genated over platinum; reduction was stopped after the uptake of 1.15 molar equivalents of hydrogen. Recrystallization of the crude product from ethanol gave colorless needles, m.p. 107–108° (lit. 105–106°,[5] 110°[32]), $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.74 μ.

Condensation of Acetone with Benzaldehyde.—Benzaldehyde (20 g.) and acetone (5.4 g.) were heated with pulverized, freshly fused zinc chloride (10 g.), following the procedure of Lippmann and Fritsch.[6] Extraction of the resulting dark brown gum with ether and precipitation with a large volume of methanol gave a yellow-brown solid. Three recrystallizations of this material from ethyl acetate gave **dibenzalacetone** (1.8 g.) as yellow leaflets, m.p. 111–112°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 6.05 and 6.16 μ, identified by infrared spectral comparison and mixed m.p. with authentic dibenzalacetone,[33] m.p. 111.5–112°. **2,4-Dinitrophenylhydrazone:** deep red rods, m.p. and mixed m.p. 176–177° (lit.[34] 179–180°). On removal of ether and methanol from the original filtrate, a dark brown, resinous mass remained (16.5 g.), from which no crystalline product could be obtained. Chromatography on alumina with benzene–petroleum ether as eluent yielded further dibenzalacetone (0.8 g., combined yield 14%); elution with ether gave a yellow resin (4.75 g.), m.p. 83–96°, from which no pure component could be separated; final elution with methanol gave a yellow-brown powder (0.2 g.), which softened *ca.* 165° with subsequent decomposition (*cf.* the m.p. of 167° dec. recorded by Lippmann and Fritsch[6] for "stilbeneacetone"). Several attempted crystallizations of this material from benzene–petroleum ether gave an amorphous, pale yellow solid, decomposing *ca.* 188°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.85(m) μ.

Anal. Found: C, 86.20, 87.70, 88.38; H, 6.30, 6.07, 6.24; mol. wt. (Rast), 1015, 1018, 1083.

Variation of the reaction conditions failed to yield a more tractable product. When the reaction was carried out at 120° for 6 hr., the yield of dibenzalacetone was increased to 51%, but again no other crystalline product could be isolated. A run at 210–220° for 11 hr. gave an increased yield of the amorphous type of product obtained in the first run, after chromatography of the crude product on silica, but again crystallization was unsuccessful.

Acknowledgment.—N. Yoda gratefully acknowledges the support of a Fulbright Exchange Fellowship.

CAMBRIDGE, MASSACHUSETTS

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[32] H. Burton and C. W. Shoppee, *J. Chem. Soc.*, 1408 (1939).

[33] C. R. Conard and M. A. Dolliver, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 167.

[34] G. D. Johnson, THIS JOURNAL, **75**, 2720 (1953).

[CONTRIBUTION NO. 2229 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

On the Ultrasonic Cleavage of Some Aromatic and Heterocyclic Rings

BY DOUGLAS L. CURRELL AND L. ZECHMEISTER

RECEIVED JULY 30, 1957

It was reported earlier that upon exposure to ultrasonic waves in the presence of silver nitrate, certain halogen derivatives yielded silver halide precipitates which contained silver acetylide, silver diacetylide and (when pyridine was treated) also silver cyanide. It has now been shown that similar cleavage reactions also can be realized in the absence of silver, with benzene, bromobenzene, phenol, tropolone, pyridine and pyrrole. Under these conditions free acetylene and/or hydrogen cyanide evolved. In some instances the ultrasonic cleavage was accelerated by the presence of argon.

When in the course of a recent study[2] some halogen derivatives such as bromobenzene, iodobenzene, α-iodothiophene, α-bromofuran, etc., were suspended in aqueous silver nitrate and exposed to ultrasonic waves, a silver halide precipitate that also contained silver acetylide and small amounts of the diacetylide appeared. However, the presence of halogen in the molecule was not necessary for the cleavage of the pyridine ring. Indeed, free pyridine yielded, in addition to the products mentioned, some silver cyanide.[3,4] Analytical methods for the separation and estimation of the three silver salts were developed,[3] and the same methods now have been applied to pyrazine and pyrrole.

While in all these experiments the acetylene formed was retained in the system, in a solid phase, we have now investigated whether or not ultrasonic ring cleavage can be realized and the evolution of acetylene gas detected in the absence of silver nitrate. For this purpose the starting material was suspended in pure water and, during the ultrasonic treatment, the volatile products were swept continuously by means of an inert gas into a trap containing ammoniacal cuprous solution. Reddish-purple cuprous acetylide appeared. This precipitate was collected and titrated for acetylene as described in our first communication.[2]

When the compound contained heterocyclic nitrogen, a parallel experiment was run in which a potassium hydroxide solution was substituted for the cuprous reagent. The alkaline solution, which trapped the hydrogen cyanide formed, was treated in the same manner as the ammoniacal extracts of silver-containing precipitates mentioned in our recent paper.[3] Finally, after conversion into prussian blue, the cyano group was estimated colorimetrically.

The results are summarized in Table I (benzene, bromobenzene, phenol, tropolone) and Table II (pyridine, pyrazine, pyrrole).

These tables show that the ultrasonic conversion does take place in the absence of silver, and hence that the formation of silver complexes is not a necessary prerequisite of the cleavage process.

When comparing the acetylene yields obtained in the presence and absence of silver, it should be noted that, with the sole exception of pyridine, the compounds treated yielded more acetylene when silver nitrate was present; this effect is very conspicuous in the case of phenol. A tempting ex-

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[1] This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command under Contract No. AF18(600)-385. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] L. Zechmeister and L. Wallcave, THIS JOURNAL, **77**, 2853 (1955).

[3] L. Zechmeister and E. F. Magoon, *ibid.*, **78**, 2149 (1956).

[4] L. Zechmeister and E. F. Magoon, "Festschrift Arthur Stoll," Birkhäuser, Basel, 1957, p. 59.

TABLE I

ULTRASONIC CLEAVAGE OF SOME AROMATIC COMPOUNDS SUSPENDED IN A SILVER NITRATE SOLUTION OR IN PURE WATER

Mmoles of compound	Mmoles of $AgNO_3$	Atmosphere[a]	Duration of treatment, hr.	% C-atoms recovd. as C_2H_2 at end of treatment
		Benzene[b]		
2.2	5.0	Air	20	1.9
2.2	5.0	Air	20	1.1
2.2	5.0	Air	20	1.2
2.2	5.0	Air	20	1.9
1.4	5.0	Nitrogen	10	2.0[b]
1.4	5.0	Nitrogen	10	1.1[b]
1.3	5.0	Argon	10	3.9[b]
1.1	5.0	Argon	10	5.0[b]
2.2	None	Nitrogen	6	0.7
2.2	None	Nitrogen	3	.8
2.2	None	Argon	5	.7
2.2	None	Argon	5	.6
		Bromobenzene		
1.0	5.0	Air	6	9.0[c]
1.0	5.0	Argon	5	11.4
1.0	5.0	Argon	5	13.2
1.0	5.0	Nitrogen	10	7.9
1.0	5.0	Nitrogen	10	10.2
1.0	None	Nitrogen	10	1.9
1.0	None	Nitrogen	10	1.1
1.0	None	Argon	5	5.2
1.0	None	Argon	5	3.5
		Phenol		
2.1	5.0	Argon	40	26.4
2.1	5.0	Argon	40	22.8
2.1	None	Nitrogen	40	2.3[d]
2.1	None	Argon	40	5.9
2.1	None	Argon	40	8.4
2.1	None	Argon	40	5.9
2.1	None	Argon	40	8.4
		Tropolone		
0.8	None	Nitrogen	20	0.9[d]
.8	None	Argon	20	3.3
.8	None	Argon	20	1.8

[a] In the experiments conducted in "air" no sweeping took place. [b] The unreacted portion of benzene was recovered (*cf.* Experimental Part), and the yields given in the table are based on the amount of benzene reacted. In the last four experiments listed under "benzene" the length of the treatment given was probably longer than was necessary for the completion of the reaction. [c] Value taken for comparison from reference 2. [d] The cleavage of phenol and tropolone in nitrogen atmosphere was not carried to completion.

TABLE II

ULTRASONIC CLEAVAGE OF PYRIDINE, PYRAZINE AND PYRROLE IN THE PRESENCE AND ABSENCE OF SILVER AND IN VARIOUS ATMOSPHERES

Mmoles of compound	Mmoles of $AgNO_3$	Atmosphere[a]	Time req. for completing reacn., hr.	Acety. formed during first 10 hr., mg.	% C-atoms recovd. after completing reaction As C_2H_2	As CN[b]	% N atoms recovd. as CN[b]
			Pyridine				
2.5	2.5	Air	40		2.0	Trace	Trace
2.5	2.5	Nitrogen	40	5.2	4.7	1.5	7.7
2.5	2.5	Nitrogen	40	3.9	3.5	1.4	7.3
2.5	2.5	Argon	10	6.4	4.0	2.3	11.7
2.5	2.5	Argon	10	6.9	4.5	2.3	11.7
2.5	None	Nitrogen	54	4.6	7.7	6.6	33.0
2.5	None	Nitrogen	54	3.6	8.5	7.5	37.6
2.5	None	Argon	20	7.9	9.5	7.1	35.4
2.5	None	Argon	20	10.6	8.9	6.1	30.6
			Pyrazine				
2.5	2.2[c]	Air	45		3.0	7.6	15.2
2.5	2.2[c]	Air	45		2.4	6.2	12.4
			Pyrrole[d]				
14.1	30.7[e]	Air	56		9.0	6.6	26.5
14.1	30.7[e]	Air	56		8.3	6.6	26.5
14.1	14.1[f]	Air	21		3.6	2.5	9.8
14.1	6.0[g]	Air	21		3.8	2.3	7.9
14.1	6.0[g]	Air	21		0.2	2.0	7.9
2.8	5.0[h]	Nitrogen	56	9.5	12.0	3.1	12.3
2.8	5.0[h]	Nitrogen	56	11.3	14.1	3.0	12.1
2.8	5.3[i]	Argon	30	20.4	17.6	14.3	57.0
2.8	5.3[i]	Argon	30	21.8	18.5	14.0	56.0
2.8	None	Nitrogen	40	3.9	6.3	6.5	26.0
2.8	None	Nitrogen	40	3.2	5.3	7.6	30.5
2.8	None	Argon	20	11.1	8.6	11.8	47.2
2.8	None	Argon	20	11.6	9.1	13.5	54.5
2.8	None	Argon	20	10.4	9.2	7.1	28.6
2.8	None	Argon	20	9.8	7.6	9.3	35.2

[a] In the experiments conducted in "air" no sweeping took place. [b] The results listed in the last three columns were obtained in two separate experiments. [c] 1.0 mmoles of silver nitrate was present initially and 0.3 more mmole was added after each 9-hr. treatment, following centrifugation. [d] All experiments with pyrrole (except the last two) were run in an ammoniacal medium since otherwise the pyrrole would have been attacked by the acid formed during the treatment. [e] 6.0 mmoles present initially, 3.5 mmoles added after each 7-hr. period. [f] Total silver present initially. [g] 2.5 mmoles present initially, 1.7 mmoles added after each 7-hr. period. [h] 1.5 mmoles present initially, 0.7 mmole added after each 10-hr. period. [i] 3.5 mmoles present initially, 0.9 mmole added after each 10-hr. period.

planation for the behavior of most of our substances is that upon the formation of acetylene in the presence of silver, the acetylene is rapidly transformed into a solid phase and thus protected from further conversions; however, such arguments should also apply to pyridine.

In contrast, the cyanide yields were in general higher in the absence of silver nitrate.

As listed in Tables I and II either nitrogen or argon was used as the inert gas during the ultrasonic treatment. It was interesting to note that in a number of instances the presence of argon increased the reaction rates considerably over those observed in a nitrogen atmosphere, especially in the absence of silver nitrate (*cf.* tropolone, pyridine and pyrrole). In the case of pyrrole not only the reaction rates but also the final yields were increased (Table II). For experiments in the presence of silver this phenomenon possibly can be explained as follows. In contrast to pyridine, pyrrole while exposed to ultrasonic waves undergoes a simultaneous non-ultrasonic reaction with silver, resulting in the formation of "pyrrole black."[13] We believe that the ultrasonic cleavage of the pyrrole ring is accelerated selectively by argon to an extent that secures a very effective competition with "pyrrole black" formation.

Griffing, *et al.*,[5] have reported an accelerating

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(5) V. Griffing, *J. Chem. Phys.*, **20**, 939 (1952); M. E. Fitzgerald, V. Griffing and J. Sullivan, *ibid.*, **25**, 926 (1956).

effect of noble gases on the ultrasonic liberation of chlorine from carbon tetrachloride. These authors propose that the conversion takes place inside the bubbles (cavities) formed in the ultrasonic field and is due to the heat developed during the adiabatic compression of the bubble. Another interpretation, based on electrical discharges inside the cavities, was offered by Harvey[6] and also by Frenkel.[7]

Acknowledgment.—We are indebted to Dr. Y. Kitahara of Tôhoku University for a tropolone sample.

Experimental

Materials.—The following starting materials were used: benzene (Eastman Kodak Co., spectro grade), bromobenzene (reagent grade, Matheson, Coleman and Bell); phenol (R.G., J. T. Baker Chem. Co.), pyridine (R.G., Baker and Adamson), pyrazine (Light and Co., England), pyrrole (practical, Matheson, Coleman and Bell; purified *via* the potassium salt and distillation in nitrogen[8]). The argon (Standard Grade) and nitrogen (High Purity Dry) were obtained from the Linde Co., Div. of Union Carbide Corp.

The following amounts were treated ultrasonically: benzene, 0.20 ml.; bromobenzene, 0.10 ml.; phenol, 0.20 g.; tropolone, 0.10 g.; pyridine, 0.20 ml.; pyrazine, 0.20 g.; and pyrrole, 0.20 or 1.0 ml.

General Methods.—Two ultrasonic generators "A" and "B" were used: A, constructed in these laboratories, had a nominal output power of 200 watts and was operated at a frequency of about 600 kilocycles per sec.; B was a Hypersonic Generator model BU-204 (250 watts, 1000 kilocycles per sec.) manufactured by Brush Electronics Co., Cleveland, Ohio (employed only in experiments involving pyridine). Cup-shaped barium titanate elements (diam., 9 cm.) with a glazed finish were used.

The reaction vessels, containing 50 ml. of solution or suspension, were 100-ml. round-bottom Pyrex flasks with necks 22 cm. long (for a sketch of the apparatus *cf.* ref. 4). The position of the flask, which was immersed in water covering the transducer, was adjusted by a screw system until maximum fountain height was observed. The same individual flask was used in parallel runs. In the experiments with argon or nitrogen the reaction flask was fitted with an inlet tube (diam., 6 mm.) whose tip was located 2 cm. above the surface of the liquid.

In order to analyze for acetylene in experiments conducted without silver nitrate, the gaseous products were swept continuously during the ultrasonic treatment (as well as 5 min. before and after) into three traps each containing 20 ml. of an ammoniacal cuprous solution prepared according to von Ilosvay.[9] The ultrasonic treatment was continued until no further precipitate appeared in this reagent which was renewed after every 10-hr. period. Each cuprous acetylide fraction was titrated separately, according to Willstätter and Maschmann[10] with slight modifications.[2] In order to analyze for cyanide, parallel experiments were conducted in which the von Ilosvay reagent was replaced in the trap by 2 *N* potassium hydroxide which retained the hydrogen cyanide formed. Upon the conclusion of the ultrasonic treatment the alkaline solution was diluted to 100 ml. in a volumetric flask; 2-ml. or 5-ml. samples were then treated as described earlier for ammoniacal extracts of silver-containing precipitates.[3] Finally, after conversion into prussian blue, the cyano group was estimated colorimetrically. The same sequence of analytical operations was performed with the liquid contained in the reaction vessel; if prussian blue did form, originating from hydrogen cyanide not swept into the traps, its (usually insignificant) colorimetric value was added to that mentioned above to give the total cyanide yield as listed in Table II.

During the exposure of the silver-containing solutions to ultrasonic waves the system was swept with argon or nitrogen. The precipitate was removed from the reaction flask by centrifugation after every 10 hr.; the reaction was considered as complete when no further precipitate appeared within 3 hr. The combined precipitates were extracted with concd. ammonia and analyzed for acetylene and cyanide.[3]

The following two control experiments were also conducted: (a) It was shown by sweeping the gases into the von Ilosvay reagent or potassium hydroxide that, in the presence of silver nitrate, both acetylene and hydrogen cyanide were retained quantitatively in the reaction vessel. (b) Since in the presence of silver the ultrasonic treatment of pyrrole had to be carried out in an ammoniacal medium, we have investigated whether in the ultrasonic field ammonia and acetylene would yield some cyanide that would increase the true analytical values. For this purpose acetylene generated from 1 g. of calcium carbide was bubbled for 1 hr. through 50 ml. of 1.5 *N* ammonia which was exposed simultaneously to ultrasonic waves; no cyanide could be detected. However, a 6-hr. treatment of bromobenzene, suspended in ammoniacal silver nitrate solution, did yield a little cyanide, corresponding to 0.6% of the carbon atoms present in the ring.

In all ultrasonic treatments conducted in the absence of silver a dark brown precipitate appeared consisting of a material which did not melt below 300° and was insoluble in most organic solvents. The weight of such precipitates varied between 3 mg. (*ex* benzene) and 50 mg. (*ex* pyridine). In the case of pyridine and pyrrole the precipitate was shown to contain nitrogen.

Special Procedures. Benzene.—To determine how much benzene was removed from the flask by sweeping before reacting in the experiments run in the presence of silver nitrate, the gases emerging from the vessel were passed through two traps, each containing 10 ml. of ice-cold hexane. The benzene retained in the traps was determined photometrically at 262 $m\mu$.[11] About half of the benzene present initially was thus recovered. It was not possible to perform the latter operations in the absence of silver, since contaminants interfering with the photometric readings appeared in the hexane trap.

In the same manner it was shown in the presence of silver nitrate that no pyridine, bromobenzene or pyrrole left the reaction flask.

Bromobenzene.—We have observed that, in contrast to the behavior of all the other compounds studied, exposure of bromobenzene to ultrasonic waves yielded strongly acid solutions. In special experiments (in the absence of silver) the gaseous products were swept with argon into an alkaline trap which would have retained hydrogen bromide. No bromide ion was found in the trap; that contained in the reaction vessel was determined gravimetrically.[12] It was thus found that about 56% of the bromine contained in the bromobenzene treated had been converted into its ionic form. (The dark brown precipitate was shown to be halogen-free.)

Pyridine.—The silver nitrate concentration was kept approximately constant during the ultrasonic treatment as described in detail in ref. 3.

Pyrrole.—In the runs without silver 1.5 ml. of concd. ammonia was used, but in the presence of silver we added the minimum volume of ammonia necessary for the dissolution of the silver oxide plus 0.5 ml. in excess. In the ultrasonic treatment of ammoniacal silver solutions it was possible to analyze for cyanide directly as described in ref. 3; however, this was made impossible following ultrasonic treatments that exceeded 20 hr. by the presence of a contaminant that interfered with the formation of prussian blue. In these instances the reaction solution was brought to 50 ml. in a volumetric flask; 2-ml. samples were then neutralized with dilute nitric acid to precipitate the silver cyanide which was removed by centrifugation, washed, re-

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(6) E. N. Harvey, THIS JOURNAL, **61**, 2392 (1939).

(7) Y. Frenkel, *Acta Physicochim. USSR*, **12**, 317 (1940). For further references *cf.*, *e.g.*, O. Lindstrom, *J. Acoust. Soc.*, **27**, 654 (1955).

(8) G. Ciamician and M. Dennstedt, *Ber.*, **19**, 173 (1886).

(9) L. von Ilosvay, *ibid.*, **32**, 2697 (1899).

(10) R. Willstätter and E. Maschmann, *ibid.*, **53**, 939 (1920).

(11) L. J. Andrews and R. M. Keefer, THIS JOURNAL, **71**, 3644 (1949).

(12) W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," 2nd ed., J. Wiley and Sons, Inc., New York, N. Y., 1940.

dissolved in a minimum volume of concd. ammonia and analyzed for cyanide.

"Pyrrole black" was prepared by refluxing for 4 hr. 50 ml. of a solution which contained 0.43 g. of silver nitrate and 1 ml. of pyrrole. The heavy black precipitate (0.36 g.) that began to appear after a few minutes was found to be free of silver cyanide and silver acetylide; it resembled the materials obtained by earlier authors through the action of certain oxidizing agents and/or metal ions on pyrrole.[13]

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[13] *Cf.*, *e.g.*, the chapter on "Pyrrolschwarzverbindungen" in H. Fischer and A. Stern, "Die Chemie des Pyrrols," Vol. II, Akademische Verlagsgesellschaft, Leipzig, 1940, pp. 437–440.

[FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

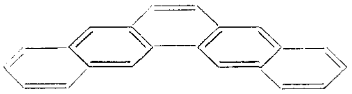
A Synthesis of 2,3,6,7-Dibenzophenanthrene

BY ERNST D. BERGMANN AND RAPHAEL IKAN

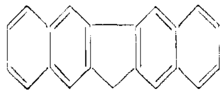
RECEIVED JULY 15, 1957

Starting from 2-methyl-3-decalone, 2,3,6,7-dibenzophenanthrene has been synthesized. The method is applicable to the synthesis of higher benzologs and of the analogous fluorene derivatives.

Among the dibenzophenanthrenes and -fluorenes, the 2,3,6,7-isomers are probably the least accessible.[1] 2,3,6,7-Dibenzophenanthrene (I) and 2,3;6,7-dibenzofluorene (II) are interrelated through 3,3′-dicarboxy-2,2′-binaphthyl (III, R = COOH) which can be cyclized *via* its lead salt to give 2,3,6,7-dibenzofluorenone.[2] On the other hand, it should be possible in analogy with previous experience[3,4] to obtain I by reduction of III (R = COOH) to the dihydroxymethyl compound III (R = CH_2OH) from which the dibromo derivative III (R = CH_2Br) would be accessible by conventional means. Treatment of the latter with lithium phenyl, followed by dehydrogenation, should give I.



I



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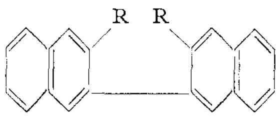
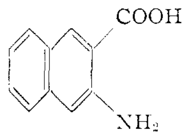


III



IV

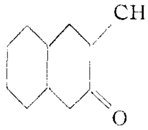
We have carried out this synthesis in an over-all yield of 21%, starting from 2-amino-3-naphthoic acid (IV) which was converted to III (R = COOH). However, this method suffers from the limitation that the preparation of IV is very cumbersome.[5] An alternative method has, therefore, been developed, which gives a lower over-all yield (10%) but has the advantage that the starting material is easily accessible.

As the above method has been described recently (after the completion of our experiments) by Badger and co-workers,[6] we refrain from a detailed discussion of this first part of our investigation.

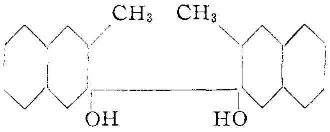
2-Methyl-3-decalone (V), available from cyclohexanone and methyl isopropenyl ketone with subsequent hydrogenation (over-all yield 82%),[7] was converted into the pinacol VI and the latter dehydrated (to VII) and dehydrogenated to 3,3′-dimethyl-2,2′-binaphthyl (III, R = CH_3). Upon treatment with NBS, this gave the same dibromo compound III (R = CH_2Br) obtained by the previous route.

By oxidation of III, R = CH_3, to III, R = COOH, the two alternative routes have been further linked to each other.

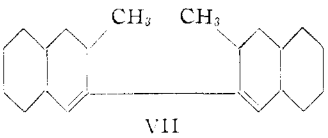
As analogs and homologs of V are easily available by similar Michael condensations,[7] this method appears applicable to the synthesis of even more highly condensed polycyclic systems.



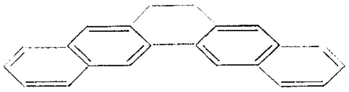
V



VI



VII



VIII

In studying the *spectra* of the compounds prepared in this investigation, some interesting observations have been made. The diene VII shows practically no selective absorption, most probably due to steric hindrance. The same effect will ex-

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[1] E. Clar and F. John, *Ber.*, **64**, 981 (1931); **62**, 3021 (1929); E. Clar, F. John and B. Hawran, *ibid.*, **62**, 940 (1929); E. Clar and D. G. Stewart, *J. Chem. Soc.*, 3215 (1951); R. H. Martin, *Helv. Chim. Acta*, **30**, 620 (1947); R. H. Martin and S. Vassart, *Bull. soc. chim. Belg.*, **61**, 234 (1952).

[2] R. H. Martin, *J. Chem. Soc.*, 679 (1941).

[3] See, also for previous literature, E. D. Bergmann and Z. Pelchowicz, *J. Org. Chem.*, **19**, 1383, 1387 (1954); G. Wittig and H. Zimmerman, *Ber.*, **86**, 629 (1953); D. M. Hall, E. E. Turner and K. E. Hamlett, *J. Chem. Soc.*, 1242 (1955).

[4] Interesting variations of this method are the preparation, from 2,2′-dibromomethylbiphenyl, of phenanthrene with sodamide in liquid ammonia (I. A. Kaye, THIS JOURNAL, **73**, 5467 (1951)) and that of 9,10-dihydrophenanthrene with sodium in the presence of catalytic quantities of tetraphenylethylene (E. Mueller and G. Roescheisen, *Ber.*, **90**, 543 (1957)).

[5] The original method of Moehlau (*Ber.*, **28**, 3096 (1895)) could not be duplicated by H. A. Harrison and F. A. Royle (*J. Chem. Soc.*, 84 (1926)). The present methods are based on the prolonged reaction of 2-hydroxy-3-naphthoic acid with ammonia and zinc chloride or ferrous sulfate at high temperature and pressure; *Org. Syntheses*, **22**, 19 (1942); German Patent 488,946 ("Beilstein," 2nd Suppl., Vol. 14, p. 323).

[6] G. M. Badger, P. R. Jefferies and R. W. L. Kimber, *J. Chem. Soc.*, 1837 (1957).

[7] E. D. Bergmann, R. Ikan and H. Weiler-Feilchenfeld, *Bull. soc. chim. France*, 290 (1957).