

manner, it darkens and shrinks at 220° without melting up to 320°. It was unaffected by water, alcohol and dilute sodium hydroxide. The crude material was analyzed, for no method of purification was discovered.

Anal. Calcd. for $C_{34}H_{22}Br_2$: C, 69.2; H, 3.9; Br, 27.1. Found: C, 68.4; H, 3.8; Br, 25.8.

Hydrogen bromide in acetic acid appears to give the same dibromide.

When solutions of the dibromide in acetone, benzene or acetic acid are refluxed, they become magenta-colored and bluish-red crystals of 6,13-diphenylpentacene separate. The solutions contain bromide ions and, from the acetone treatment, lachrymatory bromoacetone remains. When the dibromide is treated with bromine, hydrogen bromide is given off at once, indicating substitution.

F. 5,7,12,14-Tetraphenylpentacene (XXIII).—After a mixture of 0.6 g. each of the tetraol (XXII) and potassium iodide in 15 cc. of acetic acid had been refluxed for fifteen minutes, purple prisms separated. They separated easily from nitrobenzene; m. p. 306–308°; the yield was 0.4 g.

Anal. Calcd. for $C_{46}H_{30}$: C, 94.8; H, 5.2. Found: C, 94.9; H, 5.2.

A benzene solution appears red by reflected light but blue-violet by transmitted light, and exhibits an orange-red fluorescence (less intense than that of the diphenyl homolog) under an ultraviolet lamp. With acetic acid and iron this tetraol also gives a solution having the same color of red, but the fluorescence is yellowish-green. In the light, its benzene solutions were rapidly decolorized,

and a monoperoxide (XXIV), crystallizing in prisms, m. p. 250°, resulted. The solid gives a brownish melt without gas evolution.

Anal. Calcd. for $C_{46}H_{30}O_2$: C, 89.9; H, 4.9. Found: C, 90.1; H, 4.9.

Summary

6,13-Pentacenequinone appears to have a radiating bond structure. This conclusion is based upon its behavior with phenylmagnesium bromide, which resembles that of α,β -unsaturated ketones having a crossed conjugated system.

6,13-Diphenylpentacene, a bluish-red hydrocarbon, has been secured and certain of its reactions determined. In solution it takes up atmospheric oxygen (very rapidly in sunlight) and gives a peroxide.

6,13-Diphenylpentacene adds one or two equivalents of hydrogen, bromine, and maleic anhydride. The interrelation of the various products is described.

The properties and reactions of two stereoisomeric diphenylpentacene diols are described.

Certain other related highly phenylated pentacenes are described.

ROCHESTER, NEW YORK

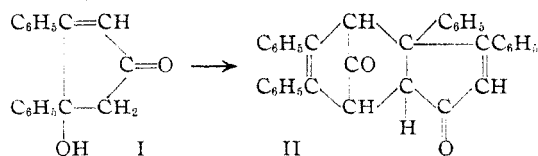
RECEIVED JANUARY 13, 1942

[COMMUNICATION NO. 843 OF THE KODAK RESEARCH LABORATORIES]

Carbonyl Bridge Compounds

BY C. F. H. ALLEN AND J. VAN ALLAN

A few years ago it was shown that the bimolecular product, formed when anhydroacetonebenzil (I) was treated with acidic dehydration agents, was a polynuclear compound containing a carbonyl bridge, (II).¹ In a series of reactions this was degraded to *o*-diphenylbenzene, showing



the presence of this ring system. Since that time, a portion of the degradation products have been synthesized,² confirming the results of some of the steps of the degradation.

In order to learn more about this type of compounds, and hoping to explain some of the un-

usual properties, attention was turned to the methylated homolog (III). This substance was selected in order to avoid any uncertainty that might be connected with the presence of mobile hydrogen atoms. α,β -Dimethylanhydroacetonebenzil (III) is now readily accessible, owing to the availability of diethyl ketone. It had been dehydrated by Gray³ long ago to give a bimolecular product, which was not further studied.

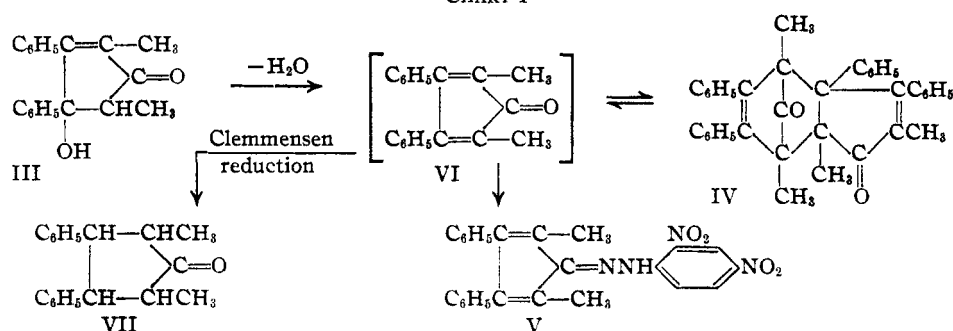
The methylated bimolecular product (IV) seemed to be homogenous, but in most reactions it behaved as though it were dissociated into its diene component, 2,5-dimethyl-3,4-diphenylcyclopentadienone (VI); this could not be isolated. Thus, on treatment with 2,4-dinitrophenylhydrazine, a monomolecular dinitrophenylhydrazone (V) resulted; this same derivative was also secured directly from the dimethylanhydroace-

(1) Allen and Spanagel, *THIS JOURNAL*, **55**, 3773 (1933).

(2) Allen, Bell, Bell and Van Allan, *ibid.*, **62**, 656 (1940).

(3) Gray, *J. Chem. Soc.*, **95**, 2134 (1909).

CHART I



tonebenzil (III). A Clemmensen reduction by Martin's procedure⁴ gave the known⁵ 2,5-dimethyl-3,4-diphenylcyclopentanone (VII).

The bimolecular product, which is white in the crystalline state, gives red solutions when heated in solvents; however, no colored substance could be isolated. At the boiling point of benzene, the apparent molecular weight is 414-417 [the calculated value for the dimer (IV) is 520], indicating about 20% dissociation. Gray³ did not determine a molecular weight, nor mention the appearance of color in solutions. This substance thus resembles the dimeric 2,3,4-triphenylcyclopentadienone⁶ which gives red solutions on heating.

The most conspicuous behavior of compounds having a carbonyl bridge is the loss of carbon monoxide when they are heated by themselves or in non-reacting solvents. At first this seemed to us an abnormal property, for compounds having a carbonyl bridge across a seven or eight-membered ring are perfectly stable when heated, being readily distillable *in vacuo*.⁷ However, this loss of carbon monoxide has been observed in so many instances that it must now be considered as characteristic for this type of substance. An inspection of the formulas reveals that all the substances that so readily lose the carbonyl bridge are of the same type (II, IV, VII, etc.), having a double bond in the same position, relative to the bridge. The loss of carbon monoxide is, in reality, a cleavage of linkages β,γ to the double bond, comparable to the production of butadiene from cyclohexene.⁸ These particular bonds are ruptured, because a very stable aromatic structure can result thereby.^{8a} If the other β,γ set of bonds

were broken, it would be simply a reversal of the diene synthesis by which these substances are prepared. Hence, it is not a question of the stability of a carbonyl bridge across a 6-membered ring; the 7- and 8-membered rings⁷ did not have a double bond in the same position relative to the bridge.

Most of the molecules so far studied have been complex, often containing more than one functional group, so that the chemical behavior of the carbonyl bridge could not be determined with assurance. For example, the bimolecular product (II) has two carbonyl groups—it forms two dioximes; in the Grignard machine it shows one active hydrogen and one addition. Also, the anhydride from tetraphenylcyclopentadienone and maleic anhydride⁹ forms neither oxime nor phenylhydrazone, but in the Grignard machine shows one active hydrogen and two additions. Hence, a simpler molecule was desired.

By the addition of styrene to the dehydration product (IV) [this reacts in the monomolecular form (VI) as previously mentioned] of α,β -dimethylanhydroacetonebenzil, such a substance was secured. A further advantage in the use of this addition product was the absence of hydrogen atoms in the position *alpha* to the carbonyl group—complications related to enolization were not encountered. Of course, it was realized that the methyl groups might act as a hindrance in reactions, owing to their spatial effect. Fortunately, this difficulty was not encountered, perhaps because, in space, the molecule resembles a cage with the carbonyl group protruding.

Addition products were prepared from the dienone (IV), styrene, and β -nitrostyrene. The first one (VIII) studied in detail resembled all previous carbonyl bridge types in losing carbon monoxide when heated, forming a dihydroben-

(4) Martin, *THIS JOURNAL*, **58**, 1440 (1936).

(5) Japp and Maitland, *J. Chem. Soc.*, **85**, 1473 (1904).

(6) Dilthey, *J. prakt. Chem.*, **136**, 294 (1933); Dilthey and Hurtig, *Ber.*, **67**, 2004 (1934).

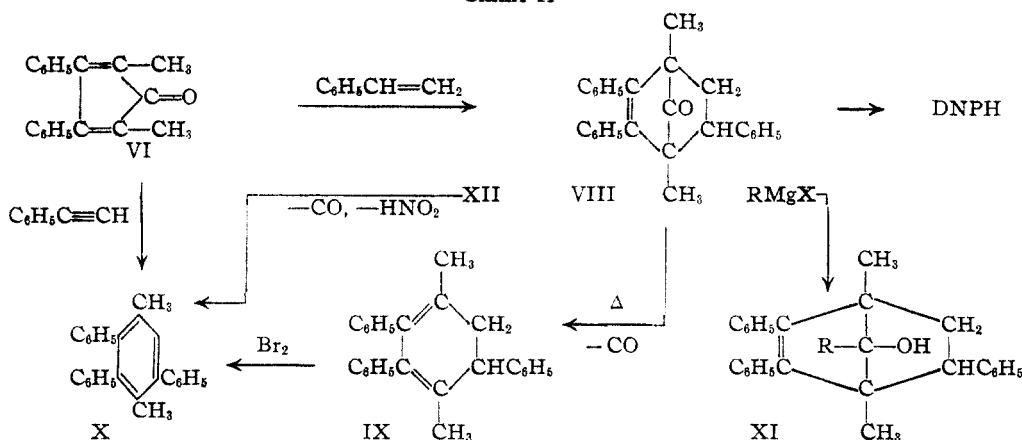
(7) Allen and Sallans, *Can. J. Res.*, **9**, 574 (1933).

(8) Schmidt, *Chem. Rev.*, **17**, 140 (1935).

(8a) The primarily-formed dihydrobenzene often loses the two hydrogen atoms during the heating to remove the carbonyl bridge.

(9) Allen and Sheps, *Can. J. Res.*, **11**, 171 (1934).

CHART II



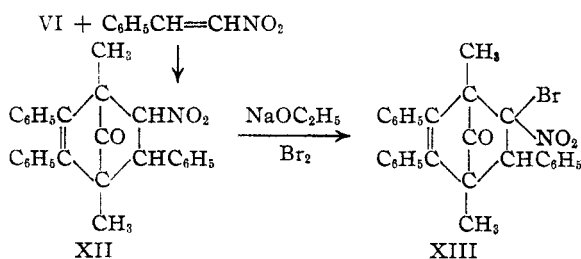
zene (IX) which was easily dehydrogenated by bromine to give the aromatic 3,6-dimethyl-1,2,4-triphenylbenzene (X). This hydrocarbon was also synthesized from the dehydration product and phenylacetylene, and resulted by loss of carbon monoxide and nitrous acid when the addition product from nitrostyrene was heated.

The bridged ketone (VIII) easily gave a 2,4-dinitrophenylhydrazone, proving the presence of a carbonyl group, and showing there was no hindrance from the methyl groups. In the Grignard machine it showed no active hydrogen, but one addition. The Grignard product was a carbinol (XI); in the Grignard machine it showed one active hydrogen and no addition. Tertiary alcohols were also secured by the use of methyl-, phenyl-, and α -naphthylmagnesium bromides. The carbonyl bridge in this type of substances is thus a normal carbonyl group, and inconsistencies observed in the more complex molecules must be related to their complicated structures. These reactions are conveniently summarized below, using the (unisolated) dienone formula (VI) for simplicity.

The behavior of a carbonyl bridge across a six-membered ring is, thus, the same as when the ring has seven or eight carbon atoms, except in stability to heat which, as already discussed, is related to the bond structure.

β -Nitrostyrene gave an addition product (XII). This is the first instance in which an isolation of a primary product with this addend has been accomplished; usually carbon monoxide or oxides of nitrogen (or both) are lost and an aromatic compound results.¹⁰ The addition product had

the properties of an aliphatic nitro compound; it dissolved in sodium ethoxide solution, and the salt so formed gave a bromonitro compound (XIII) with bromine.

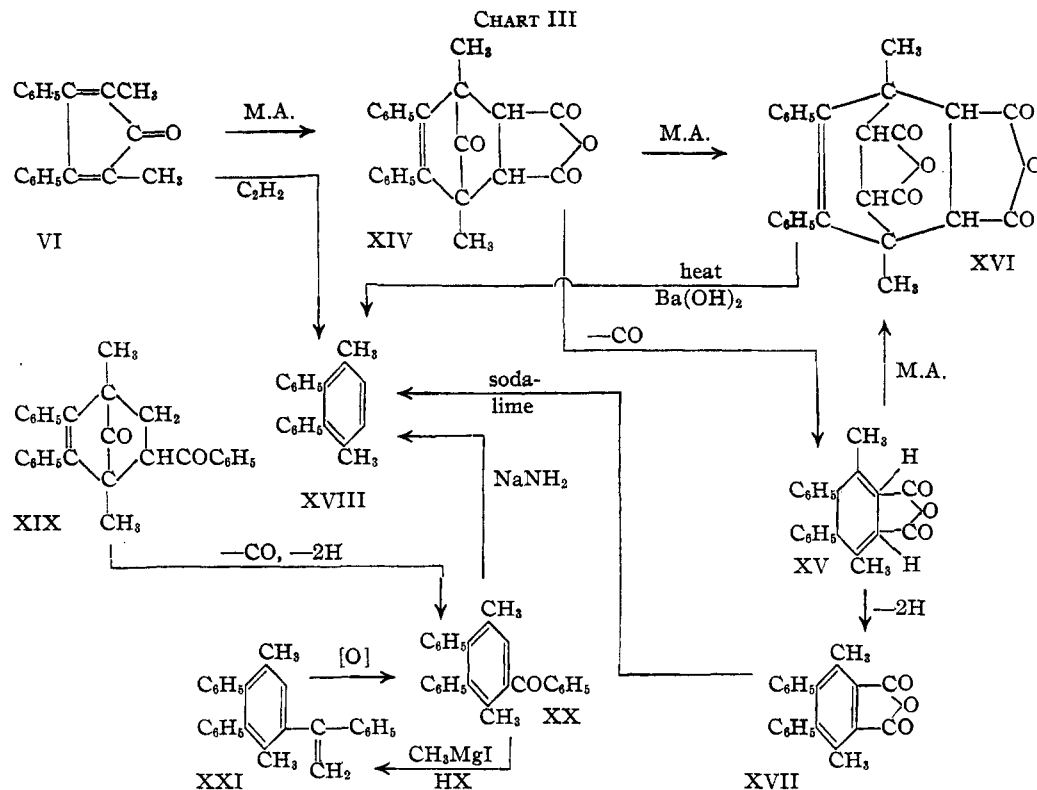


The addition of maleic anhydride is described next. The primary addition product (XIV) containing a carbonyl bridge, lost carbon monoxide on heating, as is characteristic of such compounds and gave a dihydrophthalic anhydride (XV). When excess maleic anhydride was present, this at once added to the conjugated system so formed, resulting in a dianhydride (XVI); the reaction went equally well stepwise. This behavior parallels that of the unmethylated homolog.¹ The dihydrophthalic anhydride was easily dehydrogenated and the aromatic compound XVII was heated with soda-lime for decarboxylation, resulting in 3,6-dimethyl-1,2-diphenylbenzene (XVIII).

Vinyl phenyl ketone added readily; the addition product (XIX) lost both the carbonyl bridge and the two extra hydrogen atoms on heating. The resulting benzophenone (XX) was readily cleaved by sodium amide and gave the same hydrocarbon (XVIII).

The hydrocarbon XVIII also resulted from the interaction of VI and acetylene, and on decarboxylation of XVI, the di-addition product from

(10) Allen and Bell, *THIS JOURNAL*, **61**, 521 (1939).



maleic anhydride. During this heating, one molecule of maleic anhydride was eliminated; this was first determined on the unmethylated homolog (formula XI).¹

The aromatic ketone (XX) added one equivalent of methylmagnesium iodide, but the expected carbinol was dehydrated to the hydrocarbon (XXI) during the ensuing manipulation. The hydrocarbon formed the ketone (XX) upon oxidation.

Maleic, fumaric, and acetylene dicarboxylic esters added equally well. The products (XXII) from methyl and ethyl maleate and methyl fumarate lost carbon monoxide when heated, showing they still had a carbonyl bridge. The resulting dihydro-esters (XXIII) were readily dehydrogenated by permanganate to form the same aromatic ester (XXIV); they are both dehydrogenated and hydrolyzed by Newman's¹¹ procedure, with consequent production of the anhydride (XVII).

The aromatic ester (XXIV) is also secured in the reaction using methyl acetylenedicarboxylate, the intermediate XXV losing carbon monoxide so easily it was not isolated. In accordance with the suggestion given above, the bonds β, γ to the

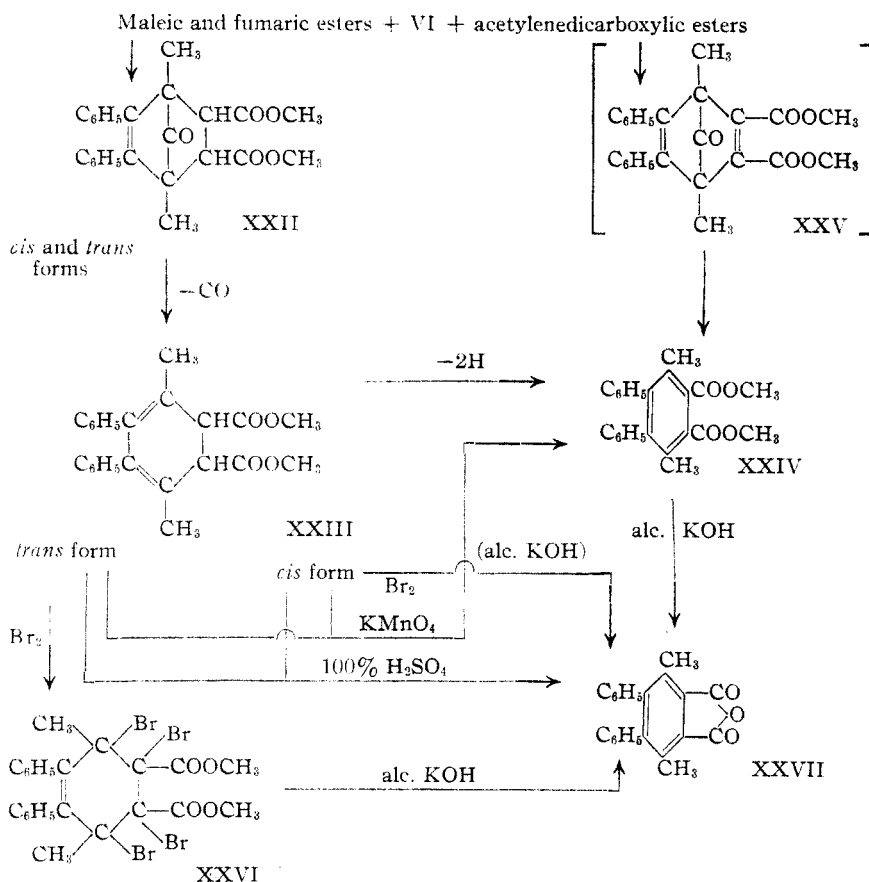
ethylenic linkage are broken—in this instance (addition of the acetylenic ester) there are two such linkages to increase the tendency to cleavage. Any acetylenic addend with cyclopentadienones would form an intermediate of such a type XXV, and, so far, in no single instance using acetylenic components has such a substance been isolated.

The configurations assigned to the esters (XXII) were based on their preparation from esters of known space relations, and supported by their difference in behavior with bromine. The *cis* form, in which the two hydrogen atoms are situated on the same side of the molecule, was readily dehydrogenated. The *trans* form, however, under the same conditions, evolved hydrogen bromide and gave a product (XXVI) containing four atoms of bromine; the halogen was eliminated from this by alcoholic potash, the anhydride (XVII) resulting on acidification of the alkaline solution.

During the removal of the bridge by heating the *cis* ester addition product (XXII), a considerable amount of a mono ester (XXVII) resulted. This was found to be methyl 2,5-dimethyl-3,4-diphenylbenzoate and synthesized from VI and methyl acrylate for confirmation. It could be

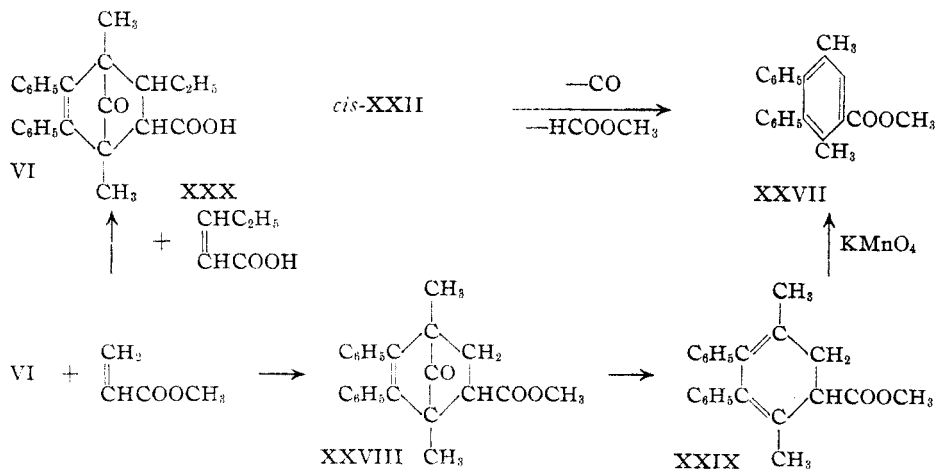
(11) Newman, THIS JOURNAL, 63, 2431 (1941).

CHART IV



formed by a splitting of methyl formate, but the latter was not detected.

larly, the chloride (XXXI) lost hydrogen chloride. This suggests that a molecular rearrange-



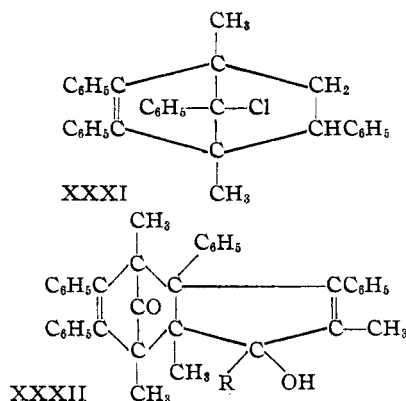
β -Ethylacrylic acid was also added, resulting in the acid (XXX).

The carbinols (XI) lost the elements of water when heated, whereas the ketones from which they were prepared lost carbon monoxide. Simi-

ment has occurred, since otherwise there is no available hydrogen. This behavior will form the subject of a subsequent paper.

The exact nature of the Grignard products from the bimolecular product (IV) and the be-

havior on pyrolysis will likewise be deferred. Since these carbinols lose carbon monoxide above their melting point, it indicates strongly that they have the structure XXXII.



Experimental Part

A. General Procedure for Preparation of the Addition Products.—For a given quantity of bimolecular product, there was used slightly more than one equivalent of addend, usually in benzene, and the mixture refluxed from ten minutes (acetylene dicarboxylic esters) to fifteen hours (fumaric ester). The products that separated on cooling were recrystallized. Exception: An excess of the addends acetylene dicarboxylic esters, ethyl maleate, maleic anhydride (to make the dianhydride), and phenylacetylene, was used as solvent; maleic anhydride was also done in trichlorobenzene (88% yield).^{11a} The properties of the addition products are collected in Table I.

B. Removal of Carbonyl Bridge.—This was performed in the usual manner for this type of addition product—heating at 200° as long as gas (carbon monoxide) was evolved. The properties of the dihydrobenzene derivatives are collected in Table II. Occasionally dehydrogenation occurs and the aromatic compound was obtained; such instances are starred (*). In some cases the oily dihydrobenzene was dehydrogenated without purification.

C. Dehydrogenation to Aromatic Series.—This was accomplished by the use of bromine in chloroform (when hydrogen bromide was evolved), or permanganate in acetone; with the second reagent, the substance in acetone solution was refluxed for an hour, filtered, and the residue, after evaporation of the acetone, recrystallized from an appropriate solvent. The properties of the hydrocarbons, 1,4-dimethyl-2,3-diphenylbenzene (XVIII), 1,4-dimethyl-2,3,5-triphenylbenzene (X), ketone 2,5-dimethyl-3,4-diphenylbenzophenone (XX), and esters, methyl and ethyl 3,6-dimethyl-4,5-diphenylphthalates (XXIV), have already been given in Tables I and II.

a.—3,6-Dimethyl-4,5-diphenylphthalic anhydride (XVII) was secured in a variety of ways as described in the introduction; *e. g.*, by dehydrogenation with bromine, hydrolysis of the esters by Newman's method, or alcoholic potash. It separates from acetic anhydride in needles; m. p. 281°.

(11a) A benzene solution of acetylene was heated in a bomb; vinyl phenyl ketone was secured from β -dimethylaminopropiophenone²; β -ethylacrylic acid was added in acetic acid as a solvent.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 80.5; H, 4.9; mol. wt., 328. Found: C, 80.2; H, 4.9; mol. wt., 322, 329 (by titration).

This anhydride was also obtained by heating the styrene addition product (VIII) with maleic anhydride; this is an illustration of the reversibility of the diene synthesis of VIII. In the Grignard machine it showed 0.8 active hydrogen and 1.5 addition.

b.—When the *trans* form of the ester (XXIII) was treated with bromine for dehydrogenation, hydrogen bromide was evolved, but the product contained four atoms of bromine; the yield was 74%. It crystallizes in prisms from chloroform-methanol; m. p. 181°.

Anal. Calcd. for $C_{24}H_{22}O_4Br_4$: C, 41.4; H, 3.2; Br, 46.1. Found: C, 41.4; H, 3.0; Br, 44.5.

All the bromine was removed by alcoholic potash; the ester was also hydrolyzed, so that on acidification the anhydride (XVII) resulted.

c.—Methyl 2,5-dimethyl-3,4-diphenylbenzoate (XXVII) crystallized out from the oily distillate [b. p. 191–193° (2 mm.)] from one addition of methyl maleate (the latter ester did *not* contain methyl acrylate). It also was secured by the permanganate dehydrogenation procedure from crude XXIX. It forms rods from methanol; m. p. 116°.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.5; H, 6.3; OCH_3 , 8.2. Found: C, 83.0; H, 6.6; OCH_3 , 8.2.

d.—1,4-Dimethyl-2,3-diphenylbenzene (XVIII) has also been prepared in other ways. The decarboxylation of the maleic anhydride addition products (XIV, XVI)^{11b} was accomplished by heating an intimate mixture of one part of anhydride and four parts of "dry" barium hydroxide monohydrate or soda-lime in a small distilling flask. The hydrocarbon (XVIII) that distilled was recrystallized from absolute ethanol or glacial acetic acid; the yield was 40%, and the melting point, 109°, was not depressed on admixture with the hydrocarbon secured by the other reactions.

When the ketone (XX) was cleaved by sodium amide in the usual manner¹² the same hydrocarbon was formed—this is the most convenient synthesis.

D.—A solution of 4 g. of the nitrostyrene addition product (XII) in 6 cc. of benzene was added to the sodium ethoxide solution from 0.3 g. of sodium and 20 cc. of absolute ethanol; after ten minutes the mixture appeared to be solid. Bromine (0.9 cc.) was added, as long as it was instantly decolorized; the salt was filtered and the bromo-nitro compound (XIII) isolated by appropriate manipulations; yield, 92%. It was recrystallized from *n*-propanol, from which it separates in long prisms; m. p. 148°.

Anal. Calcd. for $C_{27}H_{22}O_3NBr$: C, 66.4; H, 4.5. Found: C, 66.5; H, 4.4.

E.—The 2,4-dinitrophenylhydrazones—these were prepared in the customary way¹³; their properties are collected in Table III.

The 2,4-dinitrophenylhydrazone (V) was prepared equally well from the bimolecular product (IV) or the α,β -dimethylanthydroacetonebenzil (III). The molecular

(11b) For these experiments we are indebted to Dr. F. P. Pingert.

(12) Ref. 2, p. 659.

(13) Allen, *THIS JOURNAL*, **52**, 2955 (1930).

TABLE I
PROPERTIES OF ADDITION PRODUCTS

No.	Addend	Yield, %	M. p., °C.	Crystal form	Empirical formula	Analyses, %			
						Calcd. C	H	Found C	H
VIII	Styrene	90	131	Prisms ^c	C ₂₇ H ₂₄ O	88.9	6.6	88.7	6.4
XII	β-Nitrostyrene	91	176	Rods ^c	C ₂₇ H ₂₂ O ₃ N	79.3	5.6	79.5	5.8
XXII	Methyl maleate	83	144	Prisms ^d	C ₂₆ H ₂₄ O ₃	74.3	5.8	73.9	5.8
	Ethyl maleate	64	^a		C ₂₆ H ₂₈ O ₄ ^b	77.2	6.9	77.0	6.9
XXII	Methyl fumarate	73	128	Rods ^d	C ₂₆ H ₂₄ O ₅	74.3	5.8	74.2	5.8
XXIV	Methyl acetylenedicarboxylate	90	212	Prisms ^d	C ₂₄ H ₂₂ O ₄ ^g	77.0	5.9	76.7	5.8
	Ethyl acetylenedicarboxylate	81	132	Prisms ^e	C ₂₆ H ₂₆ O ₄ ^b	77.5	6.5	77.3	6.5
XXVIII	Methyl acrylate ^h	92	115	Needles ^e	C ₂₅ H ₂₂ O ₃	79.9	6.4	80.1	6.2
XXX	β-Ethylacrylic acid ⁱ	75	188	Prisms ^g	C ₂₄ H ₂₄ O ₃	80.0	6.7	79.5	6.6
XIV	Maleic anhydride ^m (one equivalent)	99	191	Needles ^f	C ₂₅ H ₁₈ O ₄	77.0	5.0	77.2	5.0
XVI	Maleic anhydride ^{i,m} (excess)	95	320	Rods ^f	C ₂₆ H ₂₀ O ₆ ^{b,i}	72.9	4.7	72.8	4.8
XIX	Vinyl phenyl ketone	77	147	Prisms ^g	C ₂₈ H ₂₄ O ₂ ^h	85.7	6.1	85.5	6.2
XVIII	Acetylene	51	109	Rods ^c	C ₂₀ H ₁₈ ^b	93.0	7.0	92.9	7.0
X	Phenylacetylene	90	157	Prisms ^g	C ₂₆ H ₂₂ ^b	93.3	6.7	93.5	6.6

^a Oil, b. p. 210–213° (3 mm.). ^b Product has lost the carbon monoxide bridge. ^c From ethanol–acetic acid. ^d From benzene–methanol. ^e From ethanol. ^f From acetic anhydride. ^g From acetic acid. ^h Some of this addition product crystallized from the vacuum-distilled oil in which methyl maleate was used. ⁱ Also obtained from α,β-dimethylanhydroacetonebenzil and excess maleic anhydride. ^j Mol. wt., calcd. 428; found (by titration, 432 ± 5). ^k In the Grignard machine shows 0.8 active hydrogen and 1.2 addition, indicating substance is enolized. ^l Von Auwers, *Ann.*, **432**, 63 (1923). ^m These two anhydrides were also formed from α,β-dimethylanhydroacetonebenzil and maleic anhydride, plus a drop of sulfuric acid. The aromatic anhydride resulted when the operation was carried out in trichlorobenzene.

TABLE II

No.	Made from no.	%	M. p., °C.	Crystal form	Empirical formula	Analyses, %			
						Calcd. C	H	Found C	H
XV	XIV		158	Needles ^d	C ₂₂ H ₁₈ O ₃	80.0	5.5	80.0	5.2
XX*	XIX		160	Plates ^a	C ₂₇ H ₂₂ O	89.0	5.6	89.5	5.9
XXIII	<i>trans</i> XXII	86	131	Prisms ^c	C ₂₄ H ₂₄ O ₄	76.7	6.4	76.1	6.4
XXIII	<i>cis</i> XXII	99	^b		C ₂₄ H ₂₄ O ₄	76.7	6.4	76.8	6.3

^a From ligroin. ^b B. p. 197–200° (2 mm.). ^c From methanol. ^d From acetic anhydride.

TABLE III

Ketone used	M. p., °C.	Solvent	Crystal form, needles	Empirical formula	C	Calcd. H	Analyses, %			
							N	C	Found H	N
VIII	200	Ethanol	Yellow	C ₃₂ H ₂₈ O ₄ N ₄			10.5			10.4
III, IV	242	Butanol	Red	C ₂₈ H ₁₀ O ₄ N ₄	68.2	4.5	12.8	68.1	4.6	13.1

TABLE IV

PROPERTIES OF PRODUCTS FROM GRIGNARD REACTIONS

No.	Solvent	Yield, %	M. p., °C.	Crystal form	Empirical formula	Analyses, %			
						Calcd. C	H	Found C	H
XXI	Butyl ether	90	151	Needles ^a	C ₂₈ H ₂₃	93.6	6.2	93.2	6.7
XXXII, R = CH ₃	Benzene	93	205	Prisms ^c	C ₃₉ H ₃₆ O ₂	87.3	6.7	87.0	6.5
XXXII, R = C ₆ H ₅	Benzene		223	Prisms	C ₄₄ H ₃₈ O ₂	88.3	6.4	88.2	6.4
XI, R = CH ₃	Benzene	93	119	Prisms ^c	C ₂₈ H ₂₈ O	88.4	7.4	88.5	7.5
XI, R = C ₆ H ₅	Benzene	89	107 d.	Needles ^{a,d}	C ₃₅ H ₃₄ O ₃	83.7	6.8	83.2	6.7
XI, R = α-C ₁₀ H ₇	Benzene	89	98	Prisms ^b	C ₃₈ H ₃₁ O	90.3	6.5	90.3	6.4

^a From acetic acid. ^b From ethanol. ^c From toluene. ^d Contains acetic acid of crystallization.

weight, determined in boiling chloroform was 425, 428; the calculated value is 440.

F.—Miscellaneous Reactions of the Bimolecular Product (IV).—A Clemmensen reduction by Martin's modification⁴ gave the known 2,5-dimethyl-3,4-diphenylcyclopentanone, m. p. 121°; oxime, m. p. 165°.⁵ The toluene layer, initially a cherry red, changed to brown when reduction was complete (about forty-eight hours).

Hydrogen bromide is evolved slowly when a solution of the bimolecular product in carbon tetrachloride or chloroform is treated with bromine, indicating substitution. The product contains halogen; it separates in prisms from alcohol; m. p. 136° (with decomposition). The same substance was also obtained from the ketone (III).

Anal. Calcd. for C₃₈H₃₂O₂Br₂: Br, 48.2. Found: Br, 48.4.

The substance decomposed at the boiling point of chloroform, so the molecular weight determination was unsatisfactory (found, 800 \pm ; calcd. for above formula, 1000).

G. Grignard Reactions.—These were all done in high-boiling solvents, *i. e.*, "forced conditions." α -Phenyl- α -(2,5-dimethyl-3,4-diphenylphenyl)-ethylene (XXI) was obtained from the benzophenone (XX); the other products were carbinols. The bimolecular product (IV) failed to react with phenylmagnesium bromide, but gave a quantitative yield of diol with phenyllithium. Their properties are collected in Table IV.

The phenylcarbinol, m. p. 107°, gave a chloride on refluxing for fifteen minutes in acetyl chloride; the chloride (85% yield) crystallizes in rods, m. p. 128°.

Anal. Calcd. for $C_{33}H_{29}Cl$: Cl, 7.6. Found: Cl, 7.4.

Summary

A considerable number and variety of com-

pounds containing a carbonyl bridge have been prepared and their chemical behavior examined. Their synthesis was made possible by the discovery that one of them, a bimolecular product resulting from the dehydration of α,β -dimethyl-anhydroacetonebenzil, is partially dissociated in most solvents. In one type, the only functional group is the $C=O$.

A carbonyl group forming a bridge is no different from any other carbonyl group; its elimination as carbon monoxide on heating is in accord with Schmidt's double bond rule.

By heating to eliminate the bridge, and dehydrogenation, highly substituted aromatic compounds have been prepared.

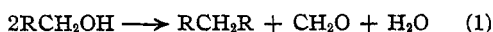
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Structural Investigations upon a Substituted Dipyrromethane. An Unusual Melting Point-Symmetry Relationship^{1,2}

BY ALSOPH H. CORWIN, WILLIAM A. BAILEY, JR.,³ AND PAUL VIOHL⁴

Dipyrromethanes have assumed great importance in the chemistry of pyrrole pigments because of the fact that they are degradation products of bile pigments and are intermediates in the synthesis of bile pigments and porphyrins as well. Substances of this type were first prepared by Pictet and Rilliet.⁵ One of the most productive methods for their preparation is that from pyrrol carbinols discovered by Fischer and Nenitzescu.⁶ This can be represented schematically by the equation



The usefulness of this synthesis was further extended by Fischer and Halbig,⁷ whose essential contribution was that pyrrol carbinols and their ethers could be produced from pyrrolmethyl halides.

By analogy with the course of many other pyrrole reactions, it has been assumed that the

points of junction of the methylene bridge were the alpha carbon atoms and not the equally available nitrogens. Only fragmentary evidence exists to support this view⁸ and, as a matter of fact, no general method is in existence for the unequivocal proof of the point. In this connection, it should be recalled that Pictet formulated his original dipyrromethane as involving N-C-N linkage. We report in this paper a method for the determination of the bridge structure of certain dipyrromethanes and a further study of the reaction of Fischer and Nenitzescu. The reactions involved in the structural argument are summarized in Chart I.

The preparation of methane IX from pyrrole II shows that it is a di-N-methylmethane. The stepwise conversion of methane VII to IX through VIII as an intermediate shows that the hydrogens open in VII are on the nitrogens. To test the possibility of intermediate rearrangements, methanes VII and VIII were regenerated from their mono-sodium salts.

The preferential methylation of the imine hydrogen over the hydroxyl hydrogen in compound V is a matter for comment. It is well known that the acidity of the imine hydrogens in pyrrole derivatives is of a different order of magnitude from

(1) Studies in the Pyrrole Series, VIII; Paper VII, Quattlebaum and Corwin, *THIS JOURNAL*, **64**, 922 (1942).

(2) The major portion of this paper is taken from the doctoral dissertation of William A. Bailey, Jr., The Johns Hopkins University, 1937.

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(5) Pictet and Rilliet, *Ber.*, **40**, 1170 (1907).

(6) Fischer and Nenitzescu, *Ann.*, **443**, 114 (1925).

(7) Fischer and Halbig, *ibid.*, **447**, 133 (1926).

(8) Feist, *Ber.*, **35**, 1647 (1902).