of aza-aromatic heterocycles toward allylmagnesium bromide with the stability of the dihydro derivatives formed upon hydrolysis. The dihydro derivatives of allyl-acridine and -phenanthridine were quite stable, and the parent heterocycles showed high reactivity. On the other hand, pyridine had a low activity and the instability of the dihydro derivatives is well known.23 This view also helps to clarify why the 4-position, rather than the 2-position, of pyridine is attacked. The superior stability of 1,4-dihydropyridine over 1,2-dihydropyridine<sup>23</sup> means, in view of our explanation, that the activation energy (hence, the localization energy) may be lower for attack at the 4position. This correlation might be placed on a quantitative basis for selective nucleophiles, in general, if the localization energies for the various dihydro derivatives were known.24

(23) J. A. Berson and E. Brown, THIS JOURNAL, 77, 444 (1955).

(24) A referee has suggested reasonably that allylmagnesium bromide may initially attack the 2-position of pyridine via a cyclic mechanism analogous to the Claisen rearrangement and rearrange to the 4position via a para-Claisen process. Indeed, such a possibility has been considered by the authors; however, they feel that such a view would be inconsistent with the behavior of unsymmetrical allylic systems in these processes. For example, benzylmagnesium chloride reacts with quinoline and isoquinoline to yield benzyl-substituted products. A cyclic mechanism would demand that o-tolyl derivatives result (cf. ref. 4)



In addition, ortho attack on acridine is extremely improbable and yet para attack occurs smoothly. Hence, it is not necessary to postulate an initial ortho attack. Another possibility considered by the authors is that the complex between pyridine and the Grignard reagent hinders attack at the 2-position. Although such steric factors may play a

Although we have offered an explanation for the attack of allylmagnesium bromide at the 4-position in pyridine, we must now consider why the similar butyllithium prefers the 2-position. For electrophilic attack on aromatic systems Brown<sup>25</sup> has noted an inverse relationship between the selectivity of an agent in choosing meta- or para-positions in toluene and its rate relative to benzene. This leads to the conclusion that the more reactive reagents react by way of looser transition states which are relatively insensitive to factors such as localization energy. Clearly, by applying this argument to nucleophilic attack on nitrogen heterocycles, this implies that the extremely reactive butyllithium in its reaction with pyridine will attain a transition shifted toward the reactants. Hence, factors such as charge density and autopolarizability of the initial pyridine molecule will become more important in determining the position attacked. Since both factors favor attack at the 2-position,<sup>17</sup> butyllithium readily gives the 2butyl-1,2-dihydrolithium salt.

It also follows from Brown's correlation<sup>24</sup> that since allylmagnesium bromide is more selective than butyllithium, it is less reactive. Supposing that the two reagents have roughly the same ionic character, the greater reactivity of the butyl carbanion is understandable, since it cannot participate in the sort of  $\pi$ -electron stabilization avail-

able to the allyl carbanion,  $CH_2$ -CH=CH<sub>2</sub>  $\leftrightarrow$ CH<sub>2</sub>=CH- $CH_2$ .

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part, this view is weakened by the observation that quinoline which also forms a complex is readily attacked at the 2-position.

(25) H. C. Brown and K. L. Nelson, THIS JOURNAL, 75, 6202 (1953). AMES, IOWA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF ILLINOIS INSTITUTE OF TECHNOLOGY]

## The Reactions of Diazonium Salts with Some Substituted Hydrazines. II. 1,6-Bisaryl-3,4-diacetyl-1,5-hexazadienes<sup>1,2</sup>

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The addition of two moles of a negatively substituted benzenediazonium salt to an alkaline solution of 1,2-diacetylhydrazine affords a 1,6-bisaryl-3,4-diacetyl-1,5-hexazadiene (I). The structure of I is established from degradative evidence.

The sole claim to the successful preparation of a (1) This work was supported by a grant from the Office of Ordnance Research, Contract DA-11-022-ORD-1276, Project TB-2-0001. (2) Previous communication on this subject, J. Org. Chem., 19, 194 (1954).

(3) Abstracted in part from a dissertation submitted by Vytautas A. Grakauskas to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

stable chain of six nitrogen atoms is contained in a report by Hofmann and Hock who obtained 1,6bis- (5'-tetrazolyl)-1,5-hexazadiene from the interaction of hydrazine and excess tetrazolediazonium chloride.<sup>4</sup> Unfortunately, the evidence in support of this structure is not unequivocal, and hence the

(4) K. A. Hofmann and H. Hock, Ber., 44, 2946 (1911).

Τ.

question as to the existence of a stable 1,5-hexazadiene remains unanswered.5

Prior to the work of Hofmann and Hock, Dimroth considered the possibility of converting a 1,6bisaryl-3,4-diacyl-1,5-hexazadiene (I) to a pentazole derivative.6 However, all attempts to prepare the requisite starting material were unsuccessful and the study apparently was abandoned.

It appeared of interest to reinvestigate the possibility of preparing a stable hexazadiene as an extension of our recent study of the formation of 1,5disubstituted tetrazoles from the interaction of a diazonium salt and a diacylhydrazine.<sup>2</sup> Accordingly, it was found that the addition of two moles of p-chlorobenzenediazonium chloride to an aqueous sodium carbonate solution of 1,2-diacetylhydrazine afforded a white solid whose elementary analysis conformed to 1,6-bis-(p-chlorophenyl)-3,4-diacetyl-1,5-hexazadiene (Ia). A modified Rast molecular weight determination<sup>7</sup> proved sufficiently close to that calculated for Ia so as to exclude 1-(p-chlorophenyl)-3-acetyltriazene (IVa) which is the only other plausible structure consis-tent with the analysis. It was subsequently observed that Ia is cleaved by warm alcoholic potassium hydroxide into p-chlorophenyl azide (IIa) and p-chloroaniline (IIIa). Distillation provided a crude separation of these degradation products and, from infrared spectrophotometric analysis, it was established that one mole of each IIa and IIIa is produced in the alkaline degradation of Ia.

A sample of Ia was next refluxed with alcoholic potassium hydroxide and the volume of evolved nitrogen measured in a nitrometer according to the procedure described by Siggia and Lohr<sup>8</sup>; 97% of the theoretical amount of nitrogen was collected within two hours. Thus all of the nitrogen contained in the original molecule Ia is accounted for in the degradation products ( $N_2$ , IIa and IIIa).

The hydrolysis of Ia with alcoholic potassium hydroxide was next performed at 5°. After approximately ten minutes the reaction was quenched with water and the mixture acidified. Under these modified conditions, two products were obtained: a yellow oil identified as *p*-chlorophenyl azide (IIa) (94% yield) and an equivalent yield of a white solid whose elementary analysis conformed to 1-



acetyl-3-(p-chlorophenyl) triazene (IVa). When a sample of IVa was warmed for a brief period with alcoholic potassium hydroxide, and the reaction mixture steam distilled, the distillate afforded IIIa in 75% yield. In a separate experiment, it was found that one mole of nitrogen is liberated on

(5) A reinvestigation of the original study will be the subject of a future communication.

(7) K. Rast, *ibid.*, **55**, 1051 (1922).
(8) S. Siggia and L. J. Lohr, J. Anal. Chem., **21**, 1201 (1949).

treatment of IVa with warm alcoholic potassium hydroxide.

The collection of the theoretical amount of nitrogen together with the isolation of IIIa substantiates the triazene structure (IVa) initially suggested by the elementary analysis. In addition, this evidence in connection with the observations described in the preceding paragraphs, suggest a relatively simple mechanism for the alkaline degradation of Ia. The proposed path is outlined below and requires no additional comment.

CHART I ale, KOH RCON N=N-Ar Ar-0 H<sub>0</sub>O

$$ArN_3 + [RCON - N = NAr \leftrightarrow RCON = N - NAr] \longrightarrow$$

In examining the scope of the reaction by which Ia was obtained, it was observed that benzene-, p-toluene- and p-anisolediazonium chlorides, on treatment with diacetylhydrazine, yield only illdefined products. On the other, p-bromo- and p-nitrobenzenediazonium chloride both afford stable 1,5-hexazadienes (Ib,c).

The interaction of 1,2-diacetylhydrazine and 2,5-dichlorobenzenediazonium chloride produced a considerable amount of 1-(2,5-dichlorophenyl)-3,4-diacetyltetrazene (Va) in addition to Id. The presence of Va was established from the observation that treatment of the mixture of coupling products with alkali afforded 1-(2,5-dichlorophenyl)-5-methyltetrazole (VIa) in 37% over-all yield. That the tetrazene (Va) must be the precursor of VIa is evident from the further observation that Id



is unaffected by the conditions necessary to bring about the cyclization of a tetrazene to a tetrazole.<sup>2</sup>

The majority of the 1,6-bisaryl-3,4-diacetyl-1,5hexazadienes (Ib,d,e,f) were successfully converted to the corresponding triazenes (IVb,c,d,e) in nearly quantitative yield on treatment with cold ethanolic potassium hydroxide.

Attempts to extend this study to include 1,5hexazadienes derived from 1,2-diformylhydrazine met with only moderate success. Thus, 1,6-bisp-chlorophenyl-3,4-diformyl-1,5-hexazadiene (Ie) was obtained in only 8% yield. Furthermore, this coupling reaction is apparently a much slower

<sup>(6)</sup> O. Dimroth and G. deMontmollin, Ber., 43, 2904 (1910).

TABLE I				
Some 1,6-Bisaryl-3,4-diacetyl-1,5-hexazadienes	ArN=N-1	NN	-N=1	JAr

I	M.p., dec., °C.	Vield, %	RCO OCR (I)						
			Formula	Carbo Caled.	n, % Found	Hydro Caled.	gen, % Found	Nitrog Caled.	en, % Found
a	132-133	70-80	$C_{15}H_{14}Cl_2O_2N_5$	48.86	48.92	3.60	3.61	21.38	21.51
b	146 - 147	70-80	$C_{16}H_{14}Br_2O_2N_6$	39.85	39.82	2.93	3.21	17.43	17.42
с	168 - 169	30 - 40	$C_{16}H_{14}O_6N_8$	46.38	46.18	3.41	3.22	27.05	26.89
d	178 - 179	20 - 30	$C_{16}H_{12}Cl_4O_2N_6$	41.58	41.83	2.62	2.87	18.19	18.28
e	124 - 125	15 - 20	$C_{14}H_{10}Cl_2O_2N_6$	46.04	45.86	2.76	2.64	23.02	23.31
f	128 - 129	10 - 15	$C_{14}H_{10}Br_{2}O_{2}N_{\pmb{6}}$	37.03	37.60	2.22	2.38	18.51	19.22

Table II

## Some 1-Arvl-3-acyltriazenes, ArN=N-NHOCR (IV)

TV	M.p., dec.,	Vield,	Transa la	Carbon, %		Hydrogen, %		Nitrogen, %	
1 V	С,	70	rornula	Calca.	Found	Caled.	Found	Caled.	Found
а	122 - 123	95	C <sub>8</sub> H <sub>8</sub> ClON <sub>3</sub>	48.62	48.73	4.08	4.27	21.26	21.14
b	108-109	90	C <sub>8</sub> H <sub>8</sub> BrON <sub>3</sub>	39.69	40.04	3.33	3.44	17.36	17.25
с	165 - 166	70	$C_8H_7Cl_2ON_3$	41.40	41.60	3.04	3.28	18.11	17.93
d	140 - 141	62	$C_7H_6C1ON_3$	45.79	45.85	3.29	3.38	22.89	22.94
e	133-134	53	C7H6BrON3	36.87	37.23	2.65	2.61	18.44	18.82

process than the corresponding reaction of 1,2diacetylhydrazine. In the latter case the product (Ia) appeared almost immediately, whereas Ie began to form only after 20-30 minutes of constant stirring.

The interaction of p-bromobenzenediazonium chloride and 1,2-diformylhydrazine afforded a 1,5hexazadiene (If) which could not be completely purified even after several recrystallizations. However, the identity of If was established by conversion to the corresponding triazene (IVe). In addition, 1-(p-bromophenyl)-tetrazole (VIb) was isolated in the course of this same transformation which indicated that the original contaminant was the corresponding tetrazene (Vb).

Dark solids were obtained from the action of either p-nitro- or 2,5-dichlorobenzenediazonium chloride on 1,2-diformylhydrazine. Purification of these crude products led only to the isolation of 1-(p-nitrophenyl)- and 1-(2,5-dichlorophenyl)-tetrazole (VIc,d), respectively. Although the corresponding 1,5-hexazadienes were not detected, it seems reasonable to assume that they were formed in low yield, only to be lost in the process of purification.

The hexazadienes are only slowly decomposed by hot aqueous hydrochloric acid. However, these same compounds readily dissolve in cold concentrated sulfuric acid and, in a matter of a few minutes, the corresponding diazonium salt is regenerated. This reversal of the original coupling reaction was detected by pouring a sulfuric acid solution of Ia on ice and treating the mixture with 2-naphthol from which 4-chlorobenzeneazo-2-naphthol was obtained in quantitative yield.

The hexazadienes react with ethanol in a manner which parallels the behavior of diazonium salts. Thus Ia, for example, on refluxing with ethanol, afforded 1,2-diacetylhydrazine in quantitative yield and a 82% yield of acetaldehyde. However, it was impossible to detect the presence of either chlorobenzene or *p*-chlorophenetole. The large amount of tarry material which is formed during the course of this reaction and which is frequently observed in the reduction of diazonium salts by ethanol<sup>9</sup> would seem to indicate that the major part of the diazonium intermediate is resinified.

### Experimental<sup>10</sup>

1,6-Bisaryl-3,4-diacetyl-1,5-hexazadienes (Ia, b, c, d).— All of the hexazadienes reported in this study were prepared by addition of excess aromatic diazonium salt solution to an aqueous sodium carbonate solution of 1,2-diacetylhydrazine. The preparation of 1,6-bis-(p-chlorophenyl)-3,4-diacetyl-1,5-hexazadiene (Ia) is presented as a typical example. See Table I for the analyses, melting point and yield of the individual 1,5-hexazadienes.

A suspension of 44.4 g. of *p*-chloroaniline (0.35 mole) in 50 ml. of water was warmed on a steam-bath until all the solid had melted. To the heterogeneous melt was added 90 ml. of concentrated hydrochloric acid followed by the addition of 200 ml. of water, which gave a clear solution. A solution of 24.5 g. of sodium nitrite (0.35 mole) in 150 ml. of water was added dropwise with stirring and external cooling.

The diazonium salt solution was added all at once with mechanical stirring to an ice-cold solution of 18.3 g. of 1,2diacetylhydrazine (0.175 mole) in *ca*. 3000 ml. of 6.0% aqueous sodium carbonate. The resulting solution remained clear for a few seconds, then a voluminous precipitate appeared which was collected after 25 minutes of stirring. The filter cake was washed with liberal amounts of water and dried in a vacuum desiccator for three days. The crude, off-white solid was triturated with 200 ml. of cold absolute ethanol, filtered and washed with 150 ml. of ether; weight 49 g. (70%), m.p. 131-133°. An analytical sample was obtained by recrystallizing the latter from benzene to give a white crystalline solid.

The crude samples of Ia and Ib were conveniently purified with small losses by recrystallization from benzene. Recrystallization from an ethanol-ether mixture also afforded a pure product, but a 10-20% loss in material was observed with this solvent, presumably due to the reducing characteristics of ethanol toward this class of compound (*vide infra*). Both Ia and Ib may also be recrystallized from ether to give white crystalline solids. Ether, unlike ethanol or benzene, does not appear to decompose the small amounts of the corresponding 1-aryl-3,4-diacetyltetrazene present in the crude hexazadiene. Therefore, ether could only be used for recrystallization of samples which were previously purified from ethanol or benzene.

The purification of 1,6-bis-(p-nitrophenyl)-3,4-diacetyl-1,5-hexazadiene (Id) is somewhat difficult and required a slightly different technique. The crude reaction product was first triturated with warm ethanol, then recrystallized from benzene and finally recrystallized several times from diox-

<sup>(9)</sup> N. Kornblum, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 265.

<sup>(10)</sup> All melting points are uncorrected. The analyses are by Micro-Tech Laboratories, Skokie, Ill.

ane. The pure compound (Id) is a yellow amorphous solid melting at 168-169° (Fisher-Johns block) with decomposi-

tion or explosion. The crude 1,6-bis-(2,5-dichlorophenyl)-3,4-diacetyl-1,5hexazadiene (Ie) exhibited a melting point at 120-150° dec. Recrystallization from ether gave a slightly greenish crystalline solid, m.p. 156-158° dec., whose elementary analysis was in a fair agreement with the requirements of the structure. Further investigation, however, showed that this solid was in reality a mixture of Ic and 1-(2,5-dichlorophenyl)-3,4-diacetyltetrazene (VIa).

To show that VIa is present in the partially purified (m.p.  $156-158^{\circ}$  dec.) product, 1 g. of the mixture was suspended in 40 ml. of 3 N sodium hydroxide and the reaction mixture held at room temperature for 12 hours. The brown solid was collected, dissolved in 40 ml. of absolute ethanol and the ethanolic solution refluxed for two hours to destroy any 1,5-hexazadiene (Ic) still present. The solution was then boiled with Norit, filtered, concentrated to ca. 10 ml. and diluted with water. 1-(2,5-Dichlorophenyl)-5-methyltetrazole (VIa), a white crystalline solid, precipitated on standing; weight  $0.3 \text{ g., m.p. } 154-155^{\circ}$ . Anal. Calcd. for  $C_6H_6Cl_2N_4$ : C, 41.94; H, 2.64; N, 24.46. Found: C, 41.92; H, 2.66; N, 24.58.

From the quantity of tetrazole (VIa, 0.3 g.) obtained, it was estimated that the crude hexazadiene Ic contained at least 37% of tetrazene Va. 1,6-Bis-(p-bromophenyl)-3,4-diformyl-1,5-hexazadiene

(If) and 1-(p-Bromophenyi)-tetrazole (VIb).—The cold pbromobenzenediazonium chloride solution, prepared from 13.8 g. of p-bromoaniline (0.08 mole), was added all at once to an ice-cold solution of 3.5 g. of 1,2-diformylhydrazine (0.04 mole) in 800 ml. of 10% aqueous sodium carbonate. The reaction mixture turned cloudy and a brown semi-solid was slowly deposited. After one hour of stirring at 0°, the product was collected and washed first with water, then with 50-70 ml. of petroleum ether ( $40-60^{\circ}$ ). The solvent removed the brown tar present in the product and left a yellow solid, weight 2.2 g., m.p. 80-105° dec. The crude solid was dissolved in 600 ml. of warm ether and the deep yellow solution was decolorized with Norit. The filtrate was concentrated to 50 ml. at reduced pressure and then diluted to 150 ml. with petroleum ether. The slightly yel-low solid which deposited was collected; weight 1.3 g., m.p. 105-108° dec. The analytical sample was recrystallized first from ether, then from benzene to yield a white crystalline solid.

The initial aqueous filtrate was cooled in a refrigerator for four hours. A brown solid was collected, washed with water, sucked dry and the filter cake then washed with lib-eral amount of petroleum ether  $(40-60^\circ)$  to give a dark yellow powder, weight 2.0 g., m.p. 85–129°. The crude produced was dissolved in 50 ml. of benzene and the solution decolorized with Norit, and finally treated with 20 ml. of off-white solid precipitated, weight 0.9 g. (10% yield), m.p. 178–180°. An analytical sample was recrystallized from benzene to give white plates VIb, m.p. 182°.

Anal. Calcd. for C<sub>7</sub>H<sub>5</sub>BrN<sub>4</sub>: C, 37.35; H, 2.24; N, 24.90. Found: C, 37.40; H, 2.45; N, 24.92.

1-(p-Nitrophenyl)- and 1-(2,5-Dichlorophenyl)-tetrazole (VIc, d).-1,2-Diformylhydrazine on treatment with a two molar ratio of either p-nitro- or 2,5-dichlorobenzenedia-zonium chloride under the conditions described above, both yielded brown oily solids. When the crude reaction prod-ucts were purified, it was found that they were not the ex-pected 1,6-bis-(*p*-nitrophenyl)- and 1,6-bis-(2,5-dichloro-phenyl)-3,4-diformyl-1,5-hexazadienes, but rather VIc and VId, respectively.

The crude mixture containing VIc apparently contained large amounts of impurities, consisting presumably of 1,2diformyl-4-(p-nitrophenyl)-tetrazene and 1,6-bis-(p-nitrophenyl)-3,4-diformyl-1,5-hexazadiene. Several recrystallizations from absolute ethanol gave a yellow solid VIc, m.p. 202-204° (lit.<sup>5</sup> 205°) in 10-20% yield.

Anal. Calcd. for C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>N<sub>5</sub>: C, 43.98; H, 2.64; N, 36.64. Found: C, 44.23; H, 2.75; N, 37.00.

Similarly, the crude 1-(2,5-dichlorophenyl)-tetrazole (VIc), m.p. 70-120°, was isolated in 20% yield. Recrystallization first from aqueous ethanol and then from petroleum ether gave white microscopic needles, m.p. 134-135° in 5% yield.

Anal. Caled. for C<sub>7</sub>H<sub>4</sub>Cl<sub>2</sub>N<sub>4</sub>: C, 39.09; H, 1.87; N, 26.06. Found: C, 38.70; H, 1.93; N, 26.46.

Complete Hydrolysis of Ia: Isolation and Identification of Solid Products.—A solution of 5.9 g. of Ia (0.015 mole) in 40 ml. of 1 N ethanolic potassium hydroxide (0.04 mole) was warmed on a steam-bath for 10-15 minutes and then steam distilled. The distillate was saturated with sodium chloride, extracted with two 50-ml. portions of ether and the extract dried over anhydrous sodium sulfate. The ether was removed at atmospheric pressure and the residue, on distillation at reduced pressure, yielded two fractions: (a) 2.48 g., b.p. 78-81° (7 mm.) and (b) 1.28 g., b.p. 90-91° (7 mm.).

Infrared measurements indicated that fraction "a" was chiefly p-chlorophenyl azide (IIa) contaminated with some p-chloroaniline (IIIa), while fraction "b" was almost pure IIIa contaminated with a small amount of IIa azide. Solutions of known concentration of p-chlorophenyl azide in carbon disulfide were prepared and a Beer's law plot of the percentage transmittancy of the azide vibration (2090 cm. $^{-1}$ ) vs. concentration afforded a fairly straight line over the desired concentration. From this plot, fraction "a" was calculated to be 70% (0.013 mole) of IIa and 30% (0.006 mole) of IIIa (by difference). As a check on the value obtained by difference, a similar plot was prepared employing known concentrations of *p*-chloroaniline. Using an N-H deformation frequency (1612 cm.<sup>-1</sup>), the amount of IIIa in fraction "a" was found to be 34% (0.0064 mole). Fraction "b" was washed with 3.0 ml. of petroleum ether (40-60°) to give 1.05 g. of IIIa (0.008 mole), m.p. 69-70

Thus from 0.015 mole of Ia, 0.014 mole of IIa and 0.013 mole of IIIa were obtained.

Gasometric Studies.—The apparatus and procedure for collecting the nitrogen is essentially that described by Siggia and Lohr.<sup>6</sup> A sample of Ia (0.393 g., 1 millimole) was weighed out and transferred to the reaction flask. Carbon dioxide was passed through the system for about one hour and then alcoholic potassium hydroxide (0.2 g., in 30 ml. of)absolute ethanol) was introduced into the reaction flask from a dropping funnel. The mixture was heated to reflux and held at this temperature while a steady stream of carbon dioxide was bubbled through the system for 110 During this period the nitrogen was collected in a minutes. gas buret filled with 50% potassium hydroxide and volume measurements were recorded at five-minute intervals. The final volume, after correcting for the blank and reducing to standard conditions, amounted to 21.5 ml. or 96% of the theoretical value.11

Partial Hydrolysis of Ia: 1-Acyl-3-aryltriazenes (IV).-A typical procedure for the degradation of a 1,5-hexazadiene to the corresponding triazene is illustrated by the following example.

To 70 ml. of 0.3 N ethanolic potassium hydroxide were added 3.0 g. of Ia (0.0078 mole) at  $10-15^\circ$ . After ten minutes of stirring, the yellow solution was cooled to  $0^\circ$ , diluted to 400 ml. with water and acidified with dilute hy-drochloric acid. The mixture was then cooled in an icewater-bath for 30 minutes and the yellow solid collected. The crude material was first washed with cold  $(0^{\circ})$  water and then with 20 ml. of petroleum ether  $(40-60^{\circ})$ ; weight 1.42 g. (95% yield), m.p. 121–123°. A single recrystalliza-tion from *ca*. 300 ml. of petroleum ether gave 1.25 g. of 1-acetyl-3-(*p*-chlorophenyl)-triazene, m.p. 122–123° (*cf*. Table II for analyses).

The aqueous filtrate and the petroleum ether washings of IVa were combined and extracted with two 25-ml. portions of petroleum ether. The combined extracts were dried over anhydrous sodium sulfate. The solvent was then removed at atmospheric pressure and the residue distilled at reduced pressure to give 1.1 g. (94% yield) of p-chlorophenyl azide, b.p. 78-81° (7 mm.). The infrared spectrum of the latter was superimposable with that of an authentic sample of pchlorophenyl azide.

A sample of IVa (0.5 g., 0.0026 mole) was dissolved in 5.0 ml. of 2 N ethanolic potassium hydroxide and the solution warmed on a steam-bath until the original deep yellow color of the mixture had changed to a straw-like color. The addition of 50 ml. of water with cooling gave 0.24 g. (75% yield) of *p*-chloroaniline, m.p. 68-69° alone, or when mixed with an authentic sample.

<sup>(11)</sup> While the actual concentration of KOH in a stream of CO2 is low, it is apparently adequate to effect the degradation.

Another sample of IVa (0.13 g., 0.68 millimole) was hydrolyzed with 25 ml. of 0.12 N ethanolic potassium hydroxide (0.003 mole) and the nitrogen collected in a manner similar to that already described. The corrected volume of nitrogen amounted to 16.8 ml. or to 97% (17.3 ml., 0.68 millimole) of the theoretical value.

Uncoupling of 1,6-Bis (*p*-chlorophenyl)-3,4-diacetyl-1,5hexazadiene (Ia) with Concentrated Sulfuric Acid.—To 5.0 ml. of cold concentrated sulfuric acid was added portionwise 0.5 g. of 1,6-bis-(*p*-chlorophenyl)-3,4-diacetyl-1,5hexazadiene (Ia) (0.0013 mole). When all the solid had dissolved, the sulfuric acid solution was poured on 50 g. of cracked ice. The resulting solution was added to a cold alkaline solution of 2-naphthol. A deep red precipitate was deposited which was collected, washed with water and dried in a vacuum desiccator. Recrystallization from ethanol gave 0.64 g. (97% yield) of 4'-chlorobenzeneazo-2naphthol, m.p. 158-159° (lit.<sup>12</sup> 158-159°). Degradation of Ia with Ethanol.—To a three-necked found-bottomed flask equipped with a refux condenser. a

Degradation of Ia with Ethanol.—To a three-necked round-bottomed flask equipped with a reflux condenser, a gas inlet tube and containing 500 ml. of absolute ethanol, was added 23.6 g. (0.06 mole) of Ia. Two traps containing an acidified aqueous ethanol solution of 2,4-dinitrophenylhydrazine (0.07 mole) were connected in series and attached by means of a short piece of rubber tubing to the top of the

(12) K. J. P. Orton and R. W. Everatt, J. Chem. Soc., 93, 1020 (1908).

reflux condenser. The mixture was warmed slowly, the liberation of nitrogen being evident almost immediately with simultaneous hydrazone formation occurring in the first trap. After the evolution of gas had subsided, a slow stream of nitrogen was passed into the flask while the reaction mixture was maintained under gentle reflux (40 minutes).

The reflux condenser was detached and the solvent removed by distillation, the distillate being caught in one of the traps. The hydrazone was collected, recrystallized from ethanol and amounted to 26.9 g. (82% of theoretical amount), m.p. 146–147° alone and when mixed with an authentic sample of acetaldehyde 2,4-dinitrophenylhydrazone.

The tarry residue remaining in the still-pot yielded, on steam distillation, a few drops of a yellow oil and 0.1 g. of a white solid, m.p.  $300^{\circ}$ . Neither of these products was identified.

The clear aqueous solution remaining in the distillation flask was decanted from the tarry insoluble material and evaporated to dryness. The white residue was dissolved in 30 ml. of ethanol, treated with Norit and diluted to a volume of 180 ml. with absolute ether. The white solid which deposited was collected (weight 6.0 g., 95% yield) and identified from mixed melting points ( $137-139^\circ$ ) as 1,2-diacetylhydrazine.

CHICAGO, ILLINOIS

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# Configuration of Free-Radicals. Non-stereospecificity of cis- and trans-2-Butene-Sulfur Dioxide Copolymerizations

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Evidence is presented that demonstrates the copolymerization of *cis*- and *trans*-2-butene with sulfur dioxide is not stereo-specific.

#### Introduction

A pyramidal structure for free radicals is indicated by two experiments in the 1-bicyclo-[2,2,1]heptyl system. Kharasch, Engelmann and Urry<sup>3</sup> found that the decomposition of the peroxide of 1-apocamphanecarboxylic acid in carbon tetrachloride produced 1-chloroapocamphane, and Blickenstaff and Hass<sup>4</sup> found that the nitro products from the high temperature nitration of bicyclo-[2,2,1]heptane were 50% 1-nitro compound.

A considerable body of evidence<sup>5</sup> has accumulated relative to the stereochemistry of free radicals which are not constrained to a rigid pyrmiadal configuration by a bicyclic system. Omitting from this discussion all consideration of radicals in which resonance requirements demand a planar configuration, the conclusion that follows from the main body of evidence is that non-bicyclic free

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 $(3)\,$  M. S. Kharasch, F. Engelmann and W. H. Urry, This Journal,  $\boldsymbol{65},\,2428$  (1943).

(4) R. T. Blickenstaff and H. B. Hass, ibid., 68, 1431 (1946).

(5) For references to much of the pertinent literature, see: (a) P. S. Skell and R. C. Woodworth, *ibid.*, **77**, 4638 (1955), (b) G. A. Russell, *ibid.*, **78**, 1038 (1956), (c) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 443, and (d) R. L. Shriner, R. Adams and C. S. Marvel, "Organic Chemistry (Gilman)," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 383.

radicals are either planar or, if they are pyramidal, inversion takes place more rapidly than any reaction which converts the radical center to a stable tetracovalent atom. For example, the 3-trichloro- $CCl_3$ 

methyl-2-butyl radical,<sup>5a</sup> CH<sub>3</sub>CH–D–CHCH<sub>3</sub>, suffers complete equilibration among all rotational conformations of both diastereomeric forms more rapidly than the radical reacts with bromotrichloromethane.

## Stereospecificity in Radical Reactions

A critical examination of the exceptions to the generalizations stated above is the main object of this paper.

One of us (P.S.S., 1947<sup>6</sup>) observed that the reaction of ethyl (-)- $\alpha$ -bromopropionate ( $\alpha D - 3.78^{\circ}$ , neat, 1 dcm.) with 1-butene in the presence of small amounts of acetyl peroxide<sup>6</sup> produced ethyl  $\alpha$ -methyl- $\gamma$ -bromocaproate ( $\alpha D - 0.07^{\circ}$ , neat 0.25 dcm.). In view of the experimental results reported in the present paper, the slight activity observed in the product is better explained by asymmetric induction than by a stable enantiomorph of the free radical.

(6) These experiments are mentioned here because references to this unpublished work have appeared in the literature. For details regarding this type of preparation see, M. S. Kharasch, P. S. Skell and P. Fisher, THIS JOURNAL, **70**, 1055 (1948).