Acetylenic Analogues of Chichibabin Hydrocarbon

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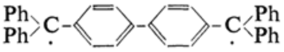
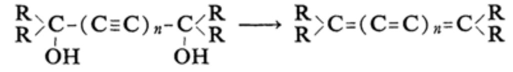
There have been many discussions of the unstable nature of Chichibabin hydrocarbon (I), which was prepared by Chichibabin as early as 1907¹⁾. Schwab and Agliardi have observed that hydrocarbon I catalyzed the interconversion of ortho- and para-hydrogen; they have attributed this catalytic activity to the presence of the biradical structure (I_b) in the hydrocarbon²⁾. On the other hand, Müller and Müller-Rodloff have assigned the quinomethane structure (I_a) on the basis of the diamagnetic behavior of this hydrocarbon³⁾. More recently, Huchison has measured the ESR spectrum of a solution of I and concluded that I in the solution contained 4～5% of the biradical (I_b)⁴⁾. However, in a private communication to Ingram, he has pointed out that

I_a



I_b

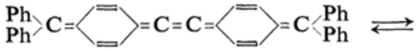
there is a distinct possibility of the presence of an impurity to which the observed signal may be attributable*. Also, there have been fairly many investigations concerning the quinomethane or biradical structure of Chichibabin type hydrocarbons⁵⁾. If there exists an equilibrium between the quinomethane and biradical structures, it would be reasonable to conclude that the energy levels corresponding to these two possible structures do not differ appreciably. If Chichibabin hydrocarbon (I) exists mainly in the form of the quinomethane (I_a), the loss of the resonance energy of the central benzene rings should be covered by an increase in the resonance energy of the newly-formed, more extended conjugate system.



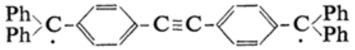
$$\underset{\text{II}}{\begin{matrix}R\\R\end{matrix}\!\!>\underset{OH}{C}-(C\equiv C)_n-\underset{OH}{C}<\!\!\begin{matrix}R\\R\end{matrix}} \longrightarrow \underset{\text{III}}{\begin{matrix}R\\R\end{matrix}\!\!>C=(C=C)_n=C<\!\!\begin{matrix}R\\R\end{matrix}}$$

On the other hand, the formation of cumulene (III) from the acetylenic glycol of type II is well-known⁶⁾. Also, the rearrangement of the acetylenic linkage to an allenic system under rather mild conditions has been shown in several instances⁷⁾. Therefore, the insertion of a triple bond to I or a substitution for the central benzene ring in I of a triple bond seems to cause a change in the valence tautomeric equilibria between the quinoid and the biradical structures of these acetylenic analogues of Chichibabin hydrocarbon.

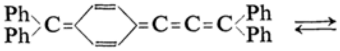
The present paper deals with the synthesis and the properties of the following acetylenic analogues of I:



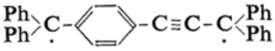
IV_a



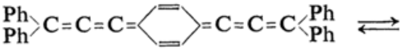
IV_b



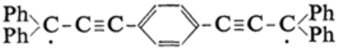
V_a



V_b



VI_a



VI_b

The Synthesis of the Precursors of the Acetylenic Analogues of Chichibabin Hydrocarbon

4, 4′-Bis(diphenylchloromethyl)-tolan (VIII). —Dibenzyl was converted to 4, 4′-dibromotolan according to the method of Barber⁸⁾.

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1) A. E. Chichibabin, *Ber.*, **40**, 1810 (1907).

2) G.-M. Schwab and N. Agliardi, ibid., **73**, 95 (1940).

3) E. Müller and I. Müller-Rodloff, *Ann.*, **517**, 134 (1935).

4) C. A. Huchison, Jr., A. Kowalsky, R. C. Paster and G. W. Wheland, *J. Chem. Phys.*, **20**, 1485 (1952).

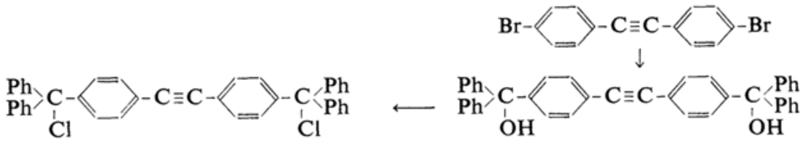
* D. J. E. Ingram, "Free Radicals as studied by Electron Spin Resonance", Butterworth Scientific Publications, London (1958), p. 229.

5) a) E. Müller and H. Pfanz, *Ber.*, **74**, 1051, 1075 (1941); b) G. Sloan and W. R. Vaughan, *J. Org. Chem.*, **22**, 750 (1957); c) G. J. Sloan, W. R. Vaughan and H. S. Jarrett, *J. Phys. Chem.*, **25**, 697 (1956); d) G. Wittig and W. Wiemer, *Ann.*, **483**, 144 (1930); e) W. Theilacker, H. Schulz, U. Baumgarte, H. G. Drössler, W. Rohde, F. Tharter and H. Uffmann, *Angew. Chem.*, **69**, 322 (1957).

6) For reviews, see P. Cadiot, W. Chodkiewicz and J. Rauss-Godineau, *Bull. soc. chim. France*, **1961**, 2176.

7) E. R. H. Jones, G. H. Whitham and M. C. Whiting, *J. Chem. Soc.*, **1957**, 4628; T. L. Jacobs and D. Danker, *J. Org. Chem.*, **22**, 1424 (1957).

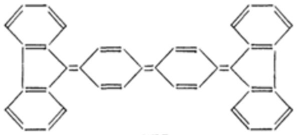
8) S. Bance, H. J. Barber and A. M. Woolman, *J. Chem. Soc.*, **1943**, 1; H. J. Barber and R. Slack, ibid., **1944**, 612.



VIII VII

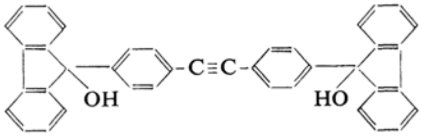
The successive treatment of the tolan with *n*-butyllithium and then with benzophenone yielded 4, 4'-bis(diphenylhydroxymethyl)-tolan (VII) in an almost quantitative yield. The reaction of thionyl chloride with the glycol VII resulted in the formation of 4, 4'-bis-(diphenylchloromethyl)-tolan (VIII) in a good yield. The dichloride VIII was found to be a fairly unstable compound which decomposed easily upon the heating of the solution or of the crystals. The development of a blue band was obseved when a solution of VIII was passed through a column of activated alumina. The blue-colored material could not be eluted with various kinds of polar solvents, and the blue color disappeared gradually without the movement of the band. From the eluate with ethyl acetate, the glycol VII was obtained as the sole decomposition product.

4, 4'-Bis(9''-chloro-9''-fluorenyl)-tolan (XI).—The synthesis and interesting properties of the biphenylene analogue of Chichibabin hydrocarbon (IX) have been reported by Theilacker[5e].

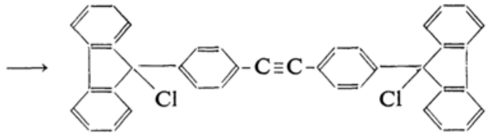


IX

In order to prepare the acetylenic analogue of IX, the corresponding dichloride (XI) was synthesized according to the following scheme. The metalation of 4, 4'-dibromotolan by means of *n*-butyllithium, followed by the reaction with fluorenone, afforded the glycol X in a good yield. It was found that the displacement of the hydroxyl groups by chlorine proceeds sluggishly compared with the case of VII. The dichloride XI was obtained in a reasonable yield after refluxing the mixture of X with a large excess of thionyl chloride for over 6 hr.

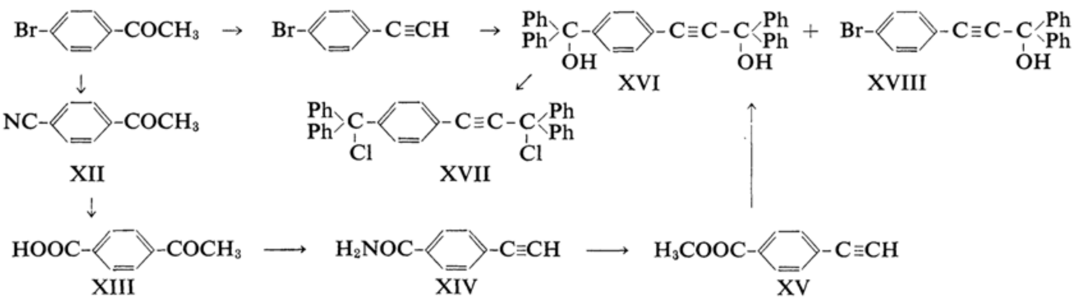


X



XI

1-Diphenylchloromethyl-4-(3'-chloro-3', 3'-diphenyl-1'-propynyl)-benzene (XVII).—The successive treatment of *p*-bromophenylacetylene with *n*-butyllithium and benzophenone gave the glycol XVI in a poor yield, together with an appreciable amount of 1, 1-diphenyl-3-(4'-bromophenyl)-propyn-1-ol (XVIII). It was found that this reaction was scarcely feasible, however, because of the poor yield and the poor reproducibility. *p*-Bromoacetophenone was converted to *p*-acetylbenzonitrile (XIII)[9]. This was hydrolyzed to give the corresponding benzoic acid XIII. Methyl *p*-ethynylbenzoate (XV) derived from XIII via two steps was treated with phenyllithium and benzophenone successively, affording the glycol XVI in a reasonable yield. The glycol XVI thus obtained was heated with a large excess of thionyl chloride in benzene or acetyl chloride in hydrochloric acid[5b], yielding the unstable dichloride XVII.



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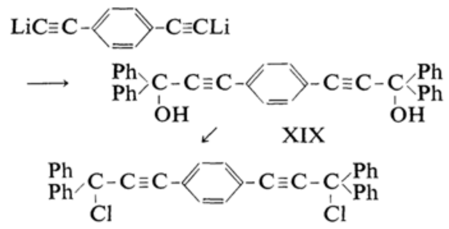
9) T. Mowry, M. Renoll and W. F. Huber, *J. Am. Chem. Soc.*, **68**, 1108 (1946) (cf. J. H. Helberger and A. von Rebay, *Ann.*, **531**, 279 (1937)).

1, 4-Bis-(3′-chloro-3, 3′-diphenyl-1′-propynyl)-benzene (XX). — 1, 4-Bis(3′-hydroxy-3′, 3′-diphenyl-1′-propynyl)-benzene (XIX) was prepared according to the method of Ried[10] by the reaction of the lithium derivative of *p*-diethynylbenzene with benzophenone. The dichloride XX was obtained by treating the glycol XIX with thionyl chloride in benzene or acetyl chloride in hydrochloric acid at a low temperature. XX was found to be extremely unstable in the presence of heat.



XIX

XX

Results

On 4, 4′-Bis-diphenylmethylyl-tolan (IV).— The rapid development of an intense blue-violet color was observed when a solution of the dichloride VIII in benzene or tetrahydrofuran was shaken with mercury or zinc dust at room temperature in an atmosphere of pure nitrogen. The solution could be kept without change of its color for several hours at the temperature of −70°C. A rapid change of the color to orange was observed when the solution was warmed to room temperature. Also, the exposure to air of the blue-violet solution caused an instant decolorization of the solution. The ultraviolet absorption spectrum of the orange solution exhibits a distinct peak at 465 mμ and the broad absorption, at a shoter wavelength. The ESR spectra were measured to determine the presence of the biradical structure IV$_b$ employing tetrahydrofuran solutions (5.1×10^{-3} mol./l. and 2.0×10^{-2} mol./l. based on the dichloride, VIII) at 21°C. The spectrum is illustrated in Fig. 1, together with that of diphenylpicrylhydrazyl (solid) for purposes of comparison. The shape of the differential absorption curve was found to be a typical one for a carbon radical. Calculation of the concentration of the biradical IV$_b$, which was carried out by a comparing the integrated differential absorption curve of IV$_b$ with that of diphenylpicrylhydrazyl, showed that 5% and 7% of IV$_b$ should be present in the above-mentioned solution, assuming that the dechlorination of the dichloride VIII by zinc dust proceeds to 100% conversion.

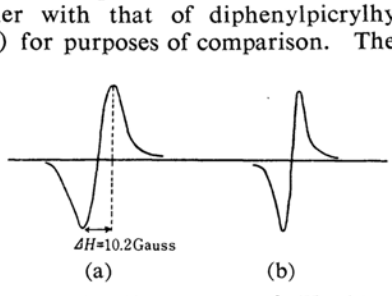


Fig. 1. The ESR spectra of IV$_b$ (a) and diphenylpicrylhydrazyl (b).

The attempts to isolate the unstable IV in a solid state failed. The concentration of the blue-violet solution in vacuo at a low temperature resulted in the formation of an orange-yellow polymeric substance.

As the structure of a cyclic dimer has been assigned to the peroxide of Chichibabin hydrocarbon by Müller[11], the formation of the same type of cyclic peroxide as XXI was expected in the case of IV$_b$. An intense blue-violet solution of IV in tetrahydrofuran was exposed to air, resulting in the formation of a light brown solution. The attempts to isolate XXI in a pure state gave unsatisfactory results. The absorption of oxygen by IV was measured using a Warburg manometer. A rapid uptake of oxygen was observed when the dichloride VIII in tetrahydrofuran was shaken with an excess of zinc dust in an atmosphere of pure oxygen. A representative absorption

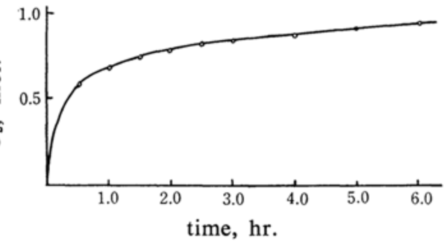
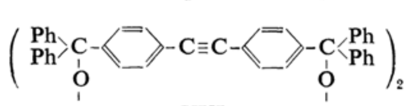


Fig. 2. The absorption of oxygen by IV$_b$.



XXI

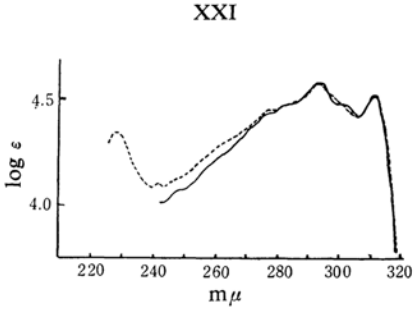


Fig. 3. The ultraviolet spectra of the peroxide (XXI, —) and the glycol (VII, ------).

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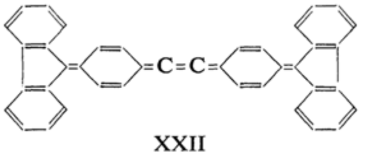
[10] W. Ried and G. Dankert, *Chem. Ber.*, **92**, 1223 (1959).

[11] E. Müller and E. Tietz, *Ber.*, **74**, 807 (1941).

curve is presented in Fig. 2. The ultraviolet spectrum of the peroxide was found to be closely related with that of the glycol VIII illustrated in Fig. 3. The peroxide solution was chromatographed on alumina, and colorless needles (m. p., 175~177°C) were isolated; these were proved to be identical with the glycol (VIII; m. p., 179~179.5°C) by a mixed melting point determination (mixed m. p., 173~178°C). The mode of the formation of the glycol VII is not clear, but it seems to arise from the peroxide XXI by a decomposition on the surface of alumina.

The ultravoilet spectrum of IV could not be measured accurately because of the unstable nature of IV. A fairly rapid change in absorption intensity was observed during the course of the measurement. Approximate absorption maxima were found at the wavelengths of 750, 678, 590 (strongest) and 439 mμ.

The Attempted Formation of 4, 4-Bis-(9″-fluorenylyl)-tolan (XXII).—The replacement of the diphenylmethylyl group in IV by a 9-fluorenyl group constitutes an interesting system XXII, which can be regarded as an acetylenic analogue of Theilacker's hydrocarbon IX[5e]. It was hoped that the terminal fluorenyl groups might stabilize the quinomethane structure, but all attempts to remove the chlorine atoms from the dichloride XI or to subtract the hydroxyl groups from the glycol X failed. No developement of an intense color was observed under various reaction conditons.



XXII

The Formation of 1-Benzhydryliden-4-(3′, 3′-diphenylpropadienyliden)-1, 4-dihydrobenzene (V_a).—Powdered anhydrous stannous chloride was added to a dilute solution of the dichloride XVIII in benzene, and the mixture was shaken for several hours. A small quantity of black-violet needles with a greenish surface luster was isolated from the reaction mixture. It was found that this substance was contaminated with a small amount of chlorine compound, but the impurity could not be removed by chromatography on alumina or by treatment with molecular silver. The ultraviolet spectrum of this substance is illustrated in Fig. 4, together with those of the related compounds. The stability of this substance in the solid state or in a benzene solution suggests the quinomethane structure of the substance V_a. However, it was observed that the reddish-violet color of a benzene solution of V_a rapidly changed to light brown on exposure to light. The measurement of the ESR spectrum showed no signal, indicating the absence of the biradical structure V_b.

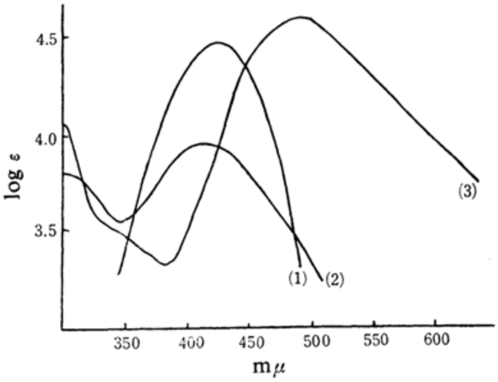
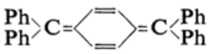


Fig. 4. The ultraviolet spectra of (1) Thiele's hydrocarbon (XXIII), (2) the mono-radical (XXV) and (3) the quinocumulene (V_a).

The characteristic features of the infrared spectrum of V_a are the absence of cumulenic absorption (1900~2050 cm^{-1})[12] and the presence of strong absorptions at 822 and 1365 cm^{-1}. The absorption at about 800 cm^{-1} is usually attributed to the out-of-plane deformations of the two adjacent hydrogen atom in a para-disubstituted benzene derivative. This argument, however, is not consistent with the structure of V_a, in which the disubstituted six-membered ring has a cyclohexadiene structure. The infrared spectrum of Thiel's hydrocarbon[13], which has been regarded as having a quinomethane structure XXIII, also exhibits absorption at 831 cm^{-1}. Quite recently, it was found that *cis*-1, 3, 5-hexatriene showed a strong absorption in this region (818 cm^{-1}) which was lacking in the spectrum of the trans-isomer[14]. Therefore, the strong absorption at 822 cm^{-1} in V_a may reasonably be attributed to the out-of-plane deformation of the hydrogen atoms of the conjugated cis-double bonds in the cyclohexadiene structure.



$$Ph_2C=C_6H_4=CPh_2$$

XXIII

A solution of the dichloride XVII in benzene was treated with molecular silver at 60°C, resulting in a deep brown solution. The solution was passed through a column of alumina, and the filtrate was evaporated, affording a red-brown solid. The free radical nature of

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[12] R. C. Lord and P. Venkateswarlu, *J. Chem. Phys.*, **20**, 1237 (1952); W. Otting, *Chem. Ber.*, **87**, 611 (1954).

[13] J. Thiele and H. Balhorn, *Ber.*, **37**, 1463 (1904).

[14] J. C. H. Hwa, P. L. de Benneville and H. J. Sims, *J. Am. Chem. Soc.*, **82**, 2537 (1960).

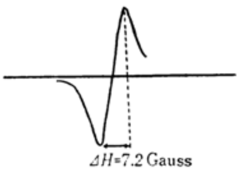
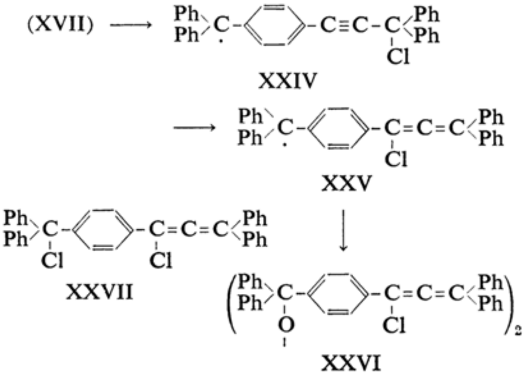


Fig. 5. The ESR spectrum of the mono-radical (XXV).

this substance was revealed by an ESR measurement employing a specimen which had been kept in an evacuated desiccator for two days (Fig. 5). The sharp and highly symmetrical absorption curve suggests that the radical center should not be an oxygen atom, but it concerns a carbon radical. The analytical data ($C_{34}H_{24}OCl$) indicates the presence of chlorine and oxygen in the molecule. From these observations, it seems highly probable that the red-brown solid consists mainly of the peroxide XXVI, containing a small amount of the mono-radical XXV. The remaining chlorine atom seems, in view of its inertness to molecular silver, to attach to an unsaturated carbon atom. There are two possibilities of the formation of such a rearranged product. One of them is that the starting dichloride was already a mixture of XVII and the rearranged dichloride XXVII which had been formed during the course of the displacement of the hydroxyl groups by chlorine atoms. Another is the rearrangement of XXIV to the isomeric radical XXV by the catalytic action of molecular silver.



Attempts to form 1, 4-Bis(3′, 3′-diphenyl-1′-propadienyliden)-1, 4-dihydrobenzene (VI$_a$) or 1, 4-bis(3′, 3′-diphenyl-1′-propynylyl)-benzene (VI$_b$).—Recently, Ried has reported that the treatment of 1, 4-bis(3′-hydroxy-3′, 3′-diphenylpropynyl)-benzene (XIX) with Stephen's reagent resulted in the formation of a dark red solution. He has assigned the biscumulene structure VI$_a$ to the reaction product on the basis of the stable color of the solution[10]. The initially-developed blue color of the reaction mixture rapidly changed to red-violet, then to reddish-brown, and finally to brown. When the glycol XIX in tetrahydrofuran was mixed with Stephen's reagent in the same solvent at −70°C, the immediate development of a transient, deep violet-blue color was observed; this color rapidly changed to red-violet, then to orange-red. The orange-red color of the solution changed to blood-red gradually at −70°C or rapidly at room temperature. The blood-red solution was found to be fairly stable, but it gradually changed to a yellow-brown solution on exposure to air at room temperature. The electronic spectra of the deep violet-blue and the red-violet solutions could not be determined because of their instability. The blood-red and the yellow-brown solutions exhibited the absorption maxima at 284, 482 mμ and 328, 540 mμ respectively. The absorption of the yellow-brown solution coincides with the reported values (333.0 and 539.5 mμ)[10]. Ried has assigned the structure of VI$_a$ to this substance, but, as has been mentioned above, the yellow-brown solution is the ultimate stage of the complex color change in the transformation of the glycol XIX. Therefore, it seems highly probable that the yellow-brown solution consists mainly of a decomposition or a polymerization product. The absorption maximum of the bloodred solution (482 mμ) shifted to a shorter wavelength than that of V$_a$ (492 mμ). In view of the presence of the more extended conjugate system in VI$_a$, this fact seems to exclude the possibility of the existence of the quinocumulene (VI$_a$) in the blood-red solution.

The treatment of the dichloride XX with various kinds of dehalogenation reagents, such as zinc dust, mercury, molecular silver, or anhydrous stannous chloride in benzene, tetrahydrofuran or dioxane, gave unsatisfactory results.

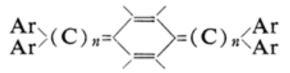
It was found from the above-mentioned experiments that the isolation of the reaction product in substantia was difficult, but the extremely unstable nature of the reaction product of the glycol XIX seems to suggest the transient formation of the biradical VI$_a$.

Discussion

As has already been mentioned, the ESR spectrum of IV showed a strong signal, indicating the presence of the double doublet IV$_a$[5b], which may be in an equilibrium with the quinocumulene structure IV$_a$. This finding indicates that the resonance energy of the central benzene nuclei in IV is large enough to prevent the complete interaction of the two unpaired electrons through the conjugate π-electron system which necessarily accompanies the transformation of benzenoid to the *p*-quinoid structure of the central nuclei. The stable triphenylmethyl structure of the radical center in IV_b may also contribute to the stabilization of IV_b.

In the case of the dechlorination of XVII, the product could be isolated in substantia and the structure of V_a assigned on the basis of analytical and ESR evidence. Although the possibility that this substance exists in a triplet state can not be excluded, the high stability of V to air in a pure state seemed to reflect the singlet state, at least at room temperature.

Recently, various kinds of stable quinocumulenes of type XXVIII bearing anthracene or pentacene nucleus in the center of the molecule have been synthesized[10,15]. VI can be regarded as a parent compound of these quinocumulenes. Therefore, it was expected that VI might



XXVIII

form a more stable quinocumulene (VI_a) than V or IV. In fact, however, the dehydroxylation of the glycol XIX gave an extremely unstable product. Because it has been well recognized that the tendency of polyacene to form a quinoid structure is more pronounced than that of benzene or naphthalene, the marked difference between XXVIII and VI seems to be attributable to the difference in the delocalization energy which accompanies the trasformation of the central aromatic system to the quinoid structure. Also, the instability of the radical seems to be related to the lack of a triphenylmethyl structure in the radical center of VI_b.

Experimental*

4, 4′-Bis(diphenylhydroxymethyl)-tolan (VII).—4, 4′-Dibromotolan was prepared according to the method of Barber[8]. The tolan (5.0 g., 0.015 mol.) in anhydrous ether (50 ml.) was mixed with *n*-butyllithium (0.04 mol.) in the same solvent (35 ml.) in an atmosphere of nitrogen. After the solution had been stirred for 15 min. at room temperature, a solution of benzophenone (6.0 g., 0.033 mol.) in anhydrous ether (50 ml.) was added drop by drop over a one-hour period, resulting in a light yellow solution. The reaction mixture was then refluxed for an hour. After standing overnight, the mixture was stirred a further 2 hr. at room temperature and 1.5 hr. under reflux. A saturated solution of ammonium chloride was added to the reaction mixture, and the organic layer was worked up according to the usual manner, affording a light yellow solid (10.0 g.). The solid was crystallized from benzene-petroleum benzine (1 : 1), yielding colorless grains; m. p., 177～179°C (8.1 g., quantitative). Further recrystallization from the same solvent gave an analytical specimen; m. p., 179～179.5°C.

Found: C, 88.57; H, 5.39. Calcd. for $C_{40}H_{30}O_2$: C, 88.53; H, 5.57%.

4, 4′-Bis(diphenylchloromethyl)-tolan (VIII).—Thionyl chloride (20 ml., 32.8 g.) was added to the suspension of the above-mentioned glycol (VII), (1.6 g., 0.003 mol.) in benzene (40 ml.). The mixture was refluxed for 2 hr., resulting in a brownish pink solution. The volatile material was removed under reduced pressure. The residue was dried over potassium hydroxide in an evacuated desiccator and then dissolved in benzene-petroleum benzine without heating. The solvent was partly removed under reduced pressure at room temperature, yielding crystals. The crystals were treated in the same way, affording pure VIII as light brown cubes; m. p., 198～203°C (1.2 g., 70%).

Found: C, 82.71; H, 4.84; Cl, 12.01. Calcd. for $C_{40}H_{28}Cl_2$: C, 82.89; H, 4.87; Cl, 12.24%.

4, 4′-Bis(9′′-hydroxy-9′′-fluorenyl)-tolan (X).—In an atmosphere of nitrogen, a solution of *n*-butyllithium in ether (36 ml., 0.042 mol.) was added over a 10-min. period to a solution of 4, 4′-dibromotolan (6.7 g., 0.02 mol.) in ether (60 ml.) and tetrahydrofuran (10 ml.). The blue-white suspension formed was stirred for 15 min., and then fluorenone (7.2 g., 0.04 mol.) in ether (60 ml.) was added drop by drop over a 15-minute period. After being stirred for 1.5 hr. at room temperature, the mixture was left to stand overnight, yielding a yellow brown suspension. The suspension was stirred another hour and then heated under reflux for 1.5 hr. The reaction mixture was decomposed by the addition of a saturated aqueous ammonium chloride. The organic layer was separated, and the aqueous layer was extracted with benzene (300 ml.). The insoluble material was filtered and washed with a small amount of benzene. The solid (8.0 g., m. p., 277～280°C) was recrystallized from aqueous acetone to yield X as colorless needles; m. p., 307～312°C (7.0 g., 64.7%).

Found: C, 89.04; H, 4.61. Calcd. for $C_{40}H_{26}O_2$: C, 89.19; H, 4.87%.

A chromatographic purification of the residue which had been obtained from the combined organic layer afforded a small amount of X.

4, 4′-Bis(9′′-chloro-9′′-fluorenyl)-tolan (XI).—The glycol (X, 0.5 g.) was added to a mixture of benzene (7 ml.) and thionyl chloride (8 ml.), and the mixture was refluxed for 6.5 hr., resulting in a brown solution. The red brown residue obtained by the evaporation of the volatile material was dried over sodium hydroxide. Recrystallization of the dried material from carbon tetrachloride-petroleum benzine yielded crude XI as brown needles; m. p., 200～226°C (0.3 g.). Further recrystallization from benzene afforded pure XI as brown plates; m. p., 224～226°C (0.2 g., 40%).

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15) N. G. Loudet, W. Chodkiewicz, P. Cadiot and A. Willemart, *Compt. rend.*, **250**, 366 (1960).

* All melting points are uncorrected. The nitrogen used was purified by passing the gas from a commercial steel cylinder through a Fieser solution. The ESR spectra were measured by Dr. S. Onishi in the Osaka Laboratories of the Japanese Association for Radiation Research on Polymers.

Found: C, 83.36; H, 4.15; Cl, 12.48. Calcd. for $C_{40}H_{24}Cl_2$: C, 83.46; H, 4.20; Cl, 12.32%.

***p*-Bromophenylacetylene.**—The acetylene was prepared from *p*-bromoacetophenone according to the well-known method[16].

***p*-Acetylbenzoic Acid (XIII)**.—*p*-Cyanoacetophenone (XII, 4.9 g., 0.034 mol.) which was prepared from *p*-bromoacetophenone[9] was heated with 58% sulfuric acid (7.8 g.) at 150°C for an hour. The yellow crystals deposited were recrystallized from boiling water, yielding XIII as yellow long needles; m. p., 207～209°C (3.8 g., 69%); lit. value[17], m. p., 205°C.

***p*-Ethynylbenzamide (XIV)**.—A mixture of the acetylbenzoic acid (XIII, 6.6 g., 0.04 mol.), phosphorus pentachloride (19.0 g., 0.09 mol.) and phosphorus oxychloride (8.0 ml.) was refluxed for 2 hr., and the oxychloride was removed under reduced pressure. The residual viscous brown oil was dissolved in ether (100 ml.) and added drop by drop into a solution of sodium amide (prepared from sodium, 6.6 g., 0.29 g. atom) in liquid ammonia (250 ml.) over a 15-min. period. The mixture was kept overnight at -70°C and was then stirred for 8.5 hr. at $-33\sim-40$°C. After evaporation of the ammonia, the reaction mixture was decomposed with a saturated aqueous ammonium chloride. The ethereal layer was separated, and the aqueous layer was extracted with ether (200 ml. × 5). The combined ether solution was washed with a saturated solution of sodium chloride and dried (Na_2SO_4). Evaporation of the solvent yielded crude XIV as light yellow powder; m. p., 172～173°C (2.7 g., 46.5%). IR ν_{max}, 3440 (NH); 1662, 1630 ($-CONH_2$); 3235 ($\equiv CH$); 2250 cm^{-1} ($-C\equiv C$).

This was used without further purification for the following reaction.

Methyl *p*-Ethynylbenzoate (XV).—A mixture of the benzamide (XIV, 2.7 g., 0.017 mol.), methanol (40 ml.) and concentrated sulfuric acid (3 ml.) was refluxed for 5 hr. on an oil-bath (110°C). The reaction mixture was poured into water (100 ml.) and extracted with ether (100 ml. × 3). The ethereal extracts were successively washed with saturated aqueous solutions of sodium chloride, sodium hydrogen carbonate and sodium chloride and dried (Na_2SO_4). Evaporation of the solvent yielded brown needles; m. p., 88～94°C (2.9 g., 96.6%). The crude crystals were recrystallized from methanol to give pure XVII; m. p., 93～95°C.

Found: C, 74.92; H, 5.02. Calcd. for $C_{10}H_8O_2$: C, 74.99; H, 5.03%.

1-Diphenylhydroxymethyl-4-(3′,3′-diphenylhydroxy-1′-propynyl)-benzene (XVI).—*a*) *From p-Bromophenylacetylene.*—Into a solution of *p*-bromophenylacetylene (6.0 g., 0.03 mol.) in ether (100 ml.) in an atmosphere of nitrogen was added an ethereal solution of *n*-butyllithium (45 ml., 0.07 mol.) over a 30-min. period. The mixture was stirred another hour at room temperature and then refluxed for an hour. Benzophenone (12.0 g., 0.067 mol.) in ether (100 ml.) was added to the mixture over a 40-min. period. The reaction mixture was kept for 2 days at room temperature and then stirred for 1.5 hr. under reflux, resulting in a pale yellow solution with a white precipitate. After decomposition with aqueous ammonium chloride, the ethereal layer was separated, washed with saturated sodium chloride solution, and dried ($MgSO_4$). Evaporation of the solvent resulted in a brown oily material (17.2 g.). A benzene solution of this substance was passed through a column of alumina and eluted with ether containing 1% of methanol. The eluate was evaporated to give a light yellow liquid. The liquid was treated with benzene-petroleum benzine (1 : 1), yielding colorless needles; m. p., 80～86°C (containing benzene of crystallization), 2.8 g. The crystals were heated at 80°C for 5 hr. in vacuo, affording XVI; m. p., 131～132°C. IR ν_{max}, 3400 cm^{-1} (OH).

Found: C, 87.21; H, 5.72. Calcd. for $C_{34}H_{26}O_2$: C, 87.52; H, 5.62%.

The mother liquor obtained by filtrating XVI was distilled, yielding viscous oil; b. p., 193°C/0.008 mmHg, (6.0 g.). Treatment of this substance with *n*-butyllithium, followed by hydrolysis, afforded a viscous oil. The oil could be crystallized by the addition of a small amount of benzene-petroleum benzine. Recrystallization from the same solvent yielded 1, 1, 3-triphenylpropyn-1-ol. It showed no depression of the melting point on admixture with an authentic specimen*. Also, the infrared spectrum was found to be identical with that of the specimen. On the basis of this evidence, the structure of XVIII was assigned to the viscous oil obtained from the mother liquor.

b) *From Methyl p-Ethynylbenzoate (XV).*—Methyl *p*-ethynylbenzoate (XV, 1.6 g., 0.01 mol.) in ether (30 ml.) was stirred drop by drop into a solution of phenyllithium (0.033 mol. in 35 ml. of ether) under an atmosphere of nitrogen. The mixture was added for 1.5 hr. at room temperature and then refluxed for another hour. To the cooled mixture, benzophenone (1.8 g., 0.01 mol.) in ether (30 ml.) was added. After being left standing overnight, the mixture was stirred for 2 hr. and mixed with a saturated aqueous ammonium chloride. The aqueous layer was extracted with ether (80 ml. × 3) and combined with the ethereal layer. The combined ethereal solution was washed with a saturated sodium chloride solution and dried (Na_2SO_4). Evaporation of the solvent gave a brown viscous oil. This was dissolved in benzene and chromatographed on alumina. Elution with ether containing 1% of methanol, followed by recrystallization from benzene-petroleum benzine, afforded XVI (2.8 g., 61.4%), which was proved to be identical with the specimen obtained by method a) by mixed melting point determination and infrared spectroscopy.

1-Diphenylchloromethyl-4-(3′-chloro-3′, 3′-diphenyl-1′-propynyl)-benzene (XVII).—A mixture of XVI (1.5 g., 0.003 mol.), benzene (15 ml.), and thionyl chloride (15 ml.) was refluxed for 2 hr., and the volatile material was removed under reduced pressure. The residue was dried over sodium hydroxide in vacuo, yielding a yellowish brown solid (XVII, 1.5 g.). XVII was also obtained by treating

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16) T. L. Jacobs, "Organic Reactions", Vol. 5, 50 (1949).

17) H. Ingle, *Ber.*, **27**, 2527 (1894).

* The authentic specimen was kindly supplied by Dr. G. Nakaminami of this Laboratory.

XVI with a mixture of acetyl chloride and hydrochloric acid[5b]. Further purification of XVII by recrystallization was proved to be difficult owing to its unstable nature in the presence of heat and light. The infrared spectrum of the crude XVII lacks the absorption of the hydroxyl group.

1-Benzhydryliden-4-(3′, 3′-diphenylpropadienyliden)-1, 4-dihydrobenzene (V_a).—A mixture of finely powdered anhydrous stannous chloride (2.0 g.), XVII (0.4 g.), and benzene (1500 ml.) was shaken for 2 hr.; then fresh anhydrous stannous chloride (2.0 g.) was added, and the shaking was continued for a further 5 hr. The reaction mixture was filtered, and the filtrate was washed with water and then dried over anhydrous sodium sulfate for 30 min. The dried solution was passed through a column (20 cm.) of alumina (25 g.). The filtrate was concentrated under reduced pressure below 40°C, yielding a partly crystallized solid. Treatment of the solid gave a small amount of deep purple needles with a green metallic surface luster. The melting point (ca. 170°C (decomp.)) could not be determined accurately because of its deep color. A qualitative analysis of this substance revealed the contamination of a chlorine compound.

Found: C, 92.96; H, 5.71; Calcd. for $C_{34}H_{24}$: C, 94.41; H, 5.59%.

Formation of 4-(3′, 3′-Diphenyl-1′-chloro-propadienyl)-phenyl-diphenylmethyl (XXV) and its Peroxide (XXVI).—A mixture of molecular silver (4.0 g.) and XVII (1.0 g.) in benzene was stirred at 60°C for 2 hr. in an atmosphere of nitrogen in a dark place, forming a dark brown solution. The molecular silver was removed by filtration, and the filtrate was passed through a column (20 cm.) of alumina (25 g.). The red-violet filtrate thus obtained was concentrated under reduced pressure in a nitrogen atmosphere, yielding a dark brown solid (0.1 g.). The solid gradually changed to a red-brown solid on being kept in an evacuated desiccator. After 2 days, the substance was subjected to ESR measurement without further purification.

Found: C, 84.11; H, 4.74; Cl, 7.49. Calcd. for $C_{34}H_{24}ClO$: C, 84.36; H, 4.99; Cl, 7.33%.

1, 4-Bis-(3′-hydroxy-3′, 3′-diphenyl-1′-propynyl)-benzene (XIX). — This substance was prepared according to the method of Ried[10] by the action of benzophenone (14.5 g.) on the dilithium derivative of *p*-diethynylbenzene (5.0 g.)[18]. Pale yellow plates; m. p., 222∼226°C (11 g., 56%) (lit. values, m. p., 226°C, 56%)[10].

1, 4-Bis(3′-chloro-3′, 3′-diphenyl-1′-propynyl)-benzene (XX).—Hydrogen chloride was introduced for 30 min. into a mixture of XIX (1.0 g.), ether (80 ml.), tetrahydrofuran (20 ml.) and acetyl chloride (0.5 ml.). The mixture was allowed to stand overnight in an ice-bath. The precipitate formed was filtered and washed repeatedly with cold ether, yielding XX as colorless needles (1.0 g., 91%). This substance decomposed at 130°C, forming a red solid which did not fuse at temperatures over 300°C. Also, the action of thionyl chloride (15 ml.) with a suspension of XIX (0.5 g.) in benzene (15 ml.) at 0.5°C resulted in the formation of XX in a low yield (0.1 g., 18%). Several attempts to purify XX failed, but the absence of a hydroxyl group was proved by infrared spectroscopy.

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[18] W. Ried, H. J. Schmidt and A. Urschel, *Chem. Ber.*, **91**, 2472 (1958).