this stirred mixture was added the catalyst. At the termination of the reaction several milliliters of isopropyl alcohol was added to destroy the catalyst and the entire reaction mixture was added to a large excess of methanol. The poylmer was filtered, washed with methanol and purified by repeated precipitation from benzene or toluene with methanol. After repeated washing with fresh methanol the polymer was dried in a vacuum oven at 40–50° for 12 hr.

E. Analysis. Infrared spectra[8a] were obtained with a Perkin-Elmer 521 grating spectrophotometer. Nuclear magnetic resonance spectra were obtained with a Varian AR-100 instrument. Glpc analyses[8b] were carried out in THF at ambient temperature with 1.5×10^5-, 1.5×10^4-, 8000-, and 800-Å columns. $\bar{A}_w$ and $\bar{A}_n$ values corresponding to molecular sizes were determined from the chromatograms. Melting points are uncorrected and were taken on a Hoover Unimelt apparatus.

Acknowledgment. We wish to acknowledge Mr. O. Need for his assistance in the synthesis of the vinyl indole monomers and Mr. G. Shrout for his aid in the interpretation of the infrared spectra.

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(8) (a) The ir spectra of all polymers are available from the authors on request. (b) ArRo Laboratories, Inc., Joliet, Ill.

Diels–Alder Polymerizations. VI.[1] Phenylated Polyphenylenes from Bis-2-pyrones and *p*-Diethynylbenzene[2]

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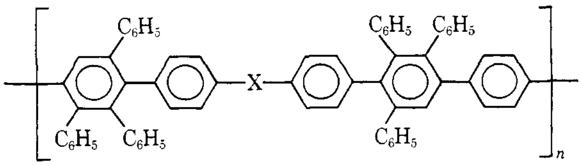
ABSTRACT: Phenylated polyphenylenes (**10, 11**) were obtained from the reactions of *p*-diethynylbenzene with 5,5′-*p*-phenylenebis-4,6-diphenyl-2-pyrone (**4**) or 6,6′-*p*-phenylenebis-4,5-diphenyl-2-pyrone (**5**), respectively, at 210–300° in toluene. The low molecular weight polymers ($[\eta] = 0.04$–0.13) obtained showed approximately the same thermal stability (TGA break = 550°, air or nitrogen) as those high molecular weight polyphenylenes obtained from the reaction of diethynylbenzenes with bistetracyclones. The polymer backbones probably have both *meta* and *para* linkages in **10** and *ortho* and *meta* linkages in **11** as demonstrated by the model reaction of 4,5,6-triphenyl-2-pyrone (**7**) with phenylacetylene which affords a 5:1 mixture of 1,2,3,4-tetraphenylbenzene (**8**) and 1,2,3,5-tetraphenylbenzene (**9**).

High molecular weight, thermally stable phenylated polyphenylenes of the general structure **1** have been prepared through Diels–Alder reactions of biscyclopentadienones and diethynylbenzenes.[3] For those polyphenylenes which do not contain methylene linkages, the pendant phenyl groups have been shown to be responsible for the initial weight loss at 550° in air or 575° in nitrogen.[3b] Since the cyclopentadienone ring must be tetrasubstituted to ensure that the cyclopentadienone will not undergo spontaneous dimerization,[4] an alternate approach was necessary for the preparation of polyphenylenes with fewer pendant phenyl groups and possibly higher thermal stability. Diels–Alder reactions of 2-pyrones and acetylenes are known to yield benzene derivatives,[5] and although 2-pyrone itself polymerizes on standing, monophenyl- and monocarboxyl-substituted 2-pyrones are stable in the monomeric form.[6] Accordingly, Diels–Alder reactions of bis-2-pyrones with *p*-diethynylbenzene were examined.



1

The bis-2-pyrones which have been reported[7,8] were unsuitable for this work since they contained aliphatic (alkylene, ether, or ester) groups linking the pyrone moieties and could not be expected to produce thermally stable polymers. Of the few general methods for the synthesis of 2-pyrones,[9] the base-catalyzed condensation of desoxybenzoin with ethyl phenylpropiolate[10] seemed suited for modification to the preparation of bis-2-pyrones fro bisdesmoxybenzoins. Thus, bis-2-pyrones **4** and **5** were prepared from 1,4-di(phenacyl)benzene (**2**) and 1,4-di(phenylacetyl)benzene (**3**).[11] Compound

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(1) For the previous paper in this series, see F. W. Harris and J. K. Stille, *Macromolecules*, **1**, 463 (1968).

(2) Reported in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968. This research was supported by the U. S. Army Research Office, Durham, N. C.

(3) (a) J. K. Stille, F. W. Harris, R. O. Rakutis, and H. Mukamal, *J. Polym. Sci., Part B*, **4**, 791 (1966); (b) H. Mukamal, F. W. Harris, and J. K. Stille, *ibid., Part A-1*, **5**, 2721 (1967); (c) J. K. Stille, R. O. Rakutis, H. Mukamal, and F. W. Harris, *Macromolecules*, **1**, 431 (1968).

(4) M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 300 (1965).

(5) C. L. Schilling, Jr., J. A. Reed, and J. K. Stille, manuscript in preparation.

(6) A. Albert, "Heterocyclic Chemistry," Essential Books, Fairlawn, N. J., 1959, p 268.

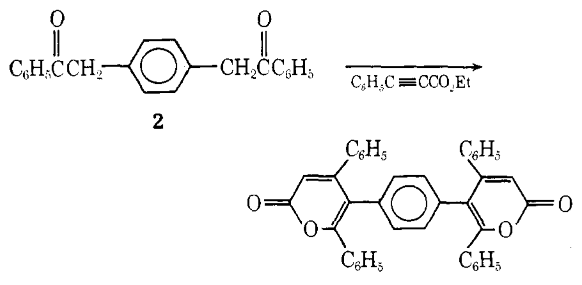
(7) Belgian Patent 643,891 (Aug 17, 1964) to Farbwerke Hoechst A.-G.; *Chem. Abstr.*, **64**, 2061c (1966).

(8) R. H. Wiley and L. H. Knabeschuh, *J. Amer. Chem. Soc.*, **77**, 1615 (1955).

(9) N. Shusherina, N. Dmitrieva, E. Luk'yanets, and R. Levina, *Usp. Khim.*, **36**, 436 (1967).

(10) S. Ruhemann, *J. Chem. Soc.*, **97**, 459 (1910).

(11) M. A. Ogliaruso and E. I. Becker, *J. Org. Chem.*, **30**, 3354 (1965).



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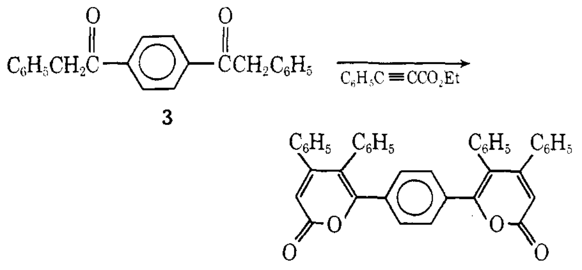
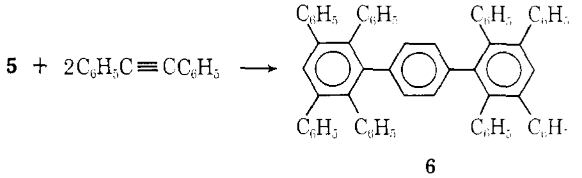


3

5

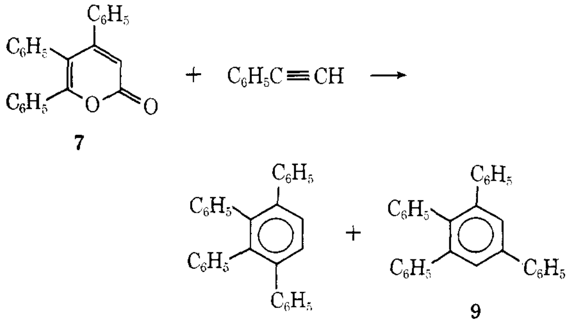
2 was synthesized by modification of the standard preparation for desoxybenzoin.[12]

The Diels–Alder reactivity of the bis-2-pyrones **4** and **5** was demonstrated by the reaction of the slightly more sterically hindered compound **5** with 2 molar equiv of diphenylacetylene to form the octaphenyl-*p*-terphenyl derivature **6**.



6

The model reaction of 4,5,6-triphenyl-2-pyrone[10] (**7**) with phenylacetylene demonstrates the probable stereochemistry of the polymerization reactions. The fact that both possible tetraphenylbenzenes, **8** and **9**, are formed *(5:1 ratio) indicates that polyphenylenes from* **4** will contain new *meta* and *para* linkages, while those from **5** will contain new *ortho* and *meta* linkages (see below).

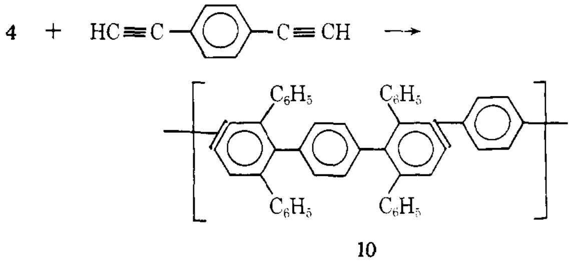


7

8

9

Bis-2-pyrones **4** and **5** were polymerized with *p*-diethynylbenzene in toluene at 200–300° for 24–176 hr, yielding low molecular weight ([η] = 0.043–0.130) nearly white polyphenylenes **10** and **11** (see Table I).



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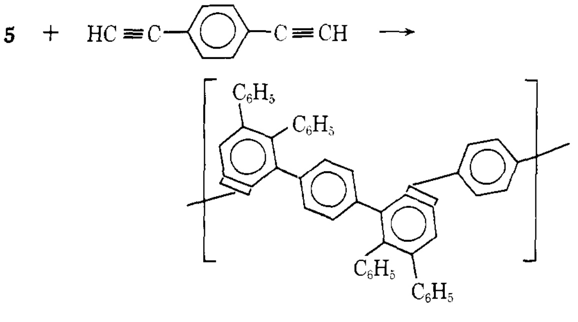

11

These polymers showed nearly the same thermal stability as the higher molecular weight polyphenylenes prepared from biscyclopentadienones.[3b] Major breaks in the TGA were observed at 550° in air or nitrogen with a smaller break at 400° (4–14% weight loss). TGA curves for the bis-2-pyrone monomers **4** and **5** were identical, showing breaks at 400 (30% weight loss) and at 550°. The 400° break for the polymers indicates the presence of 2-pyrone end groups as do the ir spectra and the elemental analyses. No capping with monoacetylenes was carried out.

Attempts to prepare tetraphenylpyridines through a new type of Diels–Alder reaction of **7** with benzonitrile, terephthalonitrile, or 3-chlorobenzonitrile did not yield the desired products. Instead, a compound, $C_{23}H_{16}O_2$, isomeric with **7**, was isolated from each reaction. At 250 or 300°, **7** alone was found to rearrange to the same compound. Tetrachloro-2-pyrone is known to undergo thermal rearrangement to 2,3,4-trichlorofuroyl chloride.[13] Any rearrangement to a Diels–Alder inactive species in the above polymerizations would destroy the necessary monomer balance and would cause low conversions, low molecular weight, and high amounts of soluble residues. Further work is in progress on the generality and mechanism of this rearrangement.

Experimental Section

1,4-Di(phenylacetyl)benzene (**3**),[11] 4,5,6-triphenyl-2-pyrone (**7**),[10] diethynylbenzene,[14] and diphenylacetylene[15] were

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(12) C. F. H. Allen and W. E. Barker, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, New York, N. Y., p 156.

(13) E. D. Weil, E. Leon, and J. Linder, *J. Org. Chem.*, **26**, 5185 (1961).

14) A. S. Hay, *ibid.*, **25**, 637 (1960).

(15) A. C. Cope, D. S. Smith, and R. J. Cotter, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, New York, N. Y., 1963, p 377.

TABLE I
POLYMERIZATIONS OF BIS-2-PYRONES[a] WITH *p*-DIETHYNYLBENZENE

Monomer (mmol)	Temp, °C	Time, hr	Product	Yield, %	$[\eta]^d$
4 (0.46)	250	36	Soluble polymer	41	0.088
			Insoluble residue[b]	52	
4 (0.709)	200	22	Acetone-insoluble polymer	45	0.074
	210	115	Petroleum ether insoluble polymer	10	0.130
			Insoluble residue[b]	6	
			Soluble residue[c]	47	
5 (0.888)	300	36	Soluble polymer	50	0.081
			Insoluble residue[b]	18	
			Soluble residue not isolated		
5 (0.607)	225	24	Soluble polymer	57	0.060
	300	24	Insoluble residue[b]	23	
			Soluble residue not isolated		
5 (0.774)	200	40	Acetone-insoluble polymer	12	0.043
	210	136	Petroleum ether insoluble polymer	16	0.061
			Insoluble residue	6	
			Soluble residue[c]	73	

[a] See Experimental Section for details. [b] Insoluble in common organic solvents including refluxing xylene. [c] Monomers **4** and **5** are insoluble under these conditions. [d] Intrinsic viscosities were obtained in toluene at 30°. TGA breaks in air or nitrogen occurred at 550° for all polymers; the decomposition in air was complete, as in the case with polymers of the general structure **1.**[3]

prepared by published procedures. Ethyl phenylpropiolate, phenylacetylene, and *p*-phenylenediacetonitrile were obtained from the Aldrich Chemical Co.

1,4-Di(phenacyl)benzene (2). *p*-Phenylenediacetonitrile (24.5 g, 0.157 mol) was heated at the reflux temperature with 175 ml of concentrated hydrochloric acid and 175 ml of water. The product was filtered, washed twice with water, and vacuum dried to yield 28.3 g (93%) of *p*-phenylenediacetic acid, mp 245–247° (lit.[16] mp 246–247°). The diacid (18.3 g, 0.095 mol) and 15.0 g (0.110 mol) of phosphorus trichloride were heated on the steam bath for 3 hr. Dry benzene (100 ml) was added and the benzene solution was suction filtered onto 25 g (0.188 mol) of aluminum chloride. This mixture was heated on the steam bath at the reflux temperature for 1 hr, after which it was poured into 200 g of cracked ice containing 175 ml of concentrated hydrochloric acid. The product was collected by suction filtration and washed with sodium carbonate solution and water. Recrystallization from ethyl acetate and vacuum drying yielded 14.7 g (50%) of 1,4-di(phenacyl)benzene, mp 204–207°.

Anal.[17] Calcd for $C_{22}H_{18}O_2$: C, 84.08; H, 5.73. Found: C, 84.33; H, 5.86.

5,5′-*p*-Phenylenebis-4,6-diphenyl-2-pyrone (4).—To a stirred suspension of 4.2 g (0.062 mol) of sodium ethoxide in 175 ml of dry ethyl ether was added 8.0 g (0.025 mol) of 1,4-di(phenacyl)benzene and 9.2 g (0.053 mol) of ethyl phenylpropiolate. The mixture was heated at the reflux temperature with stirring for 7 hr, and was poured into 400 g of cracked ice containing 100 ml of concentrated hydrochloric acid. The yellow solid was collected and washed with a few milliliters of acetone. Recrystallization from toluene yielded 3.4 g (24%) of product, mp 303–304°.

Anal. Calcd for $C_{40}H_{26}O$: C, 84.21; H, 4.56. Found: C, 83.95; H, 4.65.

6,6′-*p*-Phenylenebis-4,5-diphenyl-2-pyrone (5). The condensation of 5.8 g (0.015 mol) of 1,**4**-di(phenylacetyl)-benzene[11] and 6.6 g (0.038 mol) of ethyl phenylpropiolate with 3.0 g (0.044 mol) of sodium ethoxide in 150 ml of dry[b] ethyl ether as described for the preparation of **4** yielded 4.0 g (48%) of bright yellow product, mp 349–350°, after recrystallization from xylene.

Anal. Calcd for $C_{40}H_{26}O_4$: C, 84.21; H, 4.56. Found: C, 83.92; H, 4.69

2,2′′,3,3′′,5,5′′,6,6′′-Octaphenyl-*p*-terphenyl (6). Compound **5** (1.14 g, 2.0 mmol) and diphenylacetylene (0.71 g, 4.0 mmol) were heated with 10 ml of toluene in an evacuated tube, sealed after three freeze–thaw cycles (liquid nitrogen) under reduced pressure, at 300° for 24 hr. Evaporation of solvent and addition of methanol yielded 1.66 g (99%) of crude product. The analytical sample, after three recrystallizations from benzene–methanol, melted at 390°.

Anal. Calcd for $C_{66}H_{46}$: C, 94.44; H, 5.56. Found: C, 94.65; H, 5.65.

1,2,3,4-Tetraphenylbenzene (8) and 1,2,3,5-Tetraphenylbenzene (9). 4,5,6-Triphenyl-2-pyrone[10] (3.51 g, 10.9 mmol) and 1.11 g (10.9 mmol) of phenylacetylene were combined in a 50-ml polymerization tube with 30 ml of toluene. The tube was subjected to three freeze–thaw cycles (liquid nitrogen) under reduced pressure and was sealed under reduced pressure before being heated at 200° for 90 hr, followed by 24 hr at 225°. The tube was cooled, opened, and allowed to stand for 2 days, during which 0.753 g (21.4%) of starting 2-pyrone crystallized. Addition of a few milliliters of methanol to the toluene mother liquor caused the crystallization of two successive crops of 1,2,3,4-tetraphenylbenzene (0.727 g, 17.4%), mp 190–192° (lit.[18] mp 190–191°). Evaporation of the mother liquor and extraction of the residue with 50 ml of methanol left 1.797 g (43.2%) of products from which 1,2,3,4-tetraphenylbenzene (0.625 g, 15.1%) and 1,2,3,5-tetraphenylbenzene (0.268 g, 6.4%), mp 222–225° (lit.[19] mp 224–226°) were isolated by numerous fractional recrystallizations. Compounds **8** and **9** were isolated in a 5:1 ratio.

The same reaction, run at 300° for 24 hr with a 2:1

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(16) Kh. E. Khcheyan, A. E. Ioffe, and A. F. Pavlichev, *Zh. Prikl. Khim.*, **35,** 206 (1962); *Chem. Abstr.*, **56,** 15416*e* (1962).

(17) Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

(18) W. Dilthey and G. Hurtig, *Ber.*, **67,** 2004 (1934).

(19) G. F. Woods, J. E. Swenarton, and R. B. Isaacson, *J. Org. Chem.*, **26,** 309 (1961).

excess of phenylacetylene, yielded no recovered 2-pyrone, and compounds **8** (14%) and **9** (12%) were obtained in approximately equal amounts from 1.2 g (80%) of crude product.

Polymerizations. (See Table I.) Equimolar amounts of compounds **4** or **5** and diethynylbenzene[14] were combined with 10 ml of reagent grade toluene in 20-ml polymerization tubes. The tubes were fitted with septa and subjected to three freeze–thaw cycles (liquid nitrogen) before being sealed under reduced pressure. Each tube was heated at 200–300° in a Parr bomb containing 50–75 ml of toluene for 24–176 hr. Heat was supplied by an electric mantle, the temperature being controlled by a Jelrus automatic controller connected to a thermocouple in the bomb head. Polymers were precipitated by filtering the toluene solutions from the tube into acetone and/or petroleum ether (bp 30–60°) and were freeze-dried from benzene prior to characterization. Intrinsic viscosities were taken in toluene at 30°.

The highest molecular weight polymer ($[\eta] = 0.130$) was submitted for elemental analyses.

Anal. Calcd for $(C_{48}H_{32})_n$: C, 94.74; H, 5.26. Found: C,90.95; H, 5.24.

Compound $C_{23}H_{16}O_2$. 4,5,6-Triphenyl-2-pyrone (1.0 g, 3.0 mmol) and 10 ml of toluene were heated at 250° for 48 hr in a polymerization tube sealed in the usual manner. Cooling crystallized 0.77 g of starting material. Evaporation of solvent and extraction of the residue with methanol left another 0.06 g of starting material, identified by its nondepressed melting point on mixing with 4,5,6-triphenyl-2-pyrone. Concentration of the methanol solution and addition of water to turbidity, followed by cooling, precipitated a solid, 0.122 g, mp 200–202°, after recrystallization from methanol–water.

Anal. Calcd for $C_{23}H_{16}O_2$: C, 85.19; H, 4.93. Found: C, 85.27; H, 5.10.

The same compound was isolated from attempted reactions of 4,5,6-triphenyl-2-pyrone with benzonitrile, terephthalonitrile, and 3-chloronitrile under similar conditions.

The Degradation of Methylcellulose by Ionizing Radiation

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ABSTRACT: The degradation of methylcellulose in the solid state, induced by ionizing radiation, has been studied under a variety of conditions. Application of the theory of random chain fracture to the experimental results, along with consideration of the rate of formation of various species during the degradation, leads to several interesting conclusions regarding the mechanism of the degradation. The reaction behaves in a manner consistent with a short-chain, free-radical mechanism resulting in concurrent fragmentation and ester formation.

Although there are many reports in the literature dealing with the effects of ionizing radiation on cellulosic materials, there are relatively few which are concerned with the detailed mechanism of the over-all reactions.

The radicals formed in cellulose by ionizing radiation have been tentatively identified by means of esr spectroscopy[1] as a mixture of secondary carbon radicals and tertiary alkoxy radicals. It was also observed by these workers that the esr spectrum due to these species slowly changed into a spectrum containing relatively greater amounts of alkoxy radicals. In methylcellulose, a similar situation was observed, with a *G* value[2] for radical formation of approximately 0.8 radicals/100 eV.[1a] In cellulose, the *G* value for radical formation was calculated to be 0.9[1b] and 0.8–3.0,[1a] depending upon the type of cellulose and its physical state. The rate of production of radicals in cellulose has been found to follow an empirical relationship,[1b] $(R\bullet) = b\,(\text{dose})^a$,

Several attempts have been made to relate the rates of various reactions to the rate of energy deposited in a cellulosic system. Qualitatively, both the rate of radical disappearance and the rate of chain cleavage in cellulose have been observed to be faster in the presence of oxygen, although in both instances the differences were not great.[1b,3] Attempts at a more quantitative investigation of the rate processes involved have been made.[4-6] Several different rate laws for destruction of chain linkages in cellulose have been reported. Arthur[4] has proposed an equation of the type

$$\ln (P) = k_1 \ln (N_n) + K \qquad (1)$$

where *P* is the number of chain fractures and N_n is the total dose delivered to the system. Equation 1 is essentially the same as that derived by Charlesby,[5] who envisaged the degradation of cellulose as a random chain fracture process, leading to the relationship

$$\ln (\eta) = \frac{1}{\alpha} \ln (D + D_0) + K \qquad (2)$$

in which D_0 represents the dose necessary to degrade a polymer molecule of infinite molecular weight to a molecular weight equivalent to that of the starting ma-

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(1) (a) R. E. Florin and L. A. Wall, *J. Polym. Sci., Part A*, **1**, 1163 (1963); (b) S. Dilli, I. T. Ernst, and J. L. Garnett, *Aust. J. Chem.*, **20**, 911 (1967).

(2) *G* values are defined in terms of occurrences per 100 eV of absorbed energy.

(3) J. C. Arthur, Jr., F. A. Blouin, and R. J. Demint, *Amer. Dyestuff Reptr.*, **49**, 383 (1960).

(4) J. C. Arthur, Jr., *Textile Res. J.*, **28**, 204 (1958).

(5) A. Charlesby, *J. Polym. Sci.*, **15**, 263 (1955).

(6) M. Horio, R. Imamura, and H. Mizurkami, *Bull. Inst. Chem. Res., Kyoto Univ.*, **41**, 17 (1963).