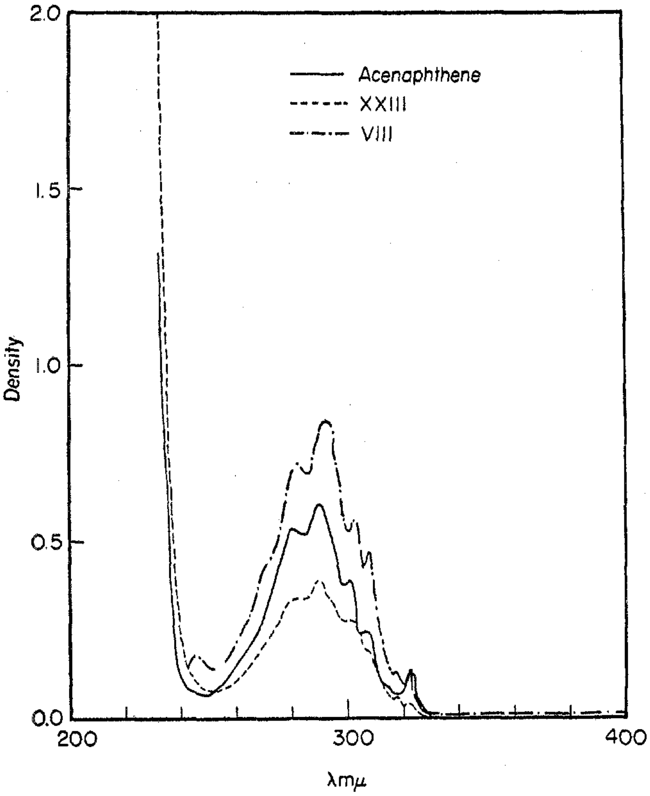


Fig. 3

The other carbinols were not isolated but were at once dehydrated by one of the above three procedures; 8–18-undecahydro-7,19-methanocyclopentadeca[*1*,*2*-*a*]acenaphthylen-20-one (X) was obtained in a 5% yield from cyclotetradecanone and acenaphthenequinone; 8–13, 16–21-dodecahydro-7,22-methanocyclooöctadeca[*1*,*2*-*a*]acenaphthylen-23-one (IX) from civetone and acenaphthenequinone, 68% yield; and 15,16-diphenylbicyclo[12.2.1]heptadeca-14,16-dien-17-one (VI) from benzil and cyclopentadecanone in a 56% yield.

The anhydrides. (*a*) *Simple adducts.* A mixture of 0.9 g. of the dienone (V), 0.2 g. of maleic anhydride, and 14 ml. of benzene was allowed to stand at room temperature until the bright red color of the solution had become yellow, and a copious precipitate had formed (about four days). After purification by dissolving in chloroform at room temperature, and precipitating with ligroin, the yellow anhydride of 21,22-dicarboxy-8–19-dodecahydro-7,20-ethano-23-methanocyclohexadeca[*1*,*2*-*a*]acenaphthylen-23-one (XI) had a melting point of 230° (dec.). Since these adducts are readily decarbonylated, the recrystallization medium should not be heated above 35°. Under the same conditions, maleic anhydride and the dienone (VI) gave the anhydride of 17,18-dicarboxy-15,16-diphenyltricyclo[12.2.2.1)nonadec-15-en-19-one (XIV).

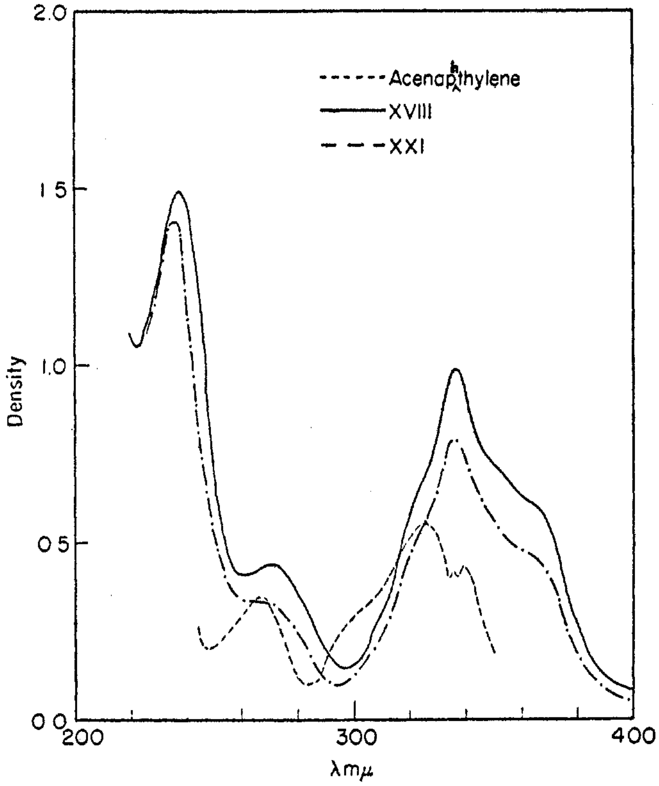


Fig. 4

The decarbonylated product, the anhydride of 21,22-dicarboxy-8–19-dodecahydro-7,20-ethanocyclohexadeca[*1*,*2*-*a*]acenaphthylene (XII), was most conveniently obtained by refluxing a mixture of 2 g. each of the dienone (V) and maleic anhydride in 50 ml. of xylene until the red color had disappeared, removing the solvent by steam, and recrystallizing the residue from benzene-ligroin; the yield of white needles, m.p. 244°, was 3.8 g. This substance was also obtained by heating the adduct (XI) at 240° for ten minutes. The anhydride (XII) does not add a second molecule of maleic anhydride to give a *bis*-anhydride. The analogous decarbonylated anhydride of 17,18-dicarboxy-15,16-diphenylbicyclo[12.2.2]octadeca-14,16-diene (XV) was made in a similar manner from the dienone (VI).

(*b*) *Decarbonylated anhydrides by use of acetylenedicarboxylic acid.* The anhydride (XIII) of 21,22-dicarboxy-8–19-dodecahydro-7,20-ethenocyclohexadeca[*1*,*2*-*a*]acenaphthylene was obtained by three minutes' fusion (at 225°) of 0.3 g. of the dienone (V) and 0.5 g. of acetylenedicarboxylic acid; the product was recrystallized from xylene. The same anhydride also resulted from a catalytic dehydrogenation of the anhydride (XII) using palladized charcoal. In a similar manner, the anhydride (XVI) of 17,18-dicarboxy-15,16-diphenylbicyclo[12.2.2]octadeca-14,16,17-triene was obtained from the dienone (VI) and the anhydride (XXIV) of 23,24-dicarboxy-8–13,16–21-dodecahydro-7,22-ethenocyclooöctadeca-[*1*,*2*-*a*]acenaphthylene from the dienone (IX).

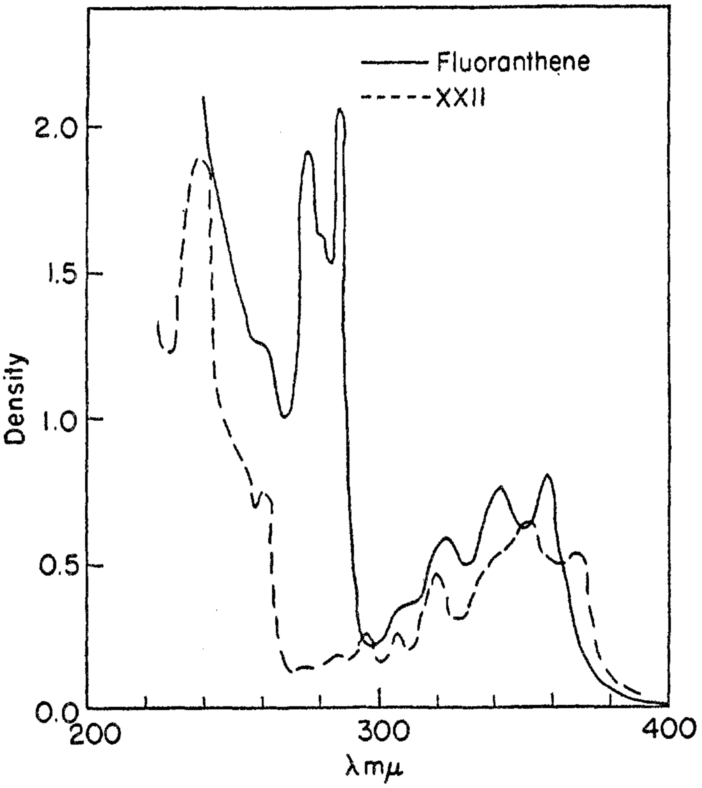


Fig. 5

The diketones. A solution of 4 g. of the dienone (V) in 200 ml. of isoöctane was exposed to a sunlamp while air was bubbled through by means of a sintered glass disperser. The initially bright red solution became yellow when the reaction was complete; the product partially separated. After the volume had been reduced, the yellow 8–19-dodecahydrocyclohexadeca[*1*,*2*-*a*]acenaphthylen-7,20-dione (XXI) was collected on a filter and recrystallized from butanol; m.p. 137°. The yield was 3.9 g. (97%). In essentially the same manner, 1,2-diisobutyrylacenaphthylene (XVIII) was obtained by aerial oxidation of the dienone (XVII) (10).

The unsaturated ketones (V, VI, XXI) were reduced catalytically at atmospheric pressure in ethyl acetate solution in the presence of a platinum oxide catalyst. The products were recrystallized from butanol. 6b-20a-Hexadehydro-7,20-methanocyclohexadeca[*1*,*2*-*a*]acenaphthylen-21-one (VIII) was obtained from the ketone (V); 6b,8–19,20a-tetradecahydrocyclohexadeca[*1,2-a*]acenaphthylen-7,20-dione (XXIII) from XXI, and 15,16-diphenylbicyclo[12.2.1]heptadecan-17-one (VII) from VI. When XXIII was treated with acetic anhydride and a drop of sulfuric acid, there was no dehydration, the starting material being recovered.

TABLE II

PROPERTIES OF NEW SUBSTANCES

NO.	RECRYST. SOLV.	M.P., °C.	YIELD, %	EMPIRICAL FORMULA	ANALYSES				Act. H	Add.
					Calc'd		Found			
					C	H	C	H		
IV	Benzene, ligroin	143	84	$C_{27}H_{32}O_2$	83.4	8.3	83.3	8.3	1.0	1.0
V	Butanol	172	90[e]	$C_{27}H_{30}O$	87.5	8.1	87.7	8.2	0.1	1.0
VI	Alcohol	111	56[d]	$C_{29}H_{34}O$	87.5	8.5	87.6	8.6	0.0	1.0
VII	Alcohol	108	70	$C_{29}H_{38}O$	86.6	9.5	86.5	9.2	0.8	0.1
VIII	Ligroin	148	83	$C_{22}H_{34}O$	86.6	9.1	86.2	8.8		
IX	Butanol	154	68[g]	$C_{27}H_{28}O$	88.1	7.6	88.1	8.1	0.0	1.0
X	Butanol	152	5[d]	$C_{26}H_{28}O$	87.6	7.9	87.8	7.7		
XI	Chloroform, methanol	230 dec.	94[a]	$C_{31}H_{32}O_4$	79.5	6.9	79.4	7.1		
XII	Benzene, ligroin	244	88	$C_{30}H_{32}O_3$	81.7	7.3	81.9	7.2		
XIII	Xylene	330	82[b]	$C_{30}H_{30}O_3$	82.2	6.9	82.2	6.8		
XIV	Chloroform, methanol	254 dec.	91	$C_{33}H_{36}O_4$	80.0	7.3	79.9	7.1		
XV	Toluene, ligroin	260	85	$C_{32}H_{36}O_3$	82.1	7.7	81.9	7.8		
XVI	Xylene	345–347	79[b]	$C_{32}H_{24}O_3$	82.5	7.3	82.2	7.0		
XVIII	Alcohol	107	95[a]	$C_{20}H_{20}O_2$	82.2	6.9	82.6	7.0	0.0	1.7
XIX	Alcohol	208	89[b]	$C_{20}H_{20}N_2$	83.1	6.9	83.5	6.8		
XX	Alcohol	142	40	$C_{21}H_{20}O_2 \cdot C_2H_6O$	78.6	5.7	78.7	6.1		
XXI	Butanol	137	97[a]	$C_{26}H_{30}O_2$	83.3	8.0	83.3	8.3	0.0	2.0
XXII	Ligroin	230	86[b]	$C_{26}H_{30}N_2$	84.4	8.1	84.5	7.8		
XXIII	Butanol	124	87[f]	$C_{26}H_{32}O_2$	83.0	8.5	83.1	8.4	0.4	1.5
XXIV	Acetic anhydride	275	64[c]	$C_{32}H_{32}O_3$	82.5	6.9	82.5	6.9		

[a] Bright yellow; [b] Light yellow; [c] Yellow brown; [d] Red; [e] Mol. Wt. Calc'd 370; Found (in boiling benzene) 361; [f] Mol. Wt. Calc'd 376; Found (in boiling benzene) 358; [g] Mol. Wt. Calc'd 368; Found (in boiling benzene) 385.

The diazines. These were prepared by warming a mixture of 0.5 g. of the unsaturated diketone, 1.5 ml. of 90% hydrazine hydrate, and 8 ml. of butanol on the steam-bath for two hours, and chilling. The yellow products were recrystallized from ligroin. 21,22-Diaza-8–19-dodecahydro-7,20-ethenocyclohexadeca[*1,2-a*]acenaphthylene (XXII)) was formed from the diketone (XXI) and 7,10-diisopropyl-8,9-diazafluoranthene (XIX) from XVIII.

SUMMARY

Macrocyclic ketones, having over 13 ring members, readily condense with benzil and acenaphthenequinone to give unsaturated macrocyclic compounds con-

taining a carbonyl bridge and two double bonds, these groups forming a crossed conjugated system. These substances comprise a new class of carbonyl bridge compounds characterized by a double bond at each bridgehead.

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