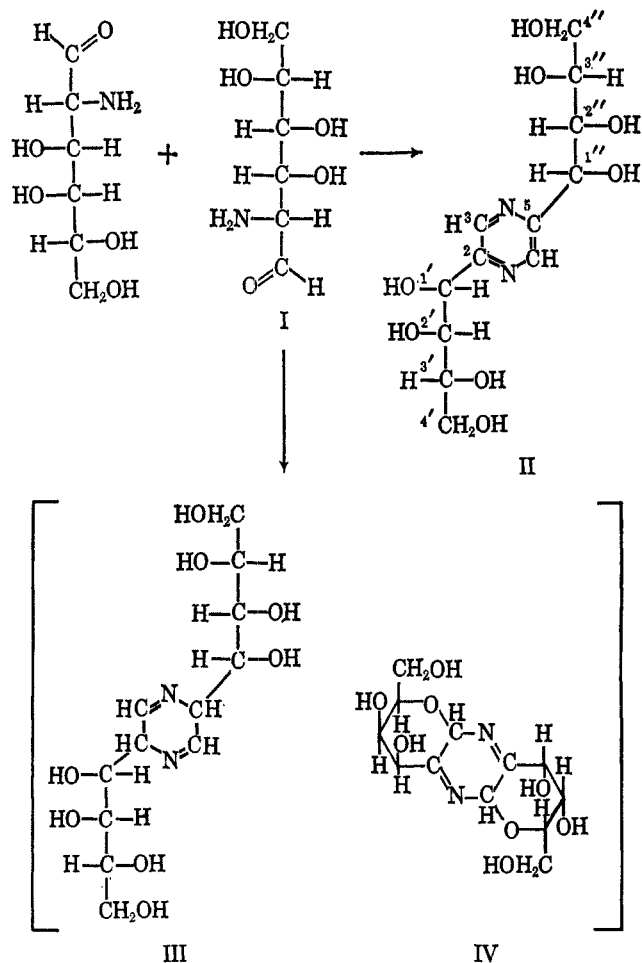


Figure 1.—Nmr spectrum of 2,5-(D-lyxo-tetraacetoxybutyl)pyrazine.

SCHEME I



galactose) appears as a low field singlet, τ 1.04, as in the case of fructosazine. This fact supports the structure II, for in the structure III the proton at C-3 would appear as a doublet through coupling with the proton at C-2. The integral value of protons appears between τ 4.0 and 6.0, corresponding to six methine protons at C-1', C-2', C-3', C-1'', C-2'', C-3'', and four methylene protons at C-4', C-4'', and between τ 7.8 and 8.2, corresponding to 24 protons of eight acetyl groups. These data exclude the possibility of structure III and IV. (See Scheme I.)

Experimental Section⁶

Tagatosazine.—Thirty grams of 2-amino-2-deoxy-D-galactose hydrochloride was suspended in 150 ml of hot methanol contain-

(6) All melting points are uncorrected.

ing 3.6 g of sodium, and after shaking, sodium chloride deposited was filtered off. The filtrate was warmed to 60–65° in water bath under reflux and oxygen was bubbled into the solution for 6 hr. After allowing to stand overnight, this reaction mixture was dissolved in 500 ml of water and passed through an Amberlite infrared-120 (H⁺) column (3 × 70 cm). The eluate together with washings was neutralized with Dowex 1 × 8 (HCO⁻), 200–400 mesh, and the resin was removed by filtration. After treatment with charcoal, the solution was concentrated *in vacuo* to a syrup. This syrup was dissolved in small amount of methanol, and ethanol was added to this solution to turbidity. Then crystals were deposited; the yield was 2.2 g (9.6%). Recrystallization from water and ethanol furnished pure crystals, mp 198° dec, $[\alpha]_{D}^{20} -14.5^{\circ}$ (*c* 1.0, water), $\lambda_{max}^{H_2O}$ 274 m μ .

Anal. Calcd for C₁₂H₂₀N₂O₈: C, 45.00; H, 6.29; N, 8.75. Found: C, 44.92; H, 6.55; N, 8.68.

2,5-Bis(D-lyxo-tetraacetoxybutyl)pyrazine.—This compound was prepared according to the method reported by Taha,² for fructosazine octaacetate, by acetylation of tagatosazine (220 mg) with acetic anhydride and pyridine. Recrystallization from acetone and petroleum ether afforded pure crystals, in the yield of 270 mg (61%): mp 143°; $[\alpha]_{D}^{20} -3.6^{\circ}$ (*c* 1.0, chloroform); ν_{max}^{Nujol} 1740 (C=O), 1230, 1060, and 870 cm⁻¹. For nmr spectrum, see Figure 1.

Anal. Calcd for C₂₈H₃₈N₂O₁₆: C, 51.22; N, 5.53; H, 4.27. Found: C, 51.18; H, 5.53; N, 4.25.

2,5-Dimethoxycarbonylpyrazine (Pyrazine-2,5-dicarboxylic Acid Dimethyl Ester) from Tagatosazine.—Tagatosazine (500 mg) was treated with potassium permanganate according to the method of Mager and Berends,⁷ and 70 mg of pyrazine-2,5-dicarboxylic acid thus gained was converted to 2,5-dimethoxycarbonylpyrazine by boiling in methanolic hydrogen chloride. Recrystallization from methanol gave 58 mg of pure product: mp 168°; the over-all yield, 19.4%; ν_{max}^{Nujol} 1720 (C=O), 1286, 1153, 1030 (C—O—C), 968, 830 (C=CH), and 763 cm⁻¹.

Anal. Calcd for C₈H₈N₂O₄: C, 48.98; H, 4.11; N, 14.28. Found: C, 49.03; H, 4.19; N, 13.98.

No depression in the melting point was observed when this material was mixed with a sample of the authentic one from fructosazine, and they showed the identical infrared spectrum.

(7) H. I. X. Mager and W. Berends, *Rec. Trav. Chim.*, **77**, 827 (1958).

An Unusual Wittig Reaction with Benzil

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The reaction of benzil with triphenylphosphine-phenylmethylene, according to Parrick,¹ leads to unilateral condensation, giving *cis*- and *trans*-1,2,3-triphenyl-1-propen-3-one. In a study of synthetic routes to pseudo-aromatic, polycyclic ring systems, we have investigated the reactions of the bisphosphorane (III), derived from 1,8-bis(bromomethyl)naphthalene (I) *via* (II) (Chart I). Since the only reaction of III which had been reported so far, was its oxidative transformation to acenaphthylene,² condensations with benzaldehyde and 2-naphthaldehyde were studied. 1,8-Distyrylnaphthalene (IV, Ar = C₆H₅) and 1,8-di- $[\beta$ -(2-naphthyl)vinyl]naphthalene (IV, Ar = 2-C₁₀H₇) were obtained.³ In the reaction with benzil, however, a yellow-greenish hydrocarbon C₃₈H₂₂ (mp

(1) J. Parrick, *Can. J. Chem.*, **42**, 190 (1964).

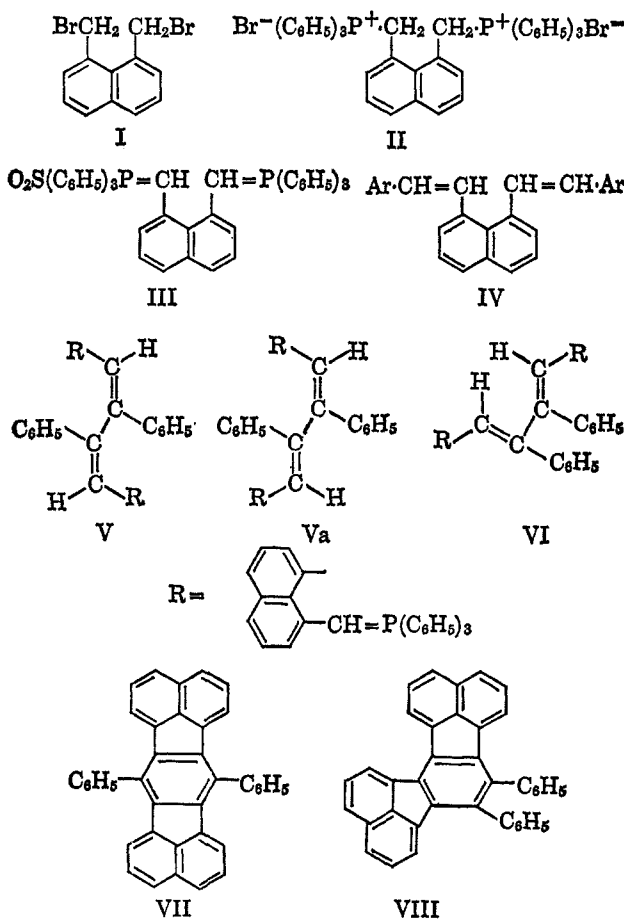
(2) H. J. Bestmann, H. Haerberlein, and O. Kratzer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 226 (1964); J. Bestmann, *ibid.*, **4**, 830 (1965).

(3) The configuration of the compounds, IV, has not been elucidated; the infrared spectrum indicates that at least one of the double bonds (and probably both) has the *trans* configuration, which would have been expected under the experimental conditions used.

TABLE I
 ULTRAVIOLET SPECTRA

Compd	Solvent	λ , $m\mu$ (log ϵ)						
		417	394			325		
Acenaphtho[1,2- <i>k</i>]fluoranthene	C ₆ H ₆	(4.24)	(4.10)			(4.72)		
Acenaphtho[1,2- <i>j</i>]fluoranthene	C ₆ H ₆		400	354	337		282	
			(3.92)	(4.74)	(4.56)		(4.14)	
Our hydrocarbon	EtOH			352	336		281	270 242
				(4.74)	(4.60)		(4.15)	(4.18) (4.68)
4,5-Di(<i>p</i> -chlorophenyl)acenaphtho[1,2- <i>j</i>]fluoranthene	C ₆ H ₆		400	358	337		280	
			(3.93)	(4.57)	(4.50)		(4.29)	
	CHCl ₃		400	357	339		275	
			(3.94)	(4.58)	(4.45)		(4.32)	
	CH ₃ CN			353	335		282 273 240 225	
				(4.65)	(4.62)		(4.33) (4.33) (4.78) (4.95)	
	Dioxane		400	355	337	325	282 273 244 224	
			(4.01)	(4.74)	(4.61)	(4.23)	(4.42) (4.43) (4.84) (5.06)	

CHART I



290°) was formed, obviously by reaction of 1 mole of benzil with 2 moles of III and spontaneous dehydrogenation or hydrogen transfer of the product, involving the elimination of four hydrogen atoms. Three intermediary diene compounds can formally be expected from this stoichiometry, *viz.* the *trans-trans* (V), the *cis-trans* (Va), and the *cis-cis* (VI) configurations. V and Va would cyclize to 7,14-diphenylacenaphtho[1,2-*k*]fluoranthene (VII) and VI to 4,5-diphenylacenaphtho[1,2-*j*]fluoranthene (VIII). The decision between these two formulas can be based on the fact that the spectra of the two nonphenylated parent substances of VII and VIII are known⁴; they

(4) See E. Clar, "Polycyclic Hydrocarbons," Vol. 2, Academic Press Inc., New York, N. Y., 1964, pp 357-360.

are characteristically different from each other, and it is justified to assume that the phenyl groups, being in highly hindered positions, will not substantially alter these spectra. Table I shows that formula VIII is preferable. Table I also contains the spectrum of the analogous product prepared from 4,4'-dichlorobenzil and III.

In fact, compounds VII and VIII have been described before^{5,6} as having mp >400 and 290-291°, respectively. The latter product is identical with our hydrocarbon (mixture melting point and superimposable ultraviolet and infrared spectra).

Experimental Section⁷

(1,8-Naphthylenedimethylene)bis[triphenylphosphonium Bromide] (II).—A solution of 26.2 g of triphenylphosphine in 150 ml of dry xylene was added to a solution of 15.7 g of 1,8-bis-(bromomethyl)naphthalene (I)⁸ in 50 ml of the same solvent and the mixture refluxed in an inert atmosphere for 1 hr. After cooling, the colorless precipitate was filtered, washed with xylene and petroleum ether and, for the analysis, recrystallized from nitromethane: yield, 37.7 g (90%), mp >300°.

Anal. Calcd for C₄₈H₄₀Br₂P₂: C, 68.7; H, 4.8; Br, 19.1; P, 7.4. Found: C, 68.7; H, 4.9; Br, 19.4; P, 6.4.

1,8-Distyrylnaphthalene (IV, Ar = C₆H₅).—In an inert atmosphere, 60 ml of 0.2 M lithium ethoxide solution was added slowly to a suspension of 4.2 g of II in a solution of 1.6 g of benzaldehyde in 60 ml of ethanol. The vivid color of the phosphoran disappeared towards the end of the reaction, and upon standing the product crystallized from the solution. After recrystallization from cyclohexane, clusters of colorless needles, mp 148°, were formed which exhibited a strong violet fluorescence in benzene solution: $\lambda_{\max}^{\text{dioxane}}$ 250 (4.72), 342 $m\mu$ (4.34); ν_{\max}^{KBr} 960 cm^{-1} (*trans*-C=C).

Anal. Calcd for C₂₆H₂₀: C, 93.9; H, 6.1. Found: C, 93.7; H, 6.2.

1,8-Di[β -(2-naphthyl)vinyl]naphthalene (IV, Ar = 2-C₁₀H₇).—In the same manner, the reaction of 4.2 g of the bisphosphonium bromide and 1.6 g of 2-naphthaldehyde in 50 ml of ethanol with 60 ml of 0.2 M lithium ethoxide solution gave an 80% yield of IV (Ar = 2-C₁₀H₇), from benzene yellowish needles of mp 214°: $\lambda_{\max}^{\text{dioxane}}$ 252 (4.94), 280 (4.40, sh), 300 (4.30, sh), 350 $m\mu$ (4.46); ν_{\max}^{KBr} 962 cm^{-1} (*trans*-C=C); fluorescence spectrum, 440 $m\mu$ (in dioxane).

Anal. Calcd for C₃₄H₂₄: C, 94.4; H, 5.6. Found: C, 94.2; H, 5.4.

4,5-Diphenylacenaphtho[1,2-*j*]fluoranthene (VIII).—In the manner described above, 4.2 g of benzil in 200 ml of ethanol was condensed with 16.8 g of II by addition of 200 ml of 0.2 M lith-

(5) W. Dilthey, S. Henkels, and A. Schaefer, *Ber.*, **71**, 974 (1938).

(6) D. B. Clapp, *J. Am. Chem. Soc.*, **61**, 2733 (1939).

(7) All melting points are uncorrected.

(8) E. D. Bergmann and J. Szmuzkovicz, *J. Am. Chem. Soc.*, **75**, 2760 (1953).

ium ethoxide solution during 10 min. The solution turned first orange, then dark red, and upon standing for 48 hr, deposited the orange-yellow crystals of VIII. Recrystallization from butanol gave needles of the same color and mp 272°; the compound sublimed at 230–240° (0.2 mm). Even so, the product was not completely pure, and only chromatography of the benzene solution on alumina gave the pure product in yellow-greenish needles of mp 290° (lit.⁶ mp 290–291°); it sublimed at 230–240° (0.2 mm) [(lit.⁶ 255–260° (3 mm)); yield, 0.6 g (12%); fluorescence, 485 m μ (in chloroform).

Anal. Calcd for C₃₃H₂₂: C, 95.4; H, 4.6. Found: C, 95.5; H, 4.7.

From the mother liquor, no other defined products could be isolated apart from triphenylphosphine oxide which was identified by melting point and mixture melting point. For comparison, the hydrocarbon VIII was synthesized according to Clapp.⁶ Chromatography of the benzene solution on neutral alumina and recrystallization from a benzene-methanol mixture gave yellow-greenish needles of mp 290°. The mixture melting point with VIII showed no depression, and the ultraviolet and infrared spectra (in chloroform and potassium bromide, respectively) were identical.

4,5-Di(*p*-chlorophenyl)acenaphtho[1,2-*j*]fluoranthene.—In a similar reaction, using 5.6 g of 4,4'-dichlorobenzil and completed by refluxing the mixture for 5 hr, yellow needles were obtained by recrystallization from benzene (0.4 g, 7%): mp >305°; fluorescence, 480 m μ (in dioxane).

Anal. Calcd for C₃₃H₂₀Cl₂: C, 83.4; H, 3.7; Cl, 13.0. Found: C, 83.4; H, 3.5; Cl, 13.0.

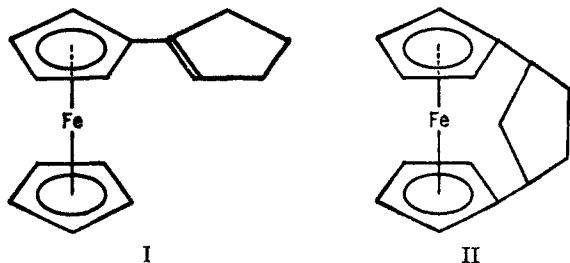
Metallocene Polymers. XIV. Metal-Ring Bond Cleavage by Water-Promoted Zinc Chloride¹

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The deleterious effects of strong Lewis acids on the ferrocene system in various solvent media, resulting in cleavage of the metal-ring bond, have been amply documented in the literature. Thus, hydrogen fluoride was reported to cleave ferrocene² to give, *via* intermediary cyclopentadiene, cyclopent-1-enylferrocene (I)³ and a compound independently prepared from ferrocene and aluminum chloride in benzene solution and identified as the heterobridged 1,1'-(1,3-cyclopentylene)-ferrocene^{3b} (II). Additional cleavage reactions were described,^{3b,c,4,5} some of them giving rise to oligomeric and polymeric cleavage products believed to be com-

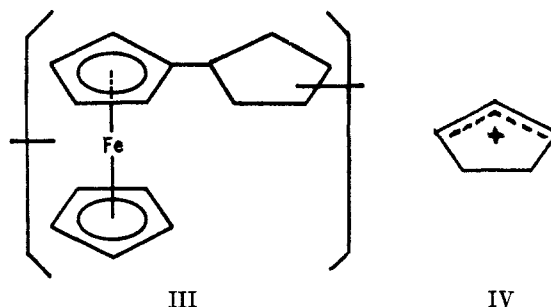


(1) Parts I–XIII of this series appeared under the general title: "Ferrocene-containing Polymers." (Part XIII: E. W. Neuse, and K. Koda, *J. Polymer Sci.*, in press.)

(2) V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3009 (1955).

(3) Structure independently ascertained by (a) K. L. Rinehart, Jr., *et al.*, *ibid.*, **82**, 4111 (1960); (b) S. G. Cottis and H. Rosenberg, *Chem. Ind.* (London), 860 (1963); (c) A. N. Nesmeyanov, N. S. Kochetkova, P. V. Petrovsky, and E. I. Fedin, *Dokl. Akad. Nauk SSSR*, **152**, 875 (1963).

posed of such recurring units as exemplified by III. All of these reported reactions proceeded in solution. To this date, however, no mentioning has been made in the literature of analogous cleavage reactions in the melt phase. Such information would be useful in connection with reactions in which molten ferrocene is exposed to the attack of Lewis acids, *e.g.*, in the melt-phase polycondensations of ferrocene with aldehydes.⁶ In these Lewis acid catalyzed polycondensation reactions, which for some time have been a major area of interest in this laboratory, the experimental conditions of temperature and heating time occasionally were severe enough to render cleavage of the metallocene system a definite possibility. Such cleavage, with subsequent further involvement of the intermediary cyclopentadiene or its protonated species, the cyclopentenyl cation IV, could conceivably affect the course



of polycondensation by causing side-chain and cross-link formation or, under less drastic conditions, merely the incorporation of cyclopentenyl and cyclopentylene groups into the products. Analytical evidence for the presence of cyclopentylene moieties in some of the polymers was indeed obtained in this earlier work.^{6d}

We have, therefore, undertaken to study the effect of the same catalyst system used in these ferrocene-aldehyde polycondensations, *viz.* water-promoted⁷ zinc chloride, on ferrocene in the molten state and in the absence of any additional reactants. When fused for 0.5–2.0 hr at 180° with zinc chloride and water in molar ratios comparable with those generally employed in the ferrocene-aldehyde condensations (*e.g.*, ferrocene-ZnCl₂-H₂O, 1.0:0.3:0.1), ferrocene was indeed found to undergo cleavage as expected. Work-up by selective extraction, chromatography, and reprecipitation furnished, aside from 70–90% unreacted ferrocene, the cyclopentylene derivatives II, V, and VI in 1–3% combined yield. The heterobridged II was identified by direct comparison with an authentic product.⁸

(4) (a) A. N. Nesmeyanov and N. S. Kochetkova, *ibid.*, **126**, 307 (1959); (b) A. N. Nesmeyanov, N. S. Kochetkova, and R. B. Materikova, *ibid.*, **136**, 1096 (1960); (c) S. J. Goldberg, *J. Am. Chem. Soc.*, **84**, 3022 (1962); (d) S. G. Cottis and H. Rosenberg, *J. Polymer Sci.*, **52**, 295 (1964).

(5) A. N. Nesmeyanov, N. S. Kochetkova, and R. B. Materikova, *Dokl. Akad. Nauk SSSR*, **147**, 113 (1962).

(6) (a) E. W. Neuse and D. S. Trifan, Abstracts, 148th National Meeting of the American Chemical Society, Sept 1964, p 5S; (b) E. W. Neuse, *Nature*, **204**, 179 (1964); (c) E. W. Neuse, K. Koda, and E. Carter, *Makromol. Chem.*, **84**, 213 (1965); (d) E. W. Neuse and E. Quo, *Bull. Chem. Soc. Japan*, in press.

(7) Water formed according to the equation (R = alkyl, aryl, etc.; see ref 6b): $(n + 1) C_{10}H_{10}Fe + nRCHO \rightarrow H-[C_{10}H_8Fe-CH(R)]_n C_{10}H_9Fe + nH_2O$.

(8) The CH out-of-plane deformation region in the infrared spectrum of II was characterized by two distinctly separated band groups, a triplet centered near 11.6 μ and a singlet at 12.50 μ , replacing the broad absorption usually exhibited by ferrocene derivatives at 12.2–12.3 μ . We have observed a similar pattern in this region with a large number of heterobridged ferrocene compounds.