groups at the same positions. This is illustrated in the simplest case, by the spectra of o-xylene and hydrindene.[1,10] While the spectrum of V does not confirm the structure attributed to this

TABLE II

ABSORPTION SPECTRA OF CHRYSENE DERIVATIVES, WAVE LENGTHS AND INTENSITIES OF THE MAXIMA

Wave lengths, Å.	Intensity, log E_{molar}	Wave lengths, Å.	Intensity, log E_{molar}
A. 6-Acetylchrysene		B. Isomeric acetyl-chrysene	
2250	4.63	2220	4.52
(2470)[a]	4.52	(2430)[a]	4.21
(2630)[a]	4.68	2530	4.32
2700	4.82	2850	4.89
(2780)[a]	4.68	3130	4.36
3350	4.10	3610	3.24
		3790	3.24
C. Diacetylchrysene		D. Substance V	
2240	4.28	2230	4.64
(2320)[a]	4.30	2420	4.42
(2440)[a]	4.55	(2520)[a]	4.60
2740	4.89	2600	4.92
2780	4.88	2690	5.16
3100	4.07	(2860)[a]	4.10
3240	4.18	2980	4.12
3390	4.19	3100	4.20
3580	3.80	3240	4.20
3780	3.76	3450	3.04
		3530	2.76
		3620	3.03

[a] Inflection only.

(10) Ramart-Lucas and Hoch, Bull. soc. chim., [5] 2, 327 (1935).

compound by Bergmann and Eschinazi, it is quite consistent with it.

Experimental

All the spectra were determined on a Beckman ultraviolet spectrophotometer in solution in ethanol; the diacetylchrysene was dissolved in ethanol containing not more than 10% of dioxane.

Summary

The similarity between the ultraviolet absorption spectra of 6-isopropenylchrysene and 6-methylchrysene is attributed to the action of steric hindrance which prevents the ethylenic group from acquiring a configuration co-planar with the chrysene ring system. In the absence of such a planar structure interaction between the aromatic ring system and the ethylenic bond of the side chain does not occur.

The spectra of certain acetylchrysenes and of a chrysene derivative containing an alicyclic ring attached at the 5,6-positions are also recorded and discussed.

KINGSTON, CANADA

The Ultraviolet Absorption Spectra of Arylethylenes

BY R. NORMAN JONES

Tetra-(9-phenanthryl)-ethylene (I) has been synthesized recently by F. Bergmann,[1] and the ultraviolet absorption spectrum of a sample of this substance, kindly supplied by Professor

I
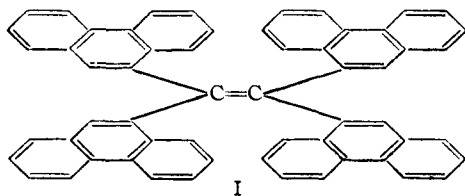
Bergmann, is shown in curve A of Fig. 1; data for the position and intensities of the maxima are

(1) Bergmann, private communication.

given in Table I. Comparison of this curve with the spectrum of a four molar solution of phenanthrene[2] (Curve B of Fig. 1) suggests that the tetra-(9-phenanthryl)-ethylene spectrum may be divided into three distinct parts: (a) a region in the neighborhood of 2500 to 2600 Å. in which the two curves are similar in shape and intensity; (b) a region between 2800 and 3000 Å. in which fine structure, characteristic of the phenanthrene chromophore, is present, but in which the intensity is enhanced; (c) a region of high intensity absorption between 3300 and 4000 Å.

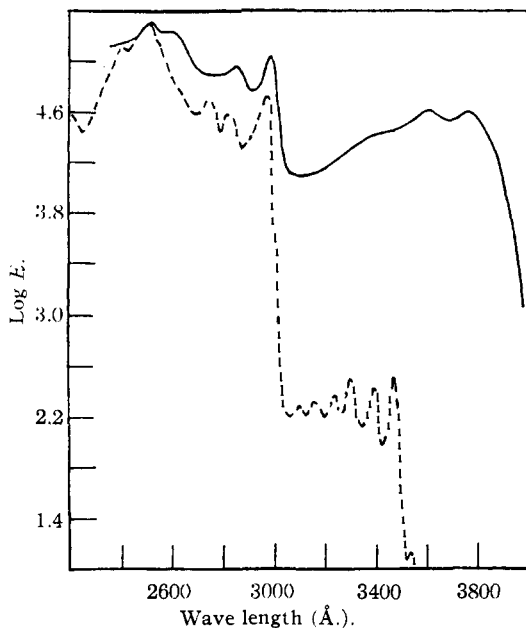(2) Calculated from the data of Mayneord and Roe, Proc. Roy. Soc. (London), A152, 299 (1935).

Fig. 1.— ———— Curve A, tetra-(9-phenanthryl)-ethylene (ethanol/dioxane); — — — Curve B, four molar solution of phenanthrene (ethanol).

which bears little resemblance to the spectrum of phenanthrene.

These observations raise interesting questions concerning the structure of tetra-(9-phenanthryl)-ethylene, and draw attention to certain factors which affect the absorption spectra of arylethylenes.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRUM OF TETRA-(9-PHENANTHRYL)-ETHYLENE, WAVE LENGTHS AND INTENSITIES OF THE MAXIMA; SOLVENT, ETHANOL.–DIOXANE

Wave length, Å.	Intensity (log E_{molar})
2520	5.31
(2550)[a]	5.20
2860	4.96
2985	5.06
(3410)[a]	4.45
3610	4.60
3770	4.60

[a] Inflection only.

Discussion

The ultraviolet absorption spectrum of benzene is modified by the introduction of an unsaturated substituent in which the side chain double bond is conjugated with the ring.[3] This effect is illustrated by comparison of the spectra of styrene and ethylbenzene in curves A and B of
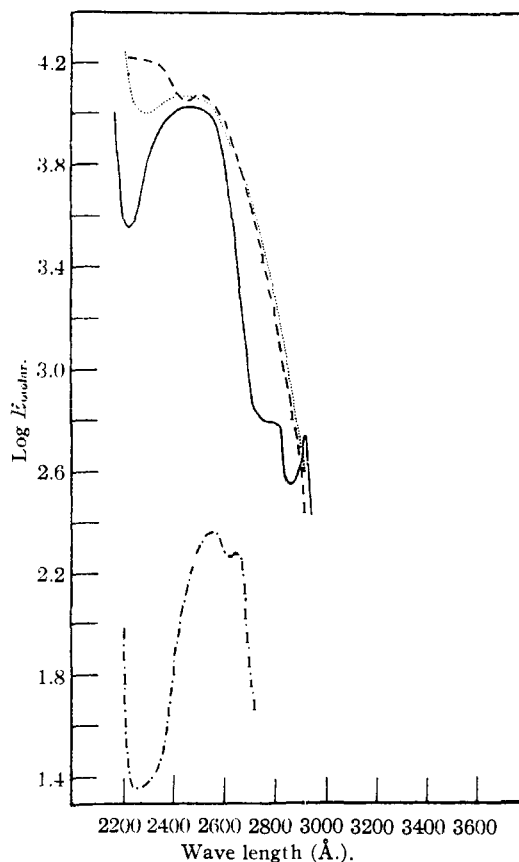
(3) Jones, *Chem. Rev.*, **32**, 1 (1943).

Fig. 2.— ———— Curve A, styrene (ethanol); — · — · — Curve B, ethylbenzene (ethanol); .... Curve C, α,β-dimethyl-*trans*-stilbene (ethanol); — — — Curve D, *asym*-diphenylethyiene (ethanol).

Fig. 2. Structures such as IIa and IIb must make a significant contribution to the ground and electronically excited states of the styrene molecule, and the bond which joins the phenyl group to the ethylenic group must be of hybrid character.
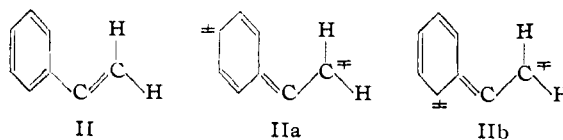
Resonance among the structures II, IIa and IIb requires that the phenyl group and the α- and β-hydrogen atoms of the ethylenic group be in the same plane; because of this, the resonance stabilization energy due to the contribution of these forms gives rise to a potential energy barrier which opposes the rotation of the phenyl group about the 1,4-axis, out of the plane of the ethylenic hydrogen atoms. This effect has been studeid more thoroughly in diphenyl, where sev-

eral investigators[4-8] have shown that the spec-
trum characteristic of the diphenyl chromophore
is modified in ortho-substituted derivatives, in
which a tendency is shown to revert to a benzene
type of chromophore. This behavior is very
marked in heavily ortho-substituted methyl de-
rivatives such as dimesityl.[4] Di-polar quinonoid
structures such as IIIa and IIIb can contribute
to the resonance stabilization energy of diphenyl
but not to that of dimesityl, as, in the latter case,
steric hindrance between the ortho substituents
on opposite rings prevents the attainment of the
necessary planar configuration. The two phenyl
groups remain "insulated" from each other and
absorb independently, as they do in diphenyl-
methane.[3]

IIIa   IIIb
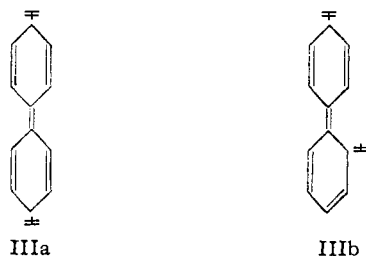
Steric factors such as these must exercise a
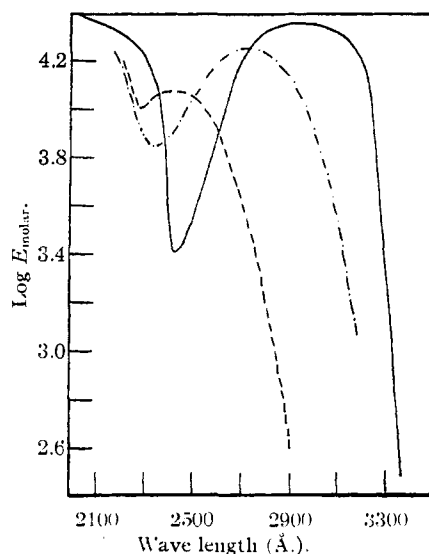controlling effect on the ultraviolet absorption

Fig. 3.— ———— Curve A, trans-stilbene (ethanol);
— —·—·— Curve B, α-methyl-trans-stilbene (ethanol);
— — — — Curve C, α,β-dimethyl-trans-stilbene (ethanol).

(4) Pickett, Walter and France, THIS JOURNAL, 58, 2296 (1936).
(5) O'Shaughnessy and Rodebush, ibid., 62, 2906 (1940).
(6) Jones, ibid., 63, 1658 (1941).
(7) Calvin, J. Org. Chem., 4, 256 (1939).
(8) Pestemer and Mayer-Pitsch, Monatsh., 70, 104 (1937).

spectra of more complex molecules, but the inter-
pretation is more difficult because of the greater
number of variables involved. The diaryl-, tri-
aryl- and tetraryl-ethylenes show some analogy
with diphenyl, and the principles which have been
found to explain changes in the spectrum of di-
phenyl on the introduction of ortho substituents
can be applied to substances of these types and
provide a reasonable explanation of certain fea-
tures of the spectra of these compounds.

X-Ray diffraction measurements by Robertson
and Woodward[9] indicate that in trans-stilbene,
the bonds joining the phenyl groups to the
ethylenic group are 1.45 Å. long, and are, there-
fore, of hybrid type. The spectrum of trans-
stilbene has been determined[10,11] and the energy
changes involved in the photo-conversion to the
cis-isomer have been discussed in relation to the
absorption spectra by Lewis, Magel and Lipkin.[12]
The spectrum (Curve A of Fig. 3) is quite differ-
ent from that of benzene and it may be presumed
that IVa, IVb and similar quinonoid structures
are contributing to the ground and electronically
excited states. The effect of substitution of
methyl groups for the ethylenic hydrogen atoms

IVa   IVb
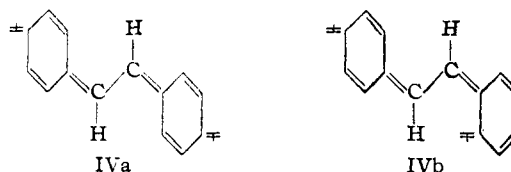
is illustrated in curves B and C of Fig. 3.[10] The
introduction of the first methyl group produces a
marked hypsochromic shift of the absorption maxi-
mum, while the second methyl group moves the
maximum still further in the same direction. The
spectra of styrene and α,β-dimethyl-trans-stilbene
differ only in the absence of vibrational fine
structure in the spectrum of the latter compound
(Curves A and C of Fig. 2).

The spectrum of asym-diphenylethylene has
been recorded by Lardy[13] and by Ramart-Lucas
and Amagat.[14] As the curves of these two observ-

(9) Robertson and Woodward, Proc. Roy. Soc. (London), A162,
568 (1937).
(10) Arends, Ber., 64, 1936 (1931).
(11) Smakula and Wassermann, Z. physik. Chem., A155, 353
(1931).
(12) Lewis, Magel and Lipkin, THIS JOURNAL, 62, 2973 (1940).
(13) Lardy, "Tables Annuelles de Constantes et Données Numér-
iques," Vol. VII, (1), 797 (1925-1926).
(14) Ramart-Lucas and Amagat, Bull. soc. chim., [4] 51 108 (1932).
It would appear that curves 2 and 5 of Fig. 2 of this paper, which are
attributed to asym-diphenylethylene and trans-stilbene should be
transposed. Unless this is done the curves do not agree with those

ers did not agree, the spectrum, has been redetermined in these Laboratories.[15] The curve (D of Fig. 2) resembles that of Lardy, and is closely similar to the spectrum of styrene and of α,β-dimethyl-*trans*-stilbene.

The spectra of triphenylethylene and of tetraphenylethylene have been recorded by Arends[10] (curves B and C of Fig. 4) and differ only slightly from the spectrum of *trans*-stilbene.
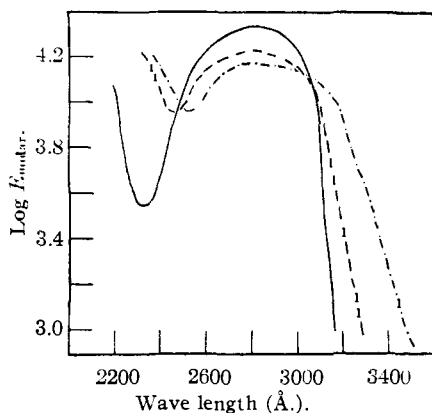
Fig. 4.— ———— Curve A, *trans*-stilbene (chloroform);
– – – – Curve B, triphenylethylene (chloroform);
– · – · – · – Curve C, tetraphenylethylene (chloroform).

These observations may be summarized in the statement that the substitution of one or more of the ethylenic hydrogen atoms of styrene and of *trans*-stilbene by phenyl groups does not necessarily produce a change in the chromophore, in spite of the apparent increase in the length and complexity of the conjugated system. The spectra of these compounds fall into two classes, depending on whether they exhibit a styrene or a *trans*-stilbene type of spectrum, as shown in Table II.

TABLE II

CLASSIFICATION OF THE SPECTRA OF ARYLETHYLENES[a]

Group I Styrene chromophore	Group II *trans*-Stilbene chromophore
Styrene	*trans*-Stilbene
asym-Diphenylethylene	Triphenylethylene
α,β-Dimethyl-*trans*-stilbene	Tetraphenylethylene

[a] The spectra of α-methyl-*trans*-stilbene and of *cis*-stilbene are intermediate between the two types.

The reasons for the restriction to two chromophoric types become apparent when due consideration is given to the steric factors involved.

recorded for these compounds by other workers; neither do they agree with the statement of the authors that "la courbe d'absorption du carbure symétrique est, comme on peut le voir, plus proche du visible que celle de son isomère dissymétrique."

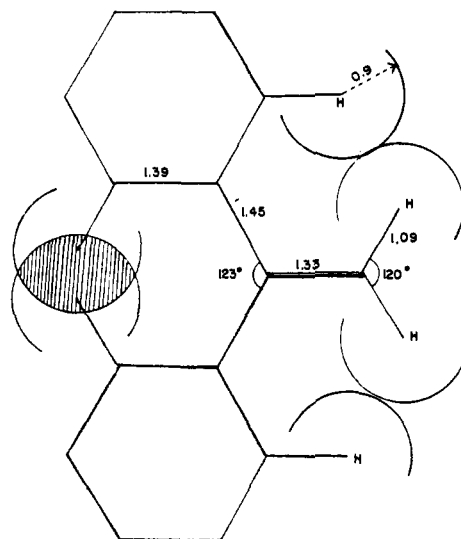(15) I wish to thank Mr. C. J. Gogek for preparing this compound.

Fig. 5.—*asym*-Diphenylethylene, diagram illustrating interference between ortho hydrogen atoms. The radius of the hydrogen atom has been taken as 0.9 Å., the "Wirkungsradius," r_t, of Stuart (*Z. physik. Chem.*, **B27**, 350 (1934)), instead of the van der Waals radius of 1.20 Å. The smaller hydrogen radius leads to better agreement between the diagrams and the estimates of atomic interference suggested by Stuart or Fisher–Hirshfelder models
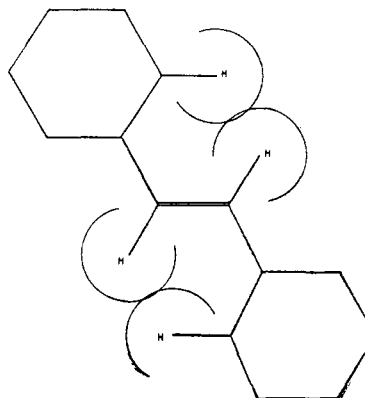
Fig. 6.—*trans*-Stilbene, diagram illustrating strainless planar configuration.

Figures 5 and 6 are approximately scale diagrams of the molecules of *asym*-diphenylethylene and *trans*-stilbene, assuming for each a planar structure. While such a structure is strainless for *trans*-stilbene, this is not true for *asym*-diphenylethylene, as interference occurs between the *ortho* hydrogen atoms of the two benzene rings. This strain may be relieved either by an increase of the angle between the bonds joining the two phenyl groups to the α-ethylenic carbon atom, or by the rotation of the benzene rings out of the plane of the ethylenic bond about their 1,4-axes.

Coates and Sutton[16] have shown, by dipole moment measurements, that the angle between the bonds is 125 ± 3°, which is insufficient to allow the two phenyl groups to be coplanar. They estimate that the rings are displaced by about 30° from the common plane. Such a displacement may involve only one of the phenyl groups, leaving the other coplanar with the ethylenic linkage or, alternatively, a lesser rotation of both of the benzene rings may occur. These displacements of either benzene ring will be opposed by a potential energy gradient resulting from the resonance stabilization energy contributed by the canonical structures of the type shown in IIa and IIb. At present we have no information available regarding the relative increase in potential energy which would result from these two alternative methods of meeting the restrictions imposed on the structure by steric necessities. The close similarity between the spectra of asym-diphenylethylene and styrene would be most readily explained by a rotation of one phenyl group only, giving rise to a molecule containing a styrene chromophore and a phenyl chromophore (V). The latter


V
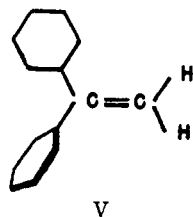
would have no appreciable influence on the resultant spectrum on account of its low relative intensity. This hypothesis requires that the two phenyl groups are not structurally equivalent to each other in asym-diphenylethylene; the activation energy necessary to accomplish an exchange of role of the two phenyl groups will be quite small, but it should give rise to a characteristic absorption band in the infrared.

In α,β-dimethyl-trans-stilbene the methyl substituents cannot be accommodated in a planar stilbene structure; experiments with Fisher-Hirschfelder atom models suggest that it is possible to release most of this strain by the rotation of one of the phenyl groups only[17] leaving a structure containing a styrene and a phenyl chromophore, comparable with the system in the strainless asym-diphenylethylene molecule.

(16) Coates and Sutton, J. Chem. Soc., 567 (1942).
(17) In this form there may be restricted rotation about the bonds joining the methyl groups to the carbon atoms of the ethylene bond.

In a similar manner it is possible to explain the presence of the trans-stilbene chromophore in the spectra of compounds of Group II of Table II. The three phenyl groups of triphenylethylene and the four phenyl groups of tetraphenylethylene cannot be accommodated in a strainless planar structure; the strain can be eased either by a small rotation of all of the phenyl groups along their 1,4-axes, or by a larger displacement of one of the phenyl groups of triphenylethylene or two of the trans-related phenyl groups of tetraphenylethylene, leaving two remaining trans-phenyl groups in the plane of the ethylene bond (VIa). This second hypothesis leaves the molecule of tetraphenylethylene with a trans-stilbene chromophoric system together with two "insulated" phenyl groups, the absorption of which is too feeble to affect the spectrum. If such a structure is correct, one pair of trans phenyl groups must differ from the other pair. Resonance degeneracy between the structures VIa and VIb cannot occur

VIa   VIb
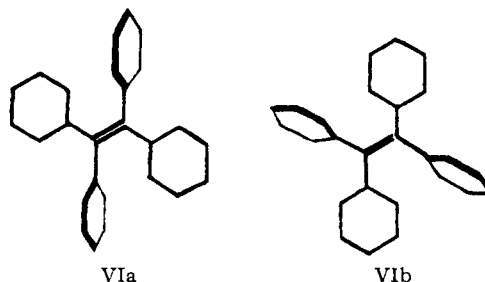
since the conversion of the one into the other requires a rotation of all the phenyl groups or a rearrangement of the atoms of the ethylenic bond. The energies associated with the interchange between these forms will be small, however, and should give rise to characteristic structure in the infrared. This type of mobile isomerism resembles, in some respects, that postulated by Lewis, Magel and Lipkin[18] for the crystal violet ion, in which the existence of two isomers is predicted, in one of which the three phenyl groups have complete screw or radial symmetry while the other has a form like a three-bladed propeller in which one of the blades is turned in the opposite direction from the other two blades.

The Spectrum of Tetra-(9-phenanthryl)-ethylene.—In this molecule the same steric factors are operative as in tetraphenylethylene, but the effects produced are more marked because of the greater size of the substituent group and the

(18) Lewis, Magel and Lipkin, THIS JOURNAL, 64, 1774 (1942).

VII   VIIa
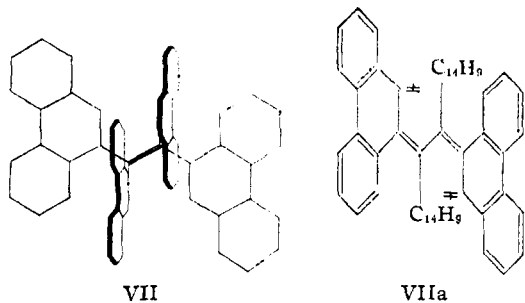
greater intensity of the phenanthrene chromophore compared with that of benzene. From Fig. 7 it is evident that in a planar arrangement of the molecule there will be an overlap of a whole benzene ring, and in the strainless structure (VII) two *trans* related phenanthrene groups will lie in a plane approximately normal to the plane of the other two phenanthrene groups and the ethylenic bond.

The region between 2400 and 2600 Å. in the spectrum of tetra-(9-phenanthryl)-ethylene is very similar to that of phenanthrene; the intensity of the maximum at 2520 Å. is almost exactly four times that of the phenanthrene maximum at the same wave length, as would be expected if each of the four phenanthryl groups in the molecule were behaving as an independent phenanthrene chromophore. The absorption in this part of the spectrum must be due, therefore, to electronic activations centered within the phenanthrene ring system, and not influenced by conjugation with the ethylenic group. Furthermore, since the position of the absorption maximum is the same as in phenanthrene, the energy difference between the ground and the activated states corresponding with this transition must be closely the same in the two molecules. The resonance stabilization energy derived from the contributions of quinonoid canonical structure such as VIIa (which lowers somewhat the energy of the ground state) must be negligible in comparison with the energy difference between the ground state and the activated state concerned in this transition.

The absorption between 3200 and 4000 Å., which has no counterpart in the phenanthrene spectrum may be attributed to the effect of resonating structures such as VIIa.

The region between 2800 and 3000 Å. in the spectrum of tetra-(9-phenanthryl)-ethylene contains fine structure bands at 2860 and 2990 Å. corresponding closely in position to two bands in the phenanthrene spectrum, but showing en-

hanced intensity. A third fine structure band at 2750 Å., prominent in the phenanthrene spectrum is missing. These maxima may be due to a third primary electronic activation process, but are more probably vibrational sub-levels associated with the electronic activation responsible for the 2520 Å. maximum. An explanation of the increase in intensity without shift of position of the maxima must await a better understanding of the factors which govern the probability of occurrence of electronic transitions. It may result from the superposition of a second component, an extension of the 3200–4000 Å. band further into the ultraviolet region.

Fig. 7.—Tetra-(9-phenanthryl)-ethylene, diagram illustrating overlap of one benzene ring in a planar configuration.

Experimental.—The spectrum of tetra-(9-phenanthryl)-ethylene was determined in a solution of ethanol–dioxane containing 12% of dioxane, by a method which has been described previously.[19] The spectrum of *asym*-diphenylethylene was determined on a Beckman spectrophotometer. *asym*-Diphenylethylene was prepared by a standard method[20] (b. p. 134–134.5° (10 mm.); $n^{20}D$ 1.6100).

Acknowledgment.—The author wishes to express his thanks to Professor L. F. Fieser, of Harvard University, in whose laboratory the spectrum of tetra-(9-phenanthryl)-ethylene was determined; to Dr. F. Bergmann for his coöperation in supplying the sample of tetra-(9-phenanthryl)-ethylene and to the International Cancer Research Foundation for financial assistance.

Summary

The ultraviolet absorption spectrum of tetra-(9-phenanthryl)-ethylene is recorded, and compared with that of a four molar solution of phenanthrene. These observations draw attention to the factors influencing the absorption spectra of arylethylenes, and it is shown that substances of the general formula $R_1R_2C{=}CR_3R{:}C_6H_5$ where R_1, R_2, and R_3 may be H or C_6H_5-, can be di-

(19) Jones, THIS JOURNAL, **62**, 148 (1940).

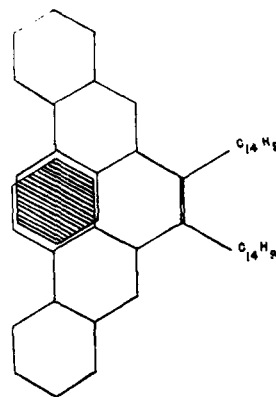(20) "Organic Syntheses," **18**, 87 (1921); Coll. Vol. 1, p. 221.

vided into two groups depending on whether their spectra resemble that of styrene or of *trans*-stilbene. *cis*-Stilbene, which has a spectrum intermediate in character between the two types, is the only exception to this generalization. An ex-

planation of this optical behavior is offered, based on a consideration of the steric factors which interfere with the attainment of the most stable resonance structures.

KINGSTON, CANADA   RECEIVED MAY 24, 1943

Rates and Temperature Coefficients of the Hydroxyl Ion Catalyzed Aldol Condensation of Benzaldehyde with Methyl Ethyl Ketone and Acetone[1]

BY JOSEPH D. GETTLER AND LOUIS P. HAMMETT

In principle and in fact,[2] a symmetrical ketone such as acetone may condense with one mole of benzaldehyde in only one way to form a primary condensation product, benzalacetone. On the other hand, it is possible for an unsymmetrical ketone, such as phenylacetone or methyl ethyl ketone, to condense with one mole of benzaldehyde to yield two isomeric ketones. Goldschmidt[3] studied the reaction between phenylacetone and benzaldehyde and reported that in acid medium stibyl methyl ketone was formed while in alkaline medium cinnamyl benzyl ketone was formed. Levinstein[4] reported that in alkaline media the methyl ethyl ketone condensation occurred at the methylene carbon. He made no mention, however, of the formation of an isomeric compound formed in acid media. In contradistinction to this Müller and Harries[5] showed that in alkaline solutions a compound which they named alpha-benzalmethyl ethyl ketone is formed while in acid media the isomeric gamma compound is formed. Ryan and Devine[6] and Massara and Di Leo[7] concerned themselves chiefly with the study of the reaction products involving more than one mole of benzaldehyde. Not one of the above-mentioned investigators, however, studied the reaction with a view of finding conditions under which the primary reaction products would be produced alone to the exclusion of higher products.

Nikitin[8] followed kinetically the reaction of benzaldehyde with acetone and reported that the

aldehyde is involved to the second power in the kinetic equation while Coombs and Evans[9] studied the reaction between acetophenone and benzaldehyde and showed it to be kinetically bimolecular, the velocity also being proportional to the concentration of the catalyst. Bell[10] found the aldolization of acetaldehyde to be first order with respect to the aldehyde and approximately a linear function of the catalyst. All these investigations were concerned with the base catalyzed reaction.

Since the authors of the present paper were primarily interested in the mechanism and kinetics of formation of the isomeric primary condensation products of the methyl ethyl ketone reaction, it was essential to repeat all the past synthetic work in order to establish under just what conditions one may obtain a reaction yielding only primary condensation products with no higher products or resins and to select a suitable solvent for the kinetic experiments.

Experimental

Synthetic Part.—The earlier workers[5,6,7] in the field reported besides the two primary condensation products, (A) α-benzalmethyl ethyl ketone and (B) γ-benzalmethyl ethyl-ketone, the existence of several other higher condensation products. These include (C) $C_{18}H_{18}O_2$, 1,5-diphenyl-4-methyl-pentene-1-one-3-ol-5; (D) $C_{25}H_{20}O$, tribenzal-methyl ethyl ketone; (E) $C_{18}H_{17}OCl$, 1,5-diphenyl-4-methyl-5-chloropentene-1-one-3.

The synthetic work of Müller and Harries[5] involving the acid and base catalyzed reaction between benzaldehyde and methyl ethyl ketone was repeated in detail during the present research. Its scope was materially extended by studying the effect of the initial concentration of the reactants on the nature and yield of the products. The experimental results are presented in tabular form.

From the data in Tables I and II the following conclusions may be drawn: (1) In both the acid and base condensations, as the ratio of aldehyde to ketone approaches

(1) Dissertation submitted by Joseph Daniel Gettler in partial fulfillment of the requirements of the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

(2) Claisen and Ponder, *Ann.*, **223**, 139 (1884).

(3) Goldschmidt and Krczmar, *Monatsh.*, **22**, 657 (1901); Goldschmidt and Knopfer, *ibid.*, **18**, 437 (1897); **19**, 406 (1898).

(4) Levinstein, Inaug. Diss., Berlin, Jan. 29, 1902.

(5) Müller and Harries, *Ber.*, **35**, 966 (1902).

(6) Ryan and Devine, *Proc. Roy. Irish Acad.*, **32**, 208 (1916).

(7) Massara and Di Leo, *Gazz. chim. ital.*, **63**, 199 (1933).

(8) Nikitin, *J. Gen. Chem. (U. S. S. R.)*, **7**, 9 (1937).

(9) Coombs and Evans, *J. Chem. Soc.*, 1295 (1940).

(10) Bell, *ibid.*, 1637 (1937).