Linear Conjugated Systems Bearing Aromatic Terminal Groups. IV.[1] The Syntheses of Some Diarylacetylenes

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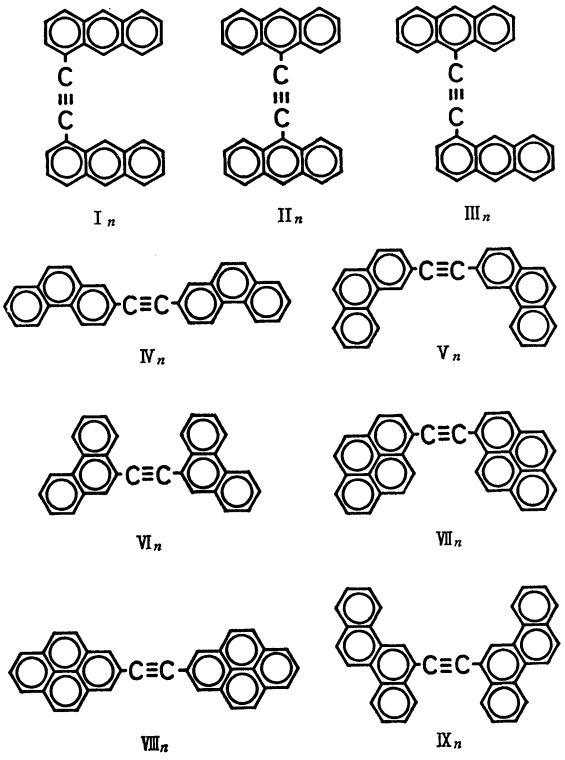
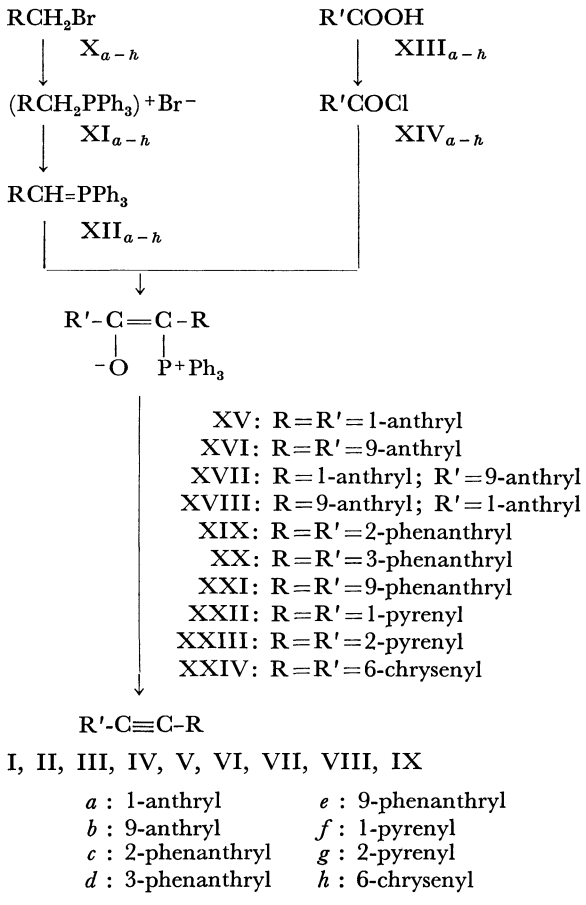
The syntheses of 1,1′-, 9,9′-, and 1,9′-dianthryl-, 2,2′-, 3,3′-, and 9,9′-diphenanthryl-, 1,1′-and 2,2′-dipyrenyl-, and 6,6′-dichrysenylacetylenes according to the pyrolytic reactions of the corresponding β-ketoalkylidenetriphenylphosphorane derivatives (intramolecular Wittig reaction) were described.

In relation to studies on the electronic spectral properties of diarylpoly-ynes,[2] we tried to prepare 1,1′-dianthryl- and 9,9′-dianthrylacetylenes (I and II). However, all attempts to prepare dianthrylacetylenes according to the usual methods were unsucessful. The well-known mercuric oxide oxidation of *bis*-hydrazone of α-diketone was not feasible for the present case, because the condensation of anthraldehydes by means of potassium cyanide and the dimerization of anthracene carboxylic acids or their acid chlorides on treatment with magnesium-magnesium iodide could not be carried out. In the case of phenanthrene series, it was found that the reaction of 9,9′-diphenanthril with hydrazine gave only monohydrazone.[3] Bromine addition to di-(1-anthryl)-and di-(9-anthryl)-ethylenes[4] could not be performed owing to the poor solubility of the ethylenes in common organic solvents.



Gough and Trippett[5], and Märkl[6] proposed a new method of formation of acetylenic bond by a pyrolytic decomposition of β-ketoalkylidenetriphenylphosphorane. This method has been applied successfully to the preparation of dianthrylacetylenes I, II, and III, diphenanthrylacetylenes IV, V, and, VI, dipyrenylacetylenes VII and VIII and 6,6′-dichrysenylacetylene IX.

As summarized in the following scheme, the bromomethyl compounds (X_{a-h}) derived from corresponding aldehydes were converted to the phosphoranes XII_{a-h} *via* triphenyl phosphonium bromides XI_{a-h}.



Scheme. Syntheses of the diarylacetylenes.

1) Part III: K. Nakasuji, S. Akiyama, K. Akashi, and M. Nakagawa, This Bulletin, **43**, 3567 (1970).

2) S. Akiyama and M. Nakagawa, *ibid.*, **40**, 340 (1967); K. Nishimoto, S. Akiyama, M. Nakagawa, and R. Fujishiro, *ibid.*, **39**, 2320 (1966); S. Akiyama and M. Nakagawa, *ibid.*, **43**, 3561 (1970).

3) Mp 255—258°C. Found: C, 84.61; H, 4.74; N, 6.53. Calcd for $C_{30}H_{20}N_2O$: C, 84.88; H, 4.75; N, 6.60%.

4) Unpublished.

5) S. T. D. Gough and S. Trippett, *Proc. Chem. Soc.*, **1961**, 302; *J. Chem. Soc.*, **1962**, 2333.

6) G. Märkl, *Chem. Ber.*, **94**, 3005 (1961).

The reaction of the phosphoranes XII_{a-h} with a half mole of the acid chlorides XIV_{a-h} in xylene, toluene or benzene afforded betaines XV-XXIV. All betaines thus obtained exhibit characteristic intense absorption due to $\nu_{C=O}$ of ylid carbonyl groups in 1500 cm^{-1} region.[7]

Pyrolyses of the betaines except for XV were performed at 200—300°C in the absence of solvent under reduced pressure resulting in the corresponding acetylenes I, III—IX in high yields. On the other hand, XV was found to decompose very easily in boiling xylene to yield II. 9,9′-Dianthrylacetylene II and 1,9′-dianthrylacetylene(III) were obtained directly when a 2 : 1 molar mixture of XII_b and XIV_b, and that of XII_b and XIV_a in xylene were heated under refulx. The same treatment of a mixture of XII_a and XIV_b gave a mixture of the betaine (XVII) and the acetylene(III). However, the same treatment of a mixture of XII_a and XIV_b gave XV containing a small amount of I. These facts observed in anthracene series seem to indicate the following sequence of thermal stability of the betaines: XVI<<XVIII XVII<<XV. The sequence of the thermal stability of the betaines clearly indicates that the steric hindrance facilitates the decomposition of betaine into acetylenes. The fact that the less hindered betaines (XIX—XXIV) of other series were obtained in good yields without decomposition is consistent with this inference.

Diarylacetylenes (I—IX) thus obtained were found to be fairly stable and scarcely soluble in common organic solvents. The electronic spectra of the dianthrylacetylenes are illustrated in Fig. 1. The sequence of the bathochromic shift was found to be I→III→II with an increasing loss of vibrational structures. The spectrum of II exhibits only a shoulder at the position corresponding to the longest-wavelength peak. The electronic spectral properties of 1,1′- dianthryl-and 9,9′-dianthrylacetylenes (I and II) have been discussed in relation to the spectral regularities of the dianthrylpoly-ynes.[2]

The electronic spectra of the diphenathryl-, the dipyrenyl- and 6,6′-dichrysenylacetylenes will be discussed in a forthcoming paper.

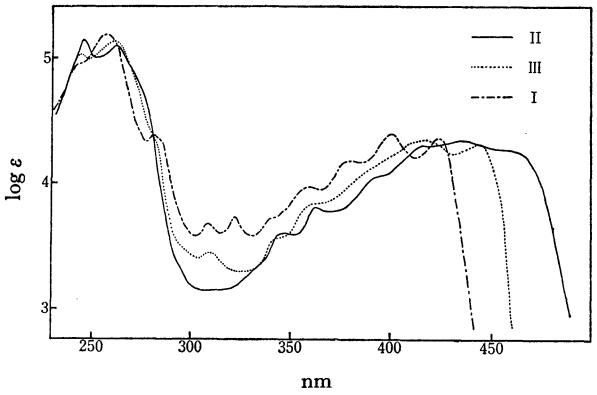


Fig.1 The electronic spectra of the dianthrylacetylenes (in tetrahydrofuran).

Experimental

All melting points are not corrected. The electronic spectra were obtained on a Hitachi EPS-3T spectrophotometer at room temperature. The IR spectra were measured with a Hitachi EPI-2 spectrophotometer by KBr-disk method.

1-Bromomethylanthracene (X_a). The bromide was prepared by the method reported previously.[8]

9-Bromomethylanthracene (X_b). Phosphorus tribromide (12.0 g, 0.044 mol) in chloroform (40 m*l*) was added over a period of 30 min to a mixture of 9-hydroxymethylanthracene (20.8 g, 0.1 mol), chloroform (350 m*l*) and pyridine (3.2 g, 0.044 mol) at −5°C. The mixture was allowed to gradually reach 20°C, after which it was stirred further for 1 hr. Cracked ice was added to the ice-cooled reaction mixture, and the organic layer separated was washed with water, sodium hydrogen carbonate solution and water, successively, and then dried. The yellow needles, mp 138—140°C, which were obtained in quantitative yield by the evaporation of the solvent *in vacuo* were recrystallized from petroleum benzine to give pure X_b as yellow needles, mp 139—140°C.

Found: C, 66.77; H, 4.19; Br, 29.54%. Calcd for $C_{15}H_{11}Br$: C, 66.44; H, 4.09; Br, 29.47%.

Anthrylmethyl-triphenylphosphonium Bromides (XI_a and XI_b). As the phosphonium bromides (XI_a and XI_b) were prepared according to a similar procedure, the preparation of XI_b will be described as an example. Triphenylphosphine (13.1 g, 0.05 mol) was added to a solution of X_b (11.1 g, 0.041 mol) in xylene (140 m*l*), and the mixture was refluxed for 17 hr. The crystals deposited were rinsed with a small amount of benzene, and then were recrystallized twice from water to give pure XI_b. Both of the salts were obtained in yields of over 90%. The physical properties and the analytical data are summarized in Table 1.

9,9′-Dianthrylacetylene (II). a) Pyrolysis of the Betaine (XVI_b) without Isolation. To a suspension of the phosphonium bromide (XI_b, 6.95 g, 0.013 mol) in xylene (70 m*l*), was added an ether solution of phenyllithium (1.18 N, 11.02 m*l*). The deep reddish-violet solution was stirred for 1 hr at 80°C, and then a hot solution of the acid chloride

Table 1. Physical properties and analytical data of XI_a and XI_b

	Mp (°C)	Crystal		Analytical data (%) C	H	Br
XI_a	275—280 (dec.)	pale yellow	Found:	73.91,	5.01,	14.62
XI_b	280 (dec.)	pale yellow	Found:	73.89,	4.91,	14.79
			Calcd for $C_{33}H_{26}BrP$:	74.30,	4.91,	14.98

7) *Cf.* A. J. Speciale and K. W. Ratts, *J. Amer. Chem. Soc.*, **85**, 2790 (1963).

8) S. Akiyama, S. Misumi, and M. Nakagawa, This Bulletin, **35**, 1826 (1962).

(XIV_b, 1.440 g, 6 mmol), prepared from 9-anthroic acid[9] and thionyl chloride in xylene (50 ml), was added. After the mixture had been stirred for 20 hr at 80°C, the mixture was refluxed for 2 hr. The hot solution was filtered to remove insoluble material which was digested with hot benzene three times (each 50 ml). The benzene extracts were combined with the filtrate, and the solvents were removed *in vacuo*. A small amount of benzene - petroleum benzine (1 : 1) was added to the residue, and the orange-yellow crystals deposited was collected by filtration (1.40 g, 62%). The crystals were re-dissolved in benzene, and the solution was percolated through a short column of alumina. The orange needles obtained by the concentration of the filtrate under reduced pressure were recrystallized from benzene to yield pure II, orange-red needles, which decomposed at *ca.* 310°C.

Found: C, 95.21; H, 4.77%; $M^+=378$. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79%; Mol. wt. 378.

b) Pyrolysis of the Isolated Betaine (XVI_b). Using benzene as solvent, the same amounts of the reagents (XI_b, phenyllithium and XIV_b) used in the case of a) were treated in a similar manner. The mixture obtained was stirred for 20 hr at 15°C and then 4 hr at 35°C. The insoluble material was filtered, and repeatedly digested with benzene (total 500 ml) at 70°C. The extracts were combined with the filtrate. The yellow fine cubes, 2.150 g (55%) which was obtained by the evaporation of the solvent *in vacuo* were dissolved in hot benzene. The insoluble acetylene(II) was removed by filtration. Evaporation of the filtrate under reduced pressure gave betaine(XVI). The crude betaine was recrystallized twice from benzene to give pure XVI as yellow cubes. The yellow crystals turned to orange needles at 280°C, which decomposed at *ca.* 310°C (decomposition point of the acetylene, II).

Found: C, 88.51; H, 5.29%. Calcd for $C_{48}H_{33}OP$: C, 87.78; H, 5.07%. IR: 1496 (C=O) cm^{-1}.

Betaine (XVI, 0.131 g, 0.2 mmol) thus obtained was dissolved in xylene (20 ml), and the solution was refluxed for 3.5 hr to give a green fluorescent orange-yellow solution. Evaporation of the solvent afforded orange-red needles, 0.069 g (91%). Triphenylphosphine oxide (0.050 g, 89%) was obtained from the filtrate. The orange-red crystals were recrystallized from benzene to yield pure II.

1,1'-Dianthrylacetylene (I). Preparation of Betaine (XV). To a suspension of the phosphonium bromide (XI_a, 3.48 g, 6.5 mmol) in xylene (30 ml), was added at room temperature an ethereal solution of phenyllithium (0.87 N, 7.51 ml) under nitrogen atmosphere. After the mixture had been stirred for 1 hr at 80°C, a hot solution of the acid chloride of 1-anthroic acid[10] (XIV_a, 0.720 g, 3 mmol) in xylene (30 ml) was added, and stirred for 20 hr at 80°C. The insoluble material was filtered, and digested repeatedly with hot toluene (total 150 ml). The extracts were combined with filtrate, and the solvent was removed under reduced pressure. Benzene (3 ml) was added to the residue, and the yellow crystalline powder was collected by filtration, and washed with a small amount of benzene (0.570 g, 29%). The crystalline powder was recrystallized twice from toluene to give yellow cubes. The crystals fused at *ca.* 180—190°C under foaming. The melt solidified at 230°C to give needles, and re-melted at 267—270°C.

Found: C, 88.42; H, 5.38%. Calcd for $C_{48}H_{33}OP$: C, 87.78; H, 5.07%. IR: 1500 (C=O) cm^{-1}.

Pyrolysis of Betaine (XV). The betaine (XV, 0.100 g, 0.15 mmol) was heated under reduced pressure (18 mmHg) at 200°C for 30 min, Evolution of triphenylphosphine oxide was observed. The solid thus obtained was mixed with a a small amount of benzene, and was filtered to remove the oxide. The crude crystals thus obtained in an almost quantitative yield were dissolved in benzene, and the solution was passed through a short column of alumina. The crystals obtained by the evaporation of the filtrate were recrystallized twice from benzene to give pure I as bright yellow needles, mp 272—273°C.

The pyrolysis of betaine(XV) in boiling xylene was found to be very slow.

Found: C, 95.07; H, 4.80%. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79%. UV in tetrahydrofuran: λ_{max} (log ε) 245* (4.96), 257(5.19), 281(4.39), 309(3.68), 322.5(3.72), 340*(3.70), 359(3.97), 380(4.18), 400(4.39), and 425(4.36) nm. (asterisks denote shoulders).

1,9'-Dianthrylacetylene (III). Preparation of Betaine (XVII). To a solution of phosphorane (XII_a), prepared according to the method used for betaine(XV), was added a xylene solution of the acid chloride of 9-anthroic acid, and the mixture was refluxed for 2 hr to complete the reaction. The yellow cubes, 0.745 g (38%), collected by filtration were recrystallized twice from benzene to give pure XVII as yellow cubes. The crystals melted at 230—250°C and turned to orange needles at 260°C. The crystals re-melted at 286—288°C.

Found: C, 88.22; H, 5.42%. Calcd for $C_{48}H_{33}OP$: C, 87.78; H, 5.07%. IR: 1497 (C=O) $cm.^{-1}$

Concentration of the filtrate gave a mixture (0.05 g) of XVII and orange-yellow needles. The mixture was recrystallized twice from benzene. The crystals thus obtained were dissolved in the same solvent, and the solution was passed through a short column of alumina. Pure III was obtained from the filtrate as orange-yellow needles, mp 286—288°C.

Pyrolysis of Betaine (XVII). Betaine(XVII) was treated according to the procedure used for the pyrolysis of XV, and the product was dissolved in benzene (40 ml). The filtrate which was obtained by the percolation of the benzene solution through a thin layer of alumina (2 g) was concentrated to afford acetylene(III), 0.036 g, 97%, mp 282—285°C. The material was recrystallized twice from benzene to yield pure III, orange-yellow needles, mp 286—288°C.

Found: C, 95.11; H, 4.79%. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79%. UV in tetrahydrofuran: λ_{max} (log ε) 244(5.02), 261.5(5.14), 320(3.46), 344*(3.39), 362*(3.85), 419(4.36), and 444(4.32). (asterisks indicate shoulders).

Preparation of Betaine (XVIII). Betaine (XVIII) was obtained as tiny yellow cubes in a yield of 24% from XII_b and XIV_a according to the method used for XV. The crude betaine was recrystallized to afford pure XIII as tiny yellow cubes, which turned to orange at 230—240°C, and then solidified to give orange needles. The crystals re-melted at 286—288°C.

Found: C, 87.32; H, 5.00%. Calcd for $C_{48}H_{33}OP$: C, 87.78; H, 5.07%. IR: 1497 (C=O) $cm.^{-1}$

Pyrolysis of the Betaine(XVIII), a) Pyrolysis without Solvent. Pyrolysis of betaine(XVIII) was carried out according to the procedure used for XV. A benzene (40 ml) solution of the product was passed through a short column of alumina (3 g). The crude crystals, 0.055 g (95%), obtained by concentration of the filtrate were recrystallized twice from benzene to yield pure III as orange-yellow needles, mp 286—288°C.

Found: C, 95.01; H, 4.83%. Calcd for $C_{30}H_{18}$: C,

9) R. R. Burtner and J. W. Cusic, *J. Amer. Chem. Soc.*, **65**, 262 (1943).

10) J. W. Cook, *J. Chem. Soc.*, **1931**, 566.

Table 2. Physical properties and analytical data of XI_c, XI_d, and XI_e

	Mp (°C)	Yield (%)	Crystal	Analytical data (%)			
					C	H	Br
XI_c	292—293 (E)	82	needles	Found:	74.41	4.91	14.90
XI_d	291—292 (W)	90	cubes	Found:	74.35	4.86	14.95
XI_e	288—289 (E)	95	plates	Found:	74.11	4.96	14.82
				Calcd for $C_{33}H_{26}BrP$:	74.30	4.91	14.98

Solvents of recrystallization are given in parentheses. E=ethanol; W=water.

Table 3. Physical properties and analytical data of XIX, XX, and XXI

	Mp (°C)	Yield (%)	Crystal	Analytical data (%)			IR (cm^{-1})
					C	H	$\nu_{C=O}$
XIX	251—251.5 (B—E)	71	pale yellow cubes	Found:	87.43	5.02	1504
XX	240—242[a] (B)	77	pale yellow needles	Found:	87.55	5.08	1490
XXI	251—252[a] (B—C)	65	pale yellow cubes	Found:	88.01	5.24	1502
				Calcd for $C_{48}H_{30}OP$:	87.78	5.07	

a) Decomposition points. B=benzene; E=ethyl acetate; C=cyclohexane.

95.21; H, 4.79%.

b) Pyrolysis in Xylene. A solution of betaine(XVIII, 0.153 g) in xylene (20 ml) was refluxed for 8 hr. The residue obtained by the evaporation of the solvent *in vacuo* was dissolved in benzene, and was passed through a short column of alumina (3 g). III was obtained from the filtrate as orange-yellow needles, 0.047 g (54%), mp 286—288°C.

Formation of Acetylene(III) without Isolation of Betaine (XVIII). A xylene solution of betaine(XVIII) prepared by the above method was refluxed for 3 hr to give orange-yellow crystals, 0.314 g (38%). This was recrystallized twice from benzene to afford pure III, mp 286—288°C.

Found: C, 94.80; H, 4.75%. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79%.

Bromomethylphenanthrenes (X_c, X_d, and X_e). According to a similar procedure used for the preparation of X_b, the hydroxymethylphenanthrenes were converted into bromomethyl derivatives. The melting points were found to be identical with reported values.[11]

Phenanthrylmethyl-triphenylphosphonium Bromides (XI_c, XI_d, and XI_e). Bromomethylphenanthrene (7.66 g, 0.028 mol) in toluene (70 ml) was mixed with triphenylphosphine (7.50 g, 0.029 mol), and the mixture was refluxed for 18 hr. The crystals deposited were washed with a small amount of benzene, and were recrystallized to give pure colorless salt. The results are summarized in Table 2.

Preparation of Betaines(XIX, XX, and XXI). Since the preparation of the betaines of phenanthrene series were performed under similar reaction conditions, that of 3-phenanthryl derivative(XX) will be described as an example. To a suspension of phosphonium bromide (XI_d, 4.700 g, 8.8 mmol) in toluene (55 ml), was added under nitrogen atmosphere a solution of phenyllithium in ether (0.64 N, 13.80 ml). After the orange-red mixture had been stirred for 30 min at 80°C, a hot solution of acid chloride (XIV_d, 0.960 g, 4 mmol) in toluene (30 ml) was added, and the mixture was stirred for 19 hr at 80°C. The insoluble material was filtered, and was digested with hot benzene (60 ml×2) and hot toluene (60 ml×2). The combined filtrate and extracts were concentrated under reduced pressure. The viscous oily residue was mixed with benzene - cyclohexane (1 : 1, 5 ml), and was warmed to give rise to crystallization. The pale yellow crystalline powder, 2.576 g (98%) was recrystallized from benzene to give pure XX. The physical properties and the analytical data are shown in Table 3.

Diphenanthrylacetylenes(IV, V, and VI). As the pyrolyses of betaines(XIX, XX and XXI) were carried out under the same conditions, the procedure employed for 3-phenanthryl derivative(XX) will be described as a typical example.

Betaine(XX, 0.329 g, 0.5 mmol) placed in an evacuated flask (18 mmHg) was gradually heated up to 250°C over a period of 15 min. Distillation of triphenylphosphine oxide was observed at 200°C. The cooled reaction mixture was digested with benzene (40 ml), and the resulting solution was passed through a short column of alumina (5 g). Concentration of the filtrate under reduced pressure afforded V

Table 4. Physical properties and analytical data of phenanthrylacetylenes (IV, V, and VI)

	Mp (°C)	Yield (%)	Crystal	Analytical data		
					C	H
IV	261—262 (E)	74	colorless fine needless	Found:	95.17	4.86
V	266—267 (T)	100	colorless cubes	Found:	94.90	4.85
VI	243—244 (B)	88	colorless columns	Found:	95.03	4.84
				Calcd for $C_{30}H_{18}$:	95.21	4.79

E=ethyl acetate; T=toluene; B=benzene.

11) E. Mosettig and J. van de Kamp, *J. Amer. Chem. Soc.*, **55**, 2995 (1933).

as almost colorless crystals in a quantitative yield. This was recrystallized to give pure V.

The physical properties and analytical data are summarized in Table 4.

Bromomethylpyrenes (X_f and X_g). To an ice-cooled suspension of 1-hydroxymethylpyrene (5.24 g, 0.023 mol) in chloroform (70 m*l*) containing pyridine (0.95 g, 0.012 mol), was added over a period of 20 min a solution of phosphorus tribromide (3.12 g, 0.012 mol) in chloroform (20 m*l*). The temperature was gradually raised to room temperature, and stirring was continued for 30 min. The reaction mixture was again chilled with an ice-bath, and cracked ice and chloroform (100 m*l*) were added. The organic layer was washed successively with water, aqueous sodium hydrogen carbonate and water, and then dried. Evaporation of the solvent under reduced pressure afforded pale yellow needles, mp 131—133°C, 6.45 g (96%). The crystals were recrystallized to give pure X_f. According to a similar procedure, X_g was obtained from 2-hydroxymethylpyrene.

The results are summarized in Table 5.

Pyrenylmethyl-triphenylphosphonium Bromides (XI_f and XI_g). A mixture of 1-bromomethylpyrene (X_f, 6.00 g, 0.020 mol), toluene (20 m*l*) and triphenylphosphine (6.55 g, 0.025 mol) was refluxed for 4 hr. The reaction mixture, upon cooling, gave phosphonium salt (XI_f) as colorless cubes in an almost quantitative yield. This was recrystallized twice from water to afforded pure XI_f. The 2-pyrenyl derivative (XI_g) was obtained under similar conditions from 2-bromomethylpyrene (X_g). The results are recorded in Table 6.

Table 5. Physical properties and analytical data of X_f and X_g

	Mp (°C)	Crystal	Analytical data (%)		
			C	H	Br
X_f	145—147[a] (B—C)	colorless cubes	Found: 69.24	3.78	27.21
X_g	160—161 (B—C)	colorless needles	Found: 69.30	3.76	26.69
			Calcd for $C_{17}H_{11}Br$: 69.17	3.76	27.07

a) Lit. value: mp 139—142°C.[12] B-C=benzene - cyclohexane

Preparation of Betaines (XXII and XXIII). An ethereal solution of phenyllithium (0.39 N, 10.0 m*l*) was added to a suspension of betaine (XI_f, 2.675 g, 3.9 mmol) in toluene (50 m*l*) in an atmosphere of nitrogen, and the mixture was stirred for 1 hr at 60°C. A hot solution of the acid chloride of pyrene-1-carboxylic acid (XIV_f, 0.476 g, 1.8 mmol) in toluene (40 m*l*) was then added to the mixture, and stirring was continued for 20 hr at 60°C. The insoluble material

Table 6. Physical properties and analytical data of XI_f and XI_g

	Mp (°C)	Crystal	Analytical data (%)		
XI_f	293—295 (dec.)[a] (W)	colorless cubes	Found: 75.12	4.64	14.32
XI_g	286—289 (dec.) (E)	colorless leaflets	Found: 75.37	4.70	14.59[b]
			Calcd for $C_{35}H_{26}BrP$: 75.41	4.70	14.33

a) Lit. value: mp265—268°C.[12]
b) The analytical specimen was dried *in vacuo* for 6 hr at 178—181°C.
W=water; E=ethanol.

Table 7. Physical properties and analytical data of XXII and XXIII

	Mp (°C)	Yield (%)	Crystal	Analytical data (%)	
				C	H
XXII	257—258 (B)	96	yellow cubes	Found: 88.55	4.72
XXIII	>300[a] (B)	88	yellow cubes	Found: 88.45	4.77
				Calcd for $C_{52}H_{33}OP$: 88.62	4.72

a) The crystals turned to colorless fine needles at *ca.* 180°C.

Table 8. Physical properties and analytical data of dipyrenylacetylenes (VII and VIII)

	Mp (°C)	Yield (%)	Crystal	Analytical data (%)	
				C	H
VII	266 (T)	93	yellow cubes	Found: 95.52	4.23
VIII	>360 (T)	88	faint yellow needles	Found: 95.93	4.29
				Calcd for $C_{34}H_{18}$: 95.75	4.25

T=toluene.

12) J. P. Greets and R. H. Martin, *Bull. Soc. Chim. Belges.*, **69**, 563 (1960).

was extracted under reflux repeatedly with toluene (total 200 ml) and then with benzene (total 300 ml). The extracts were combined with the filtrate, and the solvents were removed under reduced pressure. The crude crystals thus obtained were mixed with benzene - cyclohexane (1 : 1, 5 ml), and were filtered and washed with the same solvent. The crystals were recrystallized to give pure XXII. The 2-pyrenyl derivative(XXIII) was obtained according to the similar procedure.

The physical properties and analytical data are summarized in Table 7.

Dipyrenylacetylenes(VII and VIII). The thermal decomposition of betaines(XXII and XXIII) to give dipyrenylacetylenes (VII and VIII) was performed according to the procedure for the preparation of diphenanthrylacetylenes (IV, V and VI), and the results are summarized in Table 8.

6-Bromomethylchrysene (X_h). A solution of phosphorus tribromide (2.98 g, 0.011 mol) in tetrahydrofuran (10 ml) was added over a period of 20 min to an ice-cooled suspension of 6-hydroxymethylchrysene[13] (6.10 g, 0.024 mol) in tetrahydrofuran (140 ml) containing pyridine (0.8 g, 0.01 mol). After having been stirred for 1 hr at room temperature, the mixture was warmed to 30°C to give a homogeneous solution. Cracked ice was added to the ice-cooled solution, and the organic layer was separated. The organic layer was worked up in the usual manner to give colorless crystals in an almost quantitative yield. The crystals were recrystallized twice from dioxane to give pure X_h as colorless fine needles, mp 194—196°C.

Found: C, 70.92; H, 4.15; Br, 24.54%. Calcd for $C_{19}H_{13}Br$: C, 71.04; H, 4.08; Br, 24.88%. IR: 1500 (C=O) cm^{-1}.

6-Chrysenylmethyl-triphenylphosphonium Bromide(XI_h). The reaction of X_h with triphenylphosphine in toluene according to the usual conditions gave slightly crude XI_h. The crude material was recrystallized from methanol to give analytical specimen. The colorless plates thus obtained contained 1 mole of methanol of crystallization. The crystals cracked at *ca.* 200°C, and decomposed at 270—272°C.

Found: C, 74.09; H, 5.15; Br, 12.82%. Calcd for $C_{37}H_{28}BrP{-}CH_3OH$: C, 74.15; H, 5.24; Br, 12.98%.

Preparation of Betaine(XXIV). According to the procedure for the preparation of XXII and XXIII, the slightly crude XI_h was converted into betaine (XXIV) by the reaction with acid chloride(XIV_h).[14] The yellow cubes obtained in a yield of 89% was recrystallized twice from toluene to give pure material, yellow cubes, mp *ca.* 265°C (dec.).

Found: C, 88.70; H, 5.28%. Calcd for $C_{56}H_{37}OP$: C, 88.87; H, 4.93%.

6,6'-Dichrysenylacetylene(IX). The thermal decomposition of betaine(XXIV) under the conditions used in the preparation of diphenanthrylacetylenes(IV, V and VI) gave yellow crystals in an almost quantitative yield. The crystals were recrystallized from toluene to give pure IX as fine pale yellow needles. Acetylene(IX) was found to be highly stable, and neither fusion nor decomposition could be observed even at 330°C.

Found: C, 95.08; H, 4.63%. Calcd for $C_{38}H_{22}$: C, 95.37; H, 4.63%.

13) M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.*, **1957**, 2946.

14) K. Funke and E. Müller, *J. Prak. Chem.*, **144**, 242 (1936).