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Synthesis of Furan Derivatives. LV.[1] Macrocyclic Rings from the Reaction of Dialdehyde with Bisphosphorane and with Diamine[2]

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7,8:17,18-Dibenzo[20]annulene 1,4:11,14-dioxide all *trans* isomer (IV) has been synthesized from the Wittig reaction of di-*trans* 1,2-bis[(β-5-formyl)-2-furyl]-vinyl benzene (IIIa) with *o*-xylene-bis-(triphenylphosphonium bromide) in fairly high yield (35%). The reaction of IIIa with *o*-phenylenediamine in tetrahydrofuran has been shown to yield three annelated products, *i.e.*, 7,8:17,18-dibenzo-19,20-dihydro-16,19-diaza[20]annulene 1,4:11,14-dioxide (VI) in 15%, 16-H-7,8:17,18-dibenzo-15-keto-16,19-diaza[20]annulene 1,4:11,14-dioxide (VII) in 1.0% and oxazirino[2,3-*s*]7,8:17,18-dibenzo-16-aza[20]annulene 1,4:11,14-dioxide (VIII) in 15.7% yield. The interrelationship among these products was discussed.

The reaction of hydrazine hydrate and *cis*-α,β-di(5-formyl-2-furyl)ethylene (XIb) has been shown to yield dimeric [28]tetraazaannulene tetraoxide (XIII) in 2.5%, and no monomeric [14]diazaannulene dioxide (XII) or no other disproportionation products were obtained.

Recently, the Wittig reaction of dialdehydes with bisphosphoranes has been applicable to the synthesis of the large variety of annulenes or nonbenzenoid cyclic structures.[4] These compounds are of inherent interest in connection with the inquiry of aromaticity and have been extensively discussed in numerous publications.[5]

J.A. Elix and M.V. Sargent[6] have reported four isomeric 7,8:17,18-dibenzo[20]annulene 1,4:11,14-dioxides by the one step Wittig Reaction of equimolar portions of 2,5-furandialdehyde and *o*-xylene-bis(triphenylphosphonium bromide). It may be expected that the minor yields of isomeric annulenes (total *ca.* 5%) are attributable to the steric interferance among the internal hydrogens. On the other hand, if the structurally related nitrogen analogue, in which the vinyl groups are replaced by the azomethine groups, such as 7,8:17,18-dibenzo-16,19-diaza[20]annulene 1,4:11,14-dioxide (V) (see Chart 2), were prepared, the yield of the diazaannulene might turn out to be considerably better than that in the case of the [20]annulene, since nitrogens does not cause excessive strain.

To probe the above assumption, we attempted to prepare 1,2-bis[β-(5-formyl-2-furyl)-vinyl]benzene (III), and the reactions of III with *o*-xylene-bis(triphenylphosphonium bromide) and with *o*-phenylenediamine were examined, respectively.

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[1] Part LIV: H. Saikachi and H. Sugimoto, *Yakugaku Zasshi*, **91**, 64 (1971).

[2] Some part of this paper was presented at the second Symposium of Heterocyclic Chemistry, Nagasaki, Nov. 12, 1969. Abstract Papers pp. 224—229.

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[4] K. Grohman and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 7119 (1967); R.H. Mitchell and F. Sondheimer, *ibid.*, **90**, 530 (1968); A.P. Bindra, J.A. Elix and M.V. Sargent, *Tetrahedron Letters*, **1968**, 4335; J.A. Elix, *Chem. Commun.*, **1968**, 343; H.A. Staab, F. Graf and B. Junge, *Tetrahedron Letters*, **1966**, 743; A.P. Bindra, J.A. Elix and M.V. Sargent, *ibid.*, **1968**, 5573; J.A. Elix, M.V. Sargent and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 5080 (1967); C. Brown and M.V. Sargent, *J. Chem. Soc.* (*C*), **1969**, 1818; J.A. Elix, M.V. Sargent and F. Sondheimer, *J. Am. Chem. Soc.*, **92**, 973 (1970); A.P. Bindra, J.A. Elix, M.V. Sargent, *Aust. J. Chem.*, **22**, 1449 (1969); P.J. Garratt, K. Peter and C. Vollhardt, *Chem. Comm.*, **1970**, 109.

[5] G.M. Badger, "Aromatic Character and Aromaticity," Cambridge Univ. Press, 1969; F. Sondheimer, I.C. Calder, J.A. Elix, Y. Gaoni, P.J. Garratt, K. Grohmann, G.D. Maio, J. Meyer, M.V. Sargent and R. Wolovsky, "Special Publication No. 21," The Chemical Society, London, 1967.

[6] J.A. Elix and M.V. Sargent, *J. Am. Chem. Soc.*, **90**, 1631 (1968).

(5-Dimethoxymethyl-2-furfuryl)triphenylphosphonium chloride (II) was prepared in a straight forward manner by the acetalization of (5-formyl-2-furfuryl)triphenylphosphonium chloride[7] (I) in 93% yield. Reaction of *o*-phthalaldehyde with two molar portions of II in absolute dimethylformamide on addition of lithium methoxide and the subsequent hydrolysis of the isomeric diacetals gave a mixture of di-*trans* and di-*cis* 1,2-bis[β-(5-formyl-2-furyl)vinyl]-benzene, (IIIa) and (IIIb), respectively.

The structure and stereochemistry of di-*trans* isomer (IIIa) (25.2%) and the di-*cis* isomer (IIIb) (42.5%) were deduced from the diffrence between coupling constants of the *trans* and the *cis* olefinic protons, *i.e.*, the nuclear magnetic resonance (NMR) spectrum of the *trans* isomer exhibited the *trans* olefinic protons as two doublets centered at 6.83 and 7.70 ppm (each 2H, $J=16$ cps), while that of the *cis* isomer appeared at 6.45 and 6.80 ppm (each 2H, $J=12$ cps). The magnitude of these coupling constants is compatible with a pair of the *cis* and *trans* olefinic protons.[8]

The Wittig reaction of IIIa with *o*-xylene-bis(triphenylphosphonium bromide) in absolute dimethylformamide by lithium methoxide method gave all *trans* 7,8:17,18-dibenzo[20]annulene 1,4:11,14-dioxide (IV) in 35.3% yield. This compound is quite identical in all respects with authentic sample,[6] which was prepared by the photoisomerization of the mono-*cis* [20]annulene dioxide isomer.

As IV was obtained in fairly good yield, the assumption mentioned above was not justified, and the steric repulsion among inner hydrogens suggested less contributive to the above ring closure.

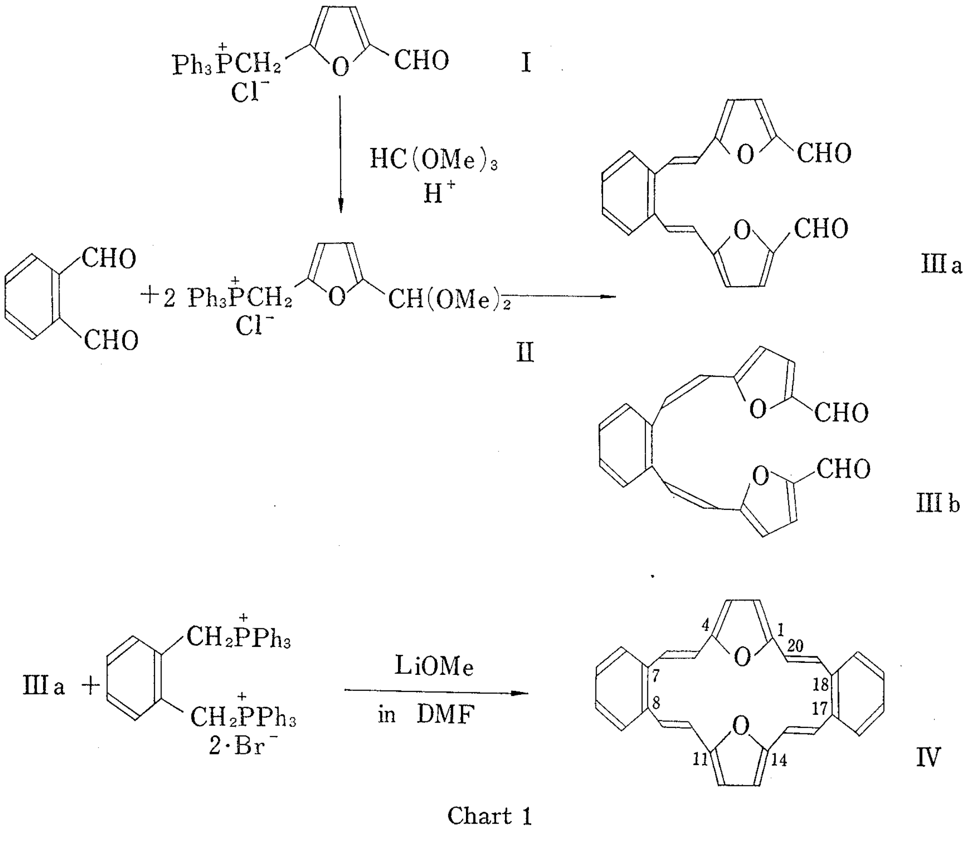

Chart 1

As an extension of the above sequence the condensation of di-*trans* 1,2-bis-[β-(5-formyl-2-furyl)vinyl]benzene (IIIa) with *o*-phenylenediamine was now examined in purified tetra-

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[7] J.A. Elix, *Chem. Commun.*, **1968**, 343.

[8] J.M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd edition, Pergamon Press, 1969, p. 301.

hydrofuran, in an effort to prepare the annelated 16,19-diaza[20]annulene dioxide (V) under a high dilution condition. The infrared (IR) spectrum of the reaction mixture showed a strong carbonyl absorption at 1670 cm^{-1}, which suggested the presence of a linear polymer and, in addition, the mass spectrum of the mixture showed another presence of a cyclic compound, whose molecular weight is corresponding to the cyclic dimer of V, by the appearance of a prominent fragment ion at *m/e* 494.174 [$(C_{26}H_{18}O_2N_2)_2—C_{20}H_{14}O_2$ requires 494.174] which resulted from the α-cleavage of $C_{20}H_{14}O_2$ group (for the eliminated group, see the illustrated part with dotted line on structure (V)).

Other three products of relatively lower molecular weight have been isolated, *i.e.*, 7,8:17, 18-dibenzo-19,20-dihydro-16,19-diaza[20]annulene 1,4:11,14-dioxide (VI), 16-H-7,8:17,18-dibenzo-15-keto-16,19-diaza[20]annulene 1,4:11,14-dioxide (VII) and oxazirino-[2,3-*s*]7,8:17,18-dibenzo-16-aza[20]annulene 1,4:11,14-dioxide (VIII), respectively.

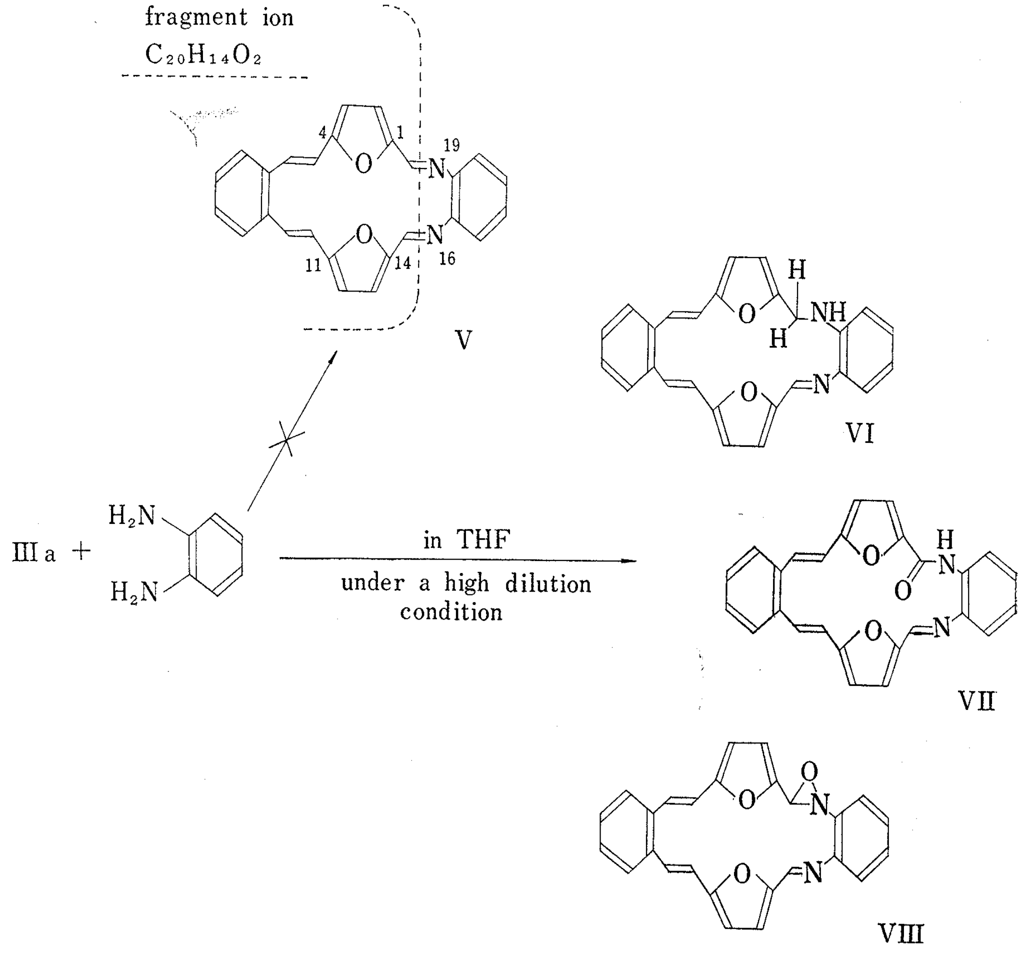

Chart 2

The column chromatography of the benzene soluble portion of the reaction mixture on silica gel with benzene afforded (VI) as beautiful red prisms, mp 268°, in 15% yield. The mass spectrum of VI exhibited a molecular ion at 392.153 ($C_{26}H_{20}O_2N_2$ requires 392.152) and no peak at 390 ($C_{26}H_{18}O_2N_2$) expected for the diazaannulene dioxide (V). The analytical data of VI was also supported the former composition. The NMR spectrum of VI lacked the aldehydic proton and exhibited a singlet (1H) at 6.87 ppm due to the N–H proton, which was exchangeable with deuterium oxide, and another singlet at 4.40 ppm characteristic of the methylene protons (2H).

The second product (VII) was isolated from the well separated second band of the above column as reddish prisms, mp 289—291°, in 1.0% yield. The structure of VII was confirmed on the basis of the spectral and analytical data, *i.e.*, the IR spectrum showed carbonyl absorption at 1653 cm^{-1}, and N–H bending absorption at 1560 cm^{-1}. Both of them suggested strongly the presence of a secondary amide group (see Fig. 1). The mass spectrum exhibited a prominent molecular peak at 406 (calcd. for $C_{26}H_{18}O_3N_2$) toghether with other major fragments at 389 and 377. Satisfactory elemental analytical data were also obtained for the above formulas. The NMR spectrum lacked aldehydic protons, and showed a broad signal at 10.25 ppm due to the associated N–H proton.

The third product (VIII) was separated, with its low solubility, from the vigorously stirred solution of the reaction residue in benzene under the illumination of diffused sunlight at room temperature for two days, and was recrystallized from toluene as organge yellow prisms, mp 180—181°, in 15.7% yield. The IR spectrum of VIII exhibited no carbonyl absorption, but showed a medium absorption at 1250 cm^{-1} characteristic of the oxyazirane ring.[9] A strong band due to nitrone was not observed in the region of N–O stretching absorption.[9] The mass spectrum of VIII exhibited a molecular ion at *m/e* 406 (calcd. for $C_{26}H_{18}O_3N_2$). The infrared and electronic spectra of VI, VII and VIII were showed in Fig. 1 and Fig. 2, respectively.

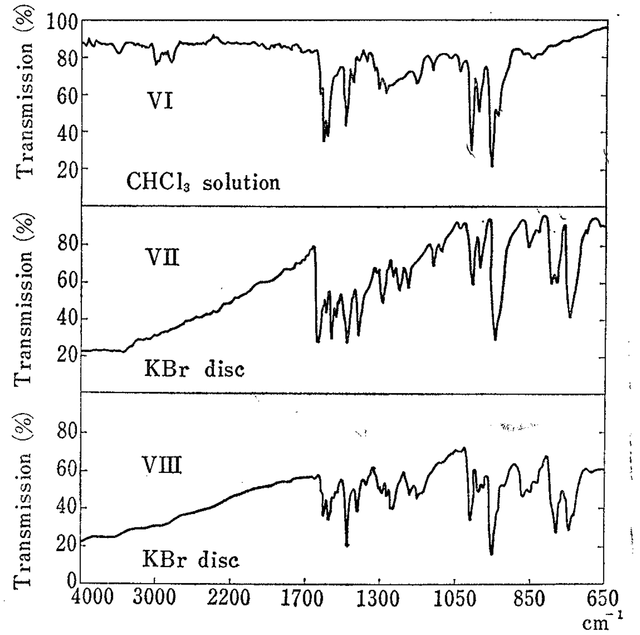

Fig. 1. The Infrared Spectra of VI, VII and VIII

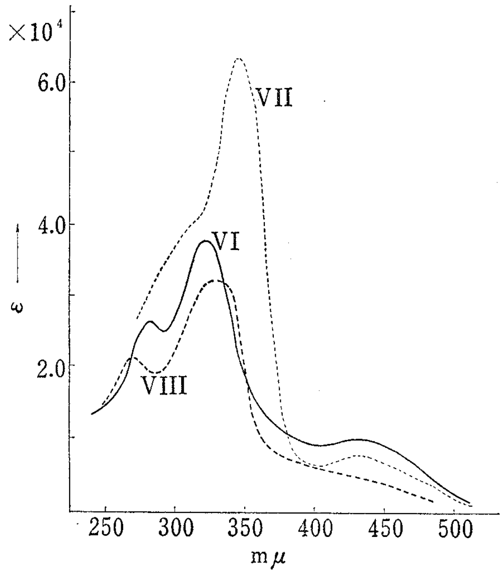

Fig. 2. The Electronic Spectra of VI, VII and VIII in Benzene

The interrelationship among these products may be well explained by the posturation of transitory existence of the nitrone structure (IX), although not isolated, as outlined below.

$$\begin{tikzcd} \text{IIIa} + o\text{-phenylene diamine} \arrow[r] \arrow[dr] \arrow[ddr] & \text{[nitrone] IX} \arrow[r, "h\nu"] & \text{oxazirane VIII} \arrow[r] & \text{second. amide VII} \\ & \text{dihydroazaannulene VI} & & \\ & \text{cyclic dimer and linear polymer} & & \end{tikzcd}$$

Since nitron is found to be very photosensitive[10] and easily to undergo light induced rearrangement to oxazirane,[11] transformation of IX into VIII may be reasonable. The path-

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[9] H. Sindo and B. Umezawa, *Chem. Pharm. Bull.* (Tokyo), **10**, 492 (1962).

[10] M.J. Kamlet and L.A. Kaplan, *J. Org. Chem.*, **22**, 776 (1957); J.S. Splitter and M. Calvin, *ibid.*, **23**, 651 (1958).

[11] D. Singh, *J. Am. Chem. Soc.*, **90**, 3894 (1968).

way to the secondary amide structure (VII) *via* the oxazirane (VIII) may also be possible, because of the three membered strain energy of VIII.[12]

It is interesting that oxydative and reductive annelated products were isolated, instead of the monomeric cyclic bis-azomethine compound (V), expected for the normal diamine and dialdehyde condensation. Both yields for the logical pair of VI and VIII were found to be comparable. An analogous disproportionation mode of diamine and dicarbonyl compound was reported in the reaction of acetonyl acetone and hydrazine hydrate in acetic acid.[13]

Another condensation of diamine with diformyl compound was carried out in the combination of *cis* α,β-bis(5-formyl-2-furyl)ethylene (XIb) and hydrazine hydrate to examine whether this reaction may afford the disproportionation products or not.

The *cis* dialdehyde (XIb), mp 120—122°, was prepared by the Wittig reaction of 5-dimethoxymethylfurfural with II, followed by the subsequent hydrolysis of the isomeric diacetals in 20% yield, together with the corresponding the *trans* isomer (XIa), mp 256—257° (56.5%).

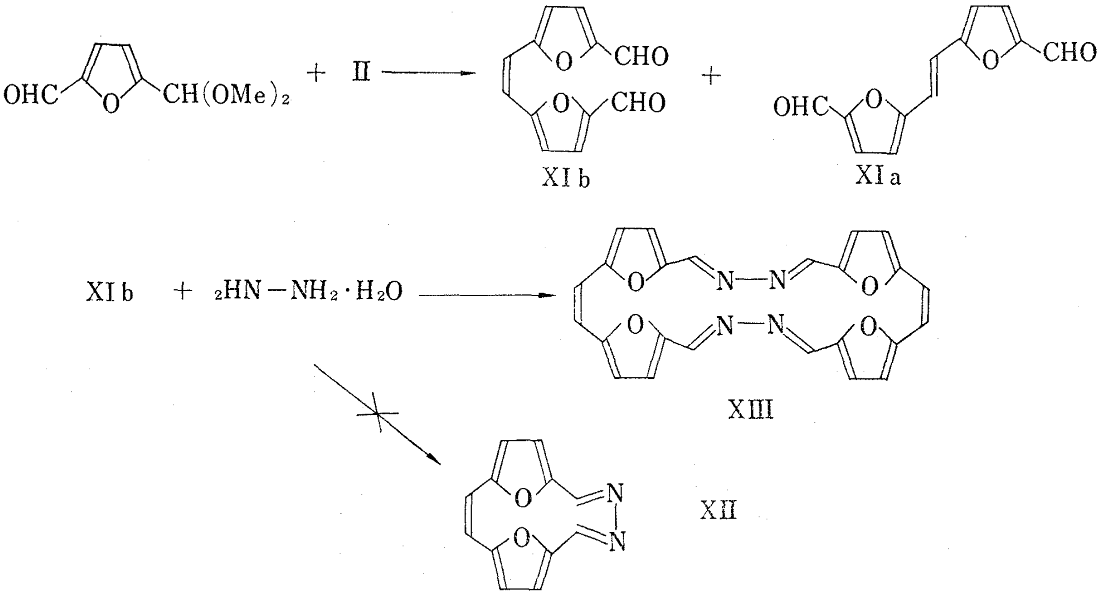

Chart 3

The condensation of XIb with hydrazine hydrate, however, gave a dark reddish polymeric substance as a major product, and 12,13,26,27-tetraaza[28]annulene 1,4:7,10:15,18:21,25-tetraoxide (XIII), mp 305°, was obtained as reddish violet prisms in 2.5% yield, and no monomeric [14]diaza-annulene dioxide (XII) or disproportionation products were obtained.

The mass spectrum of XIII showed a prominent molecular peak at *m/e* 424 (calcd. for $C_{24}H_{16}O_4N_4$) and the elemental analytical data supported above formula. The electronic spectrum of XIII in benzene showed absorption maxima at 362.5 (91000) with subsidary shoulder at 387.6 (48900).

Experimental

Melting points were not corrected. IR spectra were measured on a Koken DS-301 spectrophotometer. NMR spectra were determined in $CDCl_3$ at 60 Mc on the Nihon Denshi C 60 H recording spectrophotometer

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12) H. Krim, *Chem. Ber.*, **91**, 1057 (1958).

13) It was reported that this reaction gave principally 3,6-dimethyl-tetrahydro-pyridazine and 3,6-dimethyl-pyridazine; C.G. Overberger, N.R. Byrd and R.B. Mesrobian, *J. Am. Chem. Soc.*, **78**, 1961 (1956).

using TMS as the internal standard. Electronic spectra were determined on a Hitachi-Perkin Elmer UV-Vis spectrometer Model 139. The mass spectra were obtained on a Nihon Denshi Model JmS 01SG instrument, with visicorder recording.

(5-Formyl-2-furfuryl)triphenylphosphonium Chloride (I)——A solution of 2-chloromethylfurfural (25.0 g, 0.173 mole) and triphenylphosphine (46.5 g, 0.177 mole) in anhydrous benzene (300 ml) was refluxed for 3 hr. After cooling, the product was collected by filtration, washed throughly with anhydrous benzene. The resulting phoshonium chloride (62 g, 87%) formed pale yellow prisms, which melted at 228—230°.[14]

(5-Dimethoxymethyl-2-furfuryl)triphenylphosphonium Chloride (II)——A solution of (5-formyl-2-furfuryl)triphenylphosphonium chloride (I) (32.8 g, 0.08 mole) and methyl orthoformate (15.0 g, 0.14 mole) in absolute methanol (50 ml) was refluxed for 3 hr in the presence of a few milligrams of *p*-toluenesulfonic acid. After cooling, anhydrous sodium acetate (0.2 g) was added and then concentrated under reduced pressure, cooled, and diluted with 200 ml of dry benzene. After cooling in an ice bath, the product was filtered, washed throughly with anhydrous benzene until no further filtrate had assumed an intense red color. Air drying gave colorless prisms (33.6 g, 93%). An analytical sample was recrystallized from a mixture of benzene-chloroform (10:1), mp 175° (decomp). *Anal.* Calcd. for $C_{26}H_{26}O_3ClP$: C, 69.10; H, 5.81. Found: C, 68.68; H, 5.75. IR (KBr) cm^{-1}: 1060, 1100, 1111 (each ν-acetal).

Di-*trans* and Di-*cis* 1,2-bis[*β*-(5-Formyl-2-furyl)vinyl]benzene (IIIa and IIIb)——To a solution of *o*-phthalaldehyde (5.36 g, 0.04 mole) and (5-dimethoxymethyl-2-furyl)triphenylphosphonium chloride (II) (40.7 g, 0.09 mole) in 100 ml of anhydrous dimethylformamide was added 0.18 mole of lithium methoxide in 80 ml of methanol dropwise at 18—35° in an atmosphere of dry nitrogen. The solution was stirred at 30—32° for further 4 hr, then concentrated under reduced pressure, and diluted with water. The mixture was extracted with benzene, washed with water and dried (Na_2SO_4). After the complete removal of benzene under reduced pressure, the reddish residue was dissolved in dry ether to separate triphenylphosphine oxide, which was filtered off. The filtrate was concentrated and the obtained oily residue was heated with a solution of *p*-toluenesulfonic acid (5 g) in 125 ml of 60% aq. ethanol at 60° for 1 hr. The mixture was cooled, and separated orange red crystals were filtered and recrystallized from toluene to give the *trans* isomer (IIIa), as orange red needles, mp 147—148°, 3.2 g, in 25.2%. IR (KBr) cm^{-1}: 1675 (ν_{C-C}). Electronic spectrum, $\lambda_{max}^{benzene}$ mμ (ε), 338 (51600) and 372 (28700). NMR spectrum ($CDCl_3$) showed doublets centered at 6.83 and 7.70 ppm (each 2H, $J=16$ cps, *trans* olefinic protons) and a singlet at 9.63 ppm (2H, aldehydic protons). *Anal.* Calcd. for $C_{20}H_{14}O_4$: C, 75.46: H, 4.43. Found: C, 75.75: H, 4.61.

The aq. filtrate, from which the di-*trans* isomer was removed, was diluted with water, extracted with benzene, and dried with Na_2SO_4. After concentration, the dark reddich solution was chromatographed on silica gel with benzene to obtain 5.4 g of the di-*cis* isomer (IIIb), reddish oil (42.5%). IR (liquid film) cm^{-1}: 1673 ($\nu_{C=O}$) and 1025 (ν_{C-O-C}); electronic spectrum, $\lambda_{max}^{benzene}$ mμ (ε): 328 (24300). NMR spectrum showed two doublets centered at 6.45 and 6.80 ppm (each 2H, $J=12$ cps, the *cis*-olefinic protons) and a singlet at 9.45 ppm (2H, aldehydic protons). *Anal.* Calcd. for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.33; H, 4.36. Disemicarbazone: yellow needles, mp 214—217°.

The column was further eluated with chloroform and yielded 0.8 g of di-*trans* isomer (IIIa).

All-*trans* 7,8:17,18-dibenzo[20]annulene 1,4:11,14-Dioxide (IV)——A suspension of di-*trans* 1,2-bis[*β*-(5-formyl-2-furyl)vinyl]benzene (IIIa) (954 mg, 3 mmole) and *o*-xylene-bis(triphenylphosphonium bromide) (2.84 g, 3.6 mmole) in absolute dimethylformamide (40 ml) was stirred at room temperature, and a solution of lithium methoxide (prepared from 35 mg of lithium) in absolute methanol (20 ml) was then added dropwise over a period of 1 hr in an atmosphere of nitrogen. The temperature was rised gradually to 22—27°. The solution was continued to stirr at 30—35° for 4 hr and then cooled. The titled compound was obtained as red fine crystals, which were filtered, washed throughly with ethanol, 410 mg (35.3%), mp 300°: IR (KBr) cm^{-1}: 1010, 990, 962 (sh), 952, 937 sh, 781, 747; electronic spectrum, $\lambda_{max}^{CHCl_3}$ mμ (ε): 305 sh (56500), 314 (63000), 358 (71000) and 374 (96000) (lit[6] 303 (45100), 314 (32300), 358 (60500) and 374 (83100)).

The Reaction of Di-*trans* 1,2-bis[*β*-(5-formyl-2-furyl)vinyl]benzene (IIIa) with *o*-Phenylenediamine——To a vigorously stirred anhydrous tetrahydrofuran (150 ml, distilled over sodium), both solution of (IIIa) (2.64 g, 8.3 mmole) and *o*-phenylenediamine (0.975 g, 9 mmole) each in 100 ml of anhydrous tetrahydrofuran (100 ml) were dropwise added simultaneously over a period of 1.5 hr through high dilution apparatuses[15] with strong refluxineg. After the addition, the dark reddish solution was refluxed for a further 4.5 hr, then concentrated *in vacuo*, cooled, and diluted with benzene (30 ml). The solution was stirred for 2 days at room temperature under the diffused sunlight. Fine yellow precipitates were filtered off, washed with three 10 ml portions of cold tetrahydrofuran, and recrystallized to give 0.645 g (15.7%) of oxazirino[2,3-*s*]7,8: 17,18-dibenzo-16-aza[20]annulene 1,4:11,14-dioxide (VIII), mp 180—181°, fine yellow needles. The mass spectrum exhibited a molecular ion peak at *m/e* 406 (calcd. for $C_{26}H_{18}O_3N_2$). IR (KBr) cm^{-1}: 1560, 1495, 1425, 1250 (oxazirane), 1020, 953, 790 and 743: electronic spectrum $\lambda_{max}^{benzene}$ mμ (ε): 296 (21200) and 355—360 (plateau) (32500);

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[14] J.A. Elix, *Chem. Commun.*, **1968**, 343.

[15] N.J. Leonard and R.C. Sentz, *J. Am. Chem. Soc.*, **74**, 1708 (1952).

the NMR spectrum could not obtained to the low solubility of this compound. *Anal.* Calcd. for $C_{26}H_{18}O_3N_2$: C, 76.83; H, 4.46; N, 6.89. Found: C, 77.13; H, 4.79; N, 6.67.

The filtrate from which VIII was removed off was concentrated to a small volume *in vacuo*, and chromatographed on a column of silica gel (Mallinckrodt, 200—300 mesh) with benzene. Clearly separated two bands were developed. The fractions from the first band were evaporated to yield red crystals of 7,8:17,18-dibenzo-19,20-dihydro-16,19-diaza[20]annulene 1,4:11,14-dioxide (VI) (487 mg, 15%), which were recrystallized from ethyl acetate, red prisms, mp 268°. The mass spectrum of VI exhibited a very prominent peak at *m/e* 392.153 due to the molecular ion ($C_{26}H_{20}O_2N_2$ requires *m/e* 392.1523). IR (KBr) cm^{-1}: 3400 (N–H), 1612, 1595, 1490, 1029, 990 and 960. Electronic Spectrum, $\lambda_{max}^{benzene}$ mμ (ε): 282.5 (26800), 323 (39200) and 434 (10250). NMR spectra, see the Discussion. *Anal.* Calcd. for $C_{26}H_{20}O_2N_2$: C, 79.57; H, 5.14; N, 7.14. Found: C, 79.48; H, 5.03; N, 7.14.

On evaporation of the fraction from the second band yielded reddich prisms of 16-H-7,8:17,18-dibenzo-15-keto-16,19-diaza[20]annulene 1,4:11,14-dioxide (VII), which were recrystallized from ethyl acetate to yield 34.7 mg (1.0%) of a pure sample, mp 289—291°. IR (KBr) cm^{-1}: 1653, 1582, 1498, 1440, 1310, 1016, 995, 805, 790 and 755; electronic spectrum showed $\lambda_{max}^{benzene}$ mμ (ε): 342.5 (615000) and 435 (7200). The mass spectrum showed a prominent molecular peak at *m/e* 406. NMR spectrum, see the Discussion. *Anal.* Calcd. for $C_{26}H_{18}O_3N_2$: C, 76.83; H, 4.46; N, 6.89. Found: C, 76.76; H, 4.49; N, 6.92.

α,β-Di(5-formyl-2-furyl)ethylenes (the *trans* and the *cis* Isomer, (XIa) and (XIb))——To a solution of 5-dimethoxymethyl-2-furaldehyde[16] (11.2 g, 0.0658 mole) and (5-dimethoxymethyl-2-furfuryl)triphenylphosphonium chloride (II) (33.1 g, 0.073 mole) in absolute methanol (100 ml) was added a solution of lithium methoxide (prepared from 1.0 g of lithium) with stirring at 18—35° over a period of 1 hr under an atmosphere of nitrogen. The reddish yellow solution was stirred for more 3 hr and then concentrated to a small volume and diluted with water, extracted with benzene and dried (Na_2SO_4). After complete removal of benzene, dry ether (150 ml) was added to the residue to precipitate triphenylphosphine oxide, which was filtered off, and the filtrate was evaporated to yield the dark reddich residue, which was stirred with a solution of *p*-toluenesulfonic acid (5.0 g) in aq. 70% ethanol at room temperature for 3 hr. The *trans* α,β-di(5-formyl-2-furyl)ethylene was separated as orange red prisms, which were filtered, washed with cold ethanol, and then recrystallized from dimethylformamide, mp 256—257 (8.0 g, 56.5%). IR (KBr) cm^{-1}: 1667 ($\nu_{C=O}$). Electronic Spectrum, $\lambda_{max}^{benzene}$ mμ (ε): 365 sh (22400), 382.5 (36800) and 405 (37000). NMR spectrum showed a singlet at 7.25 ppm (2H, the *trans* olefinic protons) and another singlet at 9.58 ppm due to the aldehydic protons (2H). *Anal.* Calcd. for $C_{12}H_8O_4$: C, 66.67; H, 3.73. Found: C, 66.34; H, 3.95.

The aq. filtrate from which the *trans* isomer was removed was concentrated under reduced pressure to a small volume and diluted with water and extracted with benzene, washed several times with water and dried (Na_2SO_4). On concentration *cis* α,β-diformyl-2-furyl)ethylene (XIb) was obtained as yellow prisms, which were recrystallized from carbon tetrachloride, mp 120—122°, 2.8 g (19.7%). IR (KBr) cm^{-1}: 1665 ($\nu_{C=O}$). Electronic Spectrum, $\lambda_{max}^{benzene}$ mμ (ε): 365 sh (19200), 382.5 (28000), 405 (25800). NMR spectrum showed a singlet at 6.50 ppm (2H, the *cis* olefinic protons) and a singlet at 9.65 ppm (2H, aldehydic protons). *Anal.* Calcd. for $C_{12}H_8O_4$: C, 66.67; H, 3.73. Found: C, 66.43; H, 3.77.

Reaction of *cis* α,β-Di(5-formyl-2-furyl)ethylene (XIb) and Hydrazine Hydrate——A solution of XIb (1.41 g, 6.75 mmole) in tetrahydrofuran (150 ml) and a solution of 80% hydrazine hydrate (0.440 g, 7 mmole) in tetrahydrofuran (100 ml) were added simultaneously to boiling tetrahydrofuran (150 ml) over s period of 7 hr through dilution apparatuses. The mixture was then concentrated under reduced pressure to give a dark reddish solid mass (1.6 g), which was extracted several times with 200 ml portions of benzene and concentrated to afford violet crystals, which were washed with a few ml of cold tetrahydrofuran and recrystallized from a large volume of toluene to afford 36 mg of violet needles of 12,13,26,27-tetraaza[28]-annulene 1,4:7,10:15,18:21,25-tetraoxide (XII), mp 305°. The mass spectrum of XII, exhibited a molecular peak as a base peak at *m/e* 424. IR (KBr) cm^{-1}: 1630, 1610, 1409, 1370, 1280, 1240, 1166, 1022, 968, 952 and 800. Electronic Spectrum, $\lambda_{max}^{benzene}$ mμ (ε): 362.5 (91000) and 387.5 (48900). *Anal.* Calcd. for $C_{24}H_{16}O_4N_4$: C, 67.92; H, 3.80; N, 13.40. Found: C, 68.67; H, 3.84; N, 13.05.

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