

**756.** *Researches on Polyenes. Part VII.\* The Preparation and Electronic Absorption Spectra of Homologous Series of Simple Cyanines, Merocyanines, and Oxonols.*

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Substances of types (I—III) represent cyanines, merocyanines, and oxonols of the simplest possible type, and therefore suitable for quantum-mechanical calculations on energy levels. Several members of each series have been prepared; their electronic absorption spectra are tabulated and discussed. The merocyanines (II) differ from their charged analogues in that their absorption maxima cease, at moderate values of  $n$ , to move rapidly to longer wavelengths. This "convergent" behaviour is correlated with dipole-moment measurements.

In perhaps the first serious attempt to calculate from first principles the relation between the length of a conjugated system and the corresponding electronic absorption spectrum, Lewis and Calvin<sup>1</sup> contrasted the polyenes and the cyanine dyes, as representatives of fundamentally different systems. Their semi-classical treatment led to equations of the form  $\lambda = kn^3$  and  $\lambda = kn$ , respectively, and approximate agreement with the experimental facts was at once obvious. Recent data for simple polyenes with  $n < 7$  (ref. 2) and with  $n = 8-10$  (ref. 3) reveal very close agreement (probably closer than with any equation deduced subsequently by quantum-mechanical methods) between the facts and the first of these equations, provided that the wavelength of the longest of the bands spaced at *ca.* 1450  $\text{cm}^{-1}$  is taken as representative of the electronic transition. This is *a priori* a reasonable assumption.<sup>2</sup>

It was argued in Part III of this series<sup>2</sup> that the large and complex end-groups, and the lateral substitution with methyl groups, of natural carotenoids render them unsatisfactory for comparison with theoretical predictions. This is equally true of the cyanines in which complex heterocyclic nuclei are present. We have therefore examined a series (I) in which the end-groups are simple, and the related anionic series (III), in order to test the second Lewis-Calvin equation. We shall here refer to these compounds briefly as cyanines and oxonols, respectively, although that involves some extension of these categories<sup>4</sup> (the names are convenient and single out the essential features of cyanines and oxonols, the equal division of an electric charge, positive and negative, respectively, between heteroatoms at the ends of an odd-numbered polymethine chain; the nature of the heterocyclic nuclei is manifestly inessential to their spectroscopic properties, except insofar as it affects basicity and the length of the path between the heteroatoms). Series (I) and (III) are also of interest as perhaps the simplest possible basic and acidic dyes; members of series (III) with  $n = 0, 1$ , and 2 are known, and a claim to have investigated series (I) has been made by Simpson,<sup>5</sup> who however prepared only members with  $n = 1$  and 2, and a lateral acetoxy-derivative of compound (I;  $n = 3$ ) [his contention that this would approximate spectroscopically to (I;  $n = 3$ ) itself is now shown to be correct]. We report the preparation of compounds (I) with  $n = 0-6$  and (III) with  $n = 0-4$ , inclusive.

Polyenes  $X\cdot[\text{CH}=\text{CH}]_n\cdot\text{CH}=\text{Y}$ , where X and  $\text{CH}=\text{Y}$  are respectively (heterocyclic) groups with strong  $+M$  and  $-M$  effects, behave in many ways like cyanines and oxonols and have been called "merocyanines";<sup>6</sup> we have obtained series (II;  $n = 0-6$ ), and here

\* Part VI, *J.*, 1958, 903.

<sup>1</sup> Lewis and Calvin, *Chem. Rev.*, 1939, **25**, 273.

<sup>2</sup> Nayler and Whiting, *J.*, 1955, 3037.

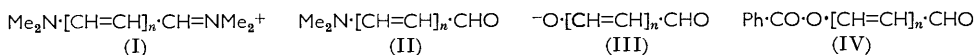
<sup>3</sup> Bohlmann and Mannhardt, *Chem. Ber.*, 1956, **89**, 1307.

<sup>4</sup> Hamer, *Quart. Rev.*, 1950, **4**, 327.

<sup>5</sup> Simpson, *J. Chem. Phys.*, 1948, **16**, 1124.

<sup>6</sup> Hamer and Winton, *J.*, 1949, 1126.

apply this term to them. They, and the *p*-methoxyphenyl-polyene aldehydes,<sup>7</sup> are successive intermediates between the fully charge-delocalised cyanines and oxonols, on the one hand, and the pure polyenes, in which "sacrificial conjugation" is involved, on the other.



*Synthetical Work.*—*Compounds with n = 0.* Though the formate anion and dimethylformamide are well known, tetramethylformamidinium compounds have not yet been prepared. In fact many methods applicable for compounds with  $n > 0$  proved unsuccessful, *e.g.*, attempted condensations between dimethylamine salts and dimethylformamide; such a compound was finally obtained, as the perchlorate, by condensation between dimethylamine, dimethylammonium perchlorate, and ethyl orthoformate. Some steric hindrance is present in the molecule of (I;  $n = 0$ ), but not in higher homologues, and may explain the difficulty in obtaining it.

*Compounds with n = 1.* Compounds (I) and (III) with  $n = 1$  are known; but convenient preparative methods are given below. The merocyanine (II;  $n = 1$ ) was readily obtained by adding dimethylamine to propynal (*cf.* similar addition to ethynyl ketones<sup>8</sup>). The compound described by Wille and Saffer<sup>9</sup> as *t*-butylaminopropadienol, and similarly prepared, is undoubtedly the corresponding *t*-butylamino-ethylenic aldehyde; the observed ferric chloride colour is explicable on that basis and in no way proves the presence of an enolic grouping.

*Compounds with n = 2.* These are the most accessible homologues ( $n > 0$ ), and at this point the interconversion of compounds (I—III) has been examined in detail. The diethyl analogue of (II;  $n = 2$ ) has been prepared from diethylamine and 1-(2,4-dinitrophenyl)-pyridinium chloride;<sup>10</sup> by a simple modification we have obtained compound (II;  $n = 2$ ) in much higher yield, as a solid which readily forms a low-melting (?mono)hydrate. Like analogues studied earlier this salt shows neither characteristic aldehydic nor strong basic properties, but behaves rather as a highly reactive tertiary amide. Thus it is fairly rapidly hydrolysed by sodium hydroxide to the salt of "glutaconic dialdehyde" (III;  $n = 2$ ). So obtained, it forms pale yellow crystals, indefinitely stable (in the solid state) at room temperature. (Earlier preparations, described as darker and less stable, may have been less pure. In acid or even neutral aqueous solution the "dialdehyde" rapidly resinifies, but it is stable in alkaline solution at moderate temperatures.) Dimethylamine salts (most conveniently the perchlorate) readily convert the merocyanine (II;  $n = 2$ ) into the corresponding cyanine (I), previously obtained by amine exchange from the dianil hydrochloride. The cyanine is hydrolysed in cold alkali almost instantaneously to the amino-aldehyde (II;  $n = 2$ ), and then to the oxonol (III;  $n = 2$ ). The cycle can be completed by treating the oxonol sodium salt (III;  $n = 2$ ) with dimethylamine perchlorate, giving the cyanine (I;  $n = 2$ ), no doubt *via* the merocyanine (II).

Benzoylation of compound (III;  $n = 2$ ) gave the known product<sup>11</sup> (IV;  $n = 2$ ), which showed the properties expected for a mixed anhydride.

*Compounds with n = 3.* In seeking synthetic routes to compounds (I—III) having  $n = 3$ , we hoped to use compounds (I—III), or variants such as (IV), with  $n = 2$ , as starting material. A chain-extension method, capable in principle of indefinite repetition, would thus be made available, giving a general synthesis for these systems. Several attempts proved unsuccessful; thus, compounds (II) and (IV), as well as the corresponding acetate,<sup>11</sup> failed to condense with sodium acetylide or ethynylmagnesium bromide at the "aldehyde" carbon atom. Evidence was obtained that pent-2-en-4-ynal, which is

<sup>7</sup> Marshall and Whiting, *J.*, 1956, 4082.

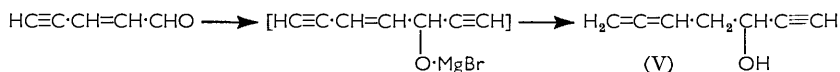
<sup>8</sup> Bowden, Braude, Jones, and Weedon, *J.*, 1945, 45.

<sup>9</sup> Wille and Saffer, *Annalen*, 1950, 568, 34.

<sup>10</sup> Knunyants and Kefeli, *J. Gen. Chem. U.S.S.R.*, 1945, 15, 628; *Chem. Abs.*, 1946, 40, 6079.

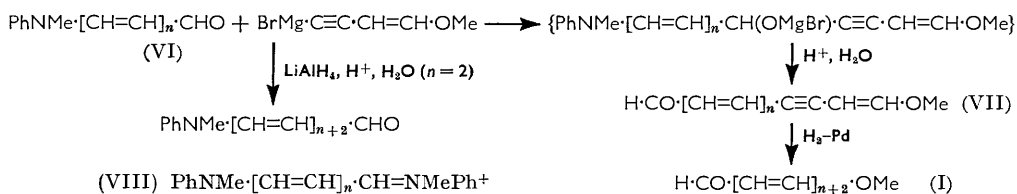
<sup>11</sup> Baumgarten, *Ber.*, 1924, 57, 1622.

closely related <sup>12</sup> to compounds (I—III;  $n = 2$ ), did do so; no attempt was made to isolate the product, but direct reduction of the complex with lithium aluminium hydride gave a product formulated, from spectroscopic data, as (V), and thus of no value for the desired chain extension.



At this point we were informed by Professor R. A. Raphael that he had condensed *N*-methylanilinopentadienal <sup>13</sup> (VI;  $n = 2$ ) with phenylethyne magnesium bromide, and, after hydrolysis, obtained 7-phenylhepta-2,4-dien-6-ynal as the semicarbazone. This reaction was repeated by us and the product was isolated as such. Similar reactions have since been reported by Jutz.<sup>14</sup> The analogous reaction with ethynylmagnesium bromide <sup>15</sup> proceeded as expected, giving hepta-2,4-dien-6-ynal in fair yield. This, in contrast to propynal and pent-2-en-4-ynal,<sup>12</sup> reacted at a negligible rate with dimethylamine, to give compound (II;  $n = 3$ ) in traces only, spectroscopically estimated. On the other hand condensation with dimethylamine and dimethylamine perchlorate to give the perchlorate of (I;  $n = 3$ ) took place rapidly and in good yield. Theoretical aspects of these differences are discussed below; meanwhile the synthesis of the merocyanine (II;  $n = 3$ ) followed as for the lower homologue. Similar derivatives of methylaniline, *e.g.*, (VI;  $n = 3$ ), were readily obtained, so that further extension of the series appeared possible. The preparation of the sodium salt of the oxonol (III;  $n = 3$ ) was not so satisfactory as that of the lower homologue, and no method was found for crystallising it without some decomposition. Treatment of the methylanilinoheptatrienal with potassium hydroxide in aqueous 1-methylpyrrolid-2-one, however, gave the potassium salt, apparently pure, in good yield. It was characterised as the benzyloxy-compound (IV;  $n = 3$ ).

*Compounds with  $n = 4$ —6.* Rather than attempt a second chain-extension cycle on the methylanilinoheptatrienal, we preferred to use methods employed in Part IV,<sup>7</sup> involving direct addition of a  $[\text{CH}=\text{CH}]_2$  grouping to the conjugated chain of methylanilinopentadienal. Condensation of the latter with the Grignard reagent from 4-methoxybut-3-en-1-yne and reduction of the complex with lithium aluminium hydride gave, on treatment with acid and isolation of the product, the desired tetraenal (VI;  $n = 4$ ), albeit in only 2% yield.



Hydrolysis of the initial Grignard complex gave the methoxynonatrienyne (VII;  $n = 2$ ) as a very unstable liquid. Catalytic hydrogenation of this over the Lindlar catalyst <sup>16</sup> gave an even more unstable product <sup>17</sup> which defeated attempts to isolate it; however, reactions with dimethylamine-dimethylamine perchlorate or with partly neutralised methylaniline gave good overall yields of the desired cyanine perchlorates.

For the hydrolysis of the cyanines to the merocyanines (II and VI;  $n = 4$ ) the conditions hitherto employed were much less successful. Use of aqueous 1-methylpyrrolid-2-one, however, resulted in satisfactory reactions. This solvent was again valuable in preparing the potassium salt of the oxonol (III;  $n = 4$ ), little or none being obtained in aqueous

<sup>12</sup> Heilbron, Jones, and Julia, *J.*, 1949, 1430; Sondheimer, Ph.D. Thesis, London, 1948.

<sup>13</sup> Zinke and Wurker, *Annalen*, 1905, **338**, 127.

<sup>14</sup> Jutz, *Chem. Ber.*, 1958, **91**, 1867.

<sup>15</sup> Jones, Skattebøl, and Whiting, *J.*, 1956, 4765.

<sup>16</sup> Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.

<sup>17</sup> Cf. Inhoffen, Bohlmann, and Rummert, *Annalen*, 1950, **569**, 226.

FIG. 1. Absorption spectra of potassium salts,  $\text{KO}\cdot[\text{CH}=\text{CH}]_n\text{CHO}$ , where  $n$  is as given on the curves. Solvent: dimethylformamide containing 3% of triethylamine, but  $\text{H}_2\text{O}$  for  $n = 1$ .

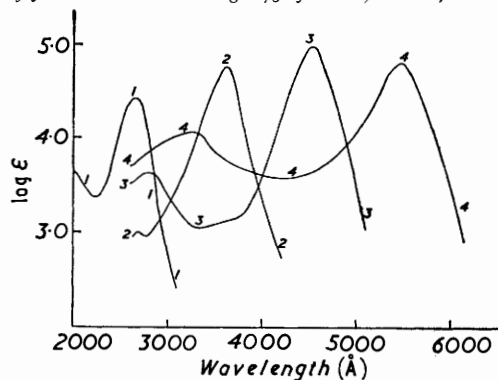


FIG. 2a.

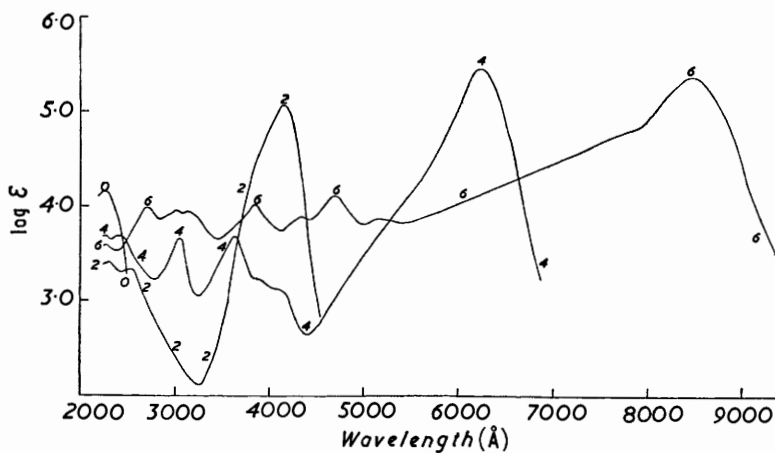


FIG. 2b.

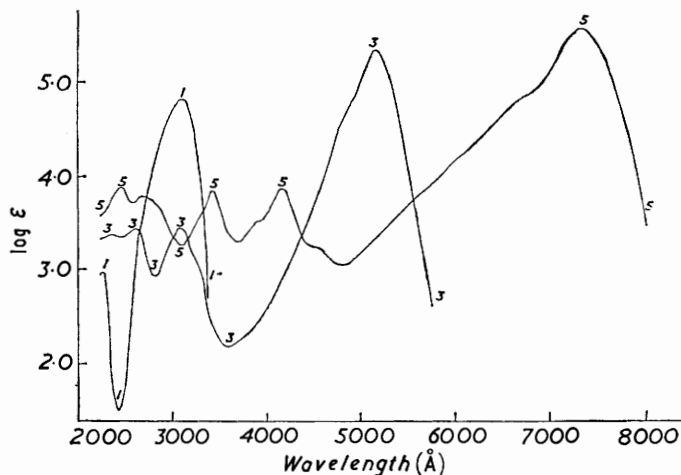
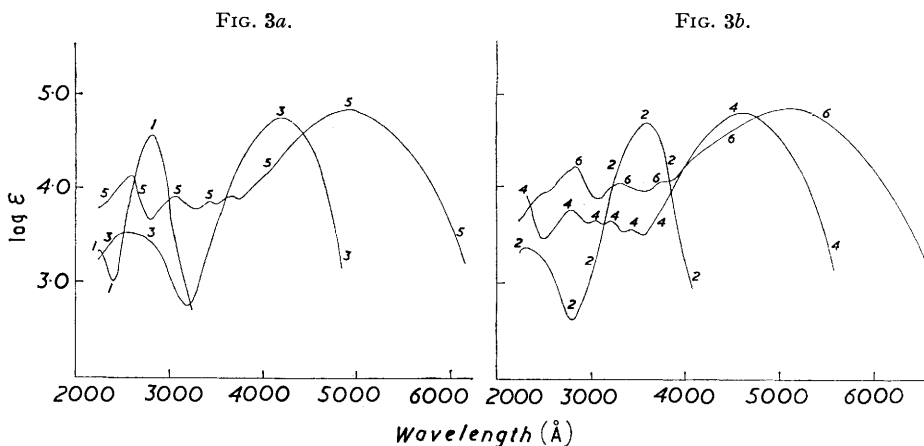


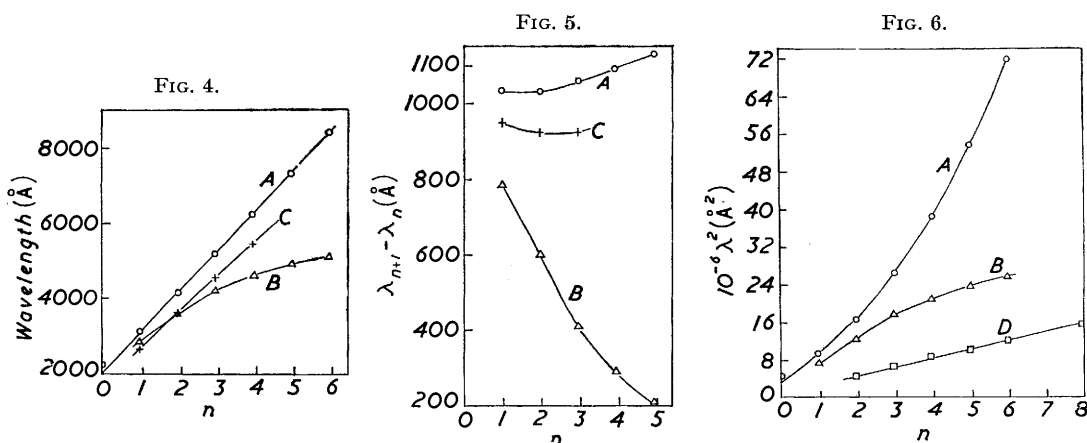
FIG. 2a & b. Absorption spectra of salts,  $\text{Me}_2\text{N}\cdot[\text{CH}=\text{CH}]_n\text{CH}=\text{NMe}_2^+\text{ClO}_4^-$ , where  $n$  is as given on the curves, in methylene dichloride.



Figs. 3a & b. Absorption spectra of compounds,  $\text{Me}_2\text{N}[\text{CH}=\text{CH}]_n\cdot\text{CHO}$ , where  $n$  is as given on the curves, in methylene dichloride.

Principal absorption maxima.

$n$	(I)		(II)		(III)		(VIII)		(VI)		(VII)		(IV)	
	$\lambda$ (Å)	$10^{-3}\epsilon$	$\lambda$ (Å)	$10^{-3}\epsilon$	$\lambda$ (Å)	$10^{-3}\epsilon$	$\lambda$ (Å)	$10^{-3}\epsilon$	$\lambda$ (Å)	$10^{-3}\epsilon$	$\lambda$ (Å)	$10^{-3}\epsilon$	$\lambda$ (Å)	$10^{-3}\epsilon$
0	2240	14.5												
1	3125	64.5	2830	37	2675	27.1								
2	4160	119.5	3615	51	3625	56	4540	111	3715	65	3615	23	2850	47.6
3	5190	207	4215	56	4550	75.5	5625	141	4215	74	3765	40.5	3240	58
4	6250	295	4625	65	5475	(63)	6715	203	4545	(57)	3915	53	3565	69
5	7345	353	4915	68										
6	8480	(220)	5125	72										



Figs. 4—6. Lewis-Calvin plots. FIG. 4: plot of  $\lambda$  against  $n$ . FIG. 5: plot of  $(\lambda_{n+1} - \lambda_n)$  against  $n$ . FIG. 6: plot of  $\lambda^2$  against  $n$ .

A, Series (I); B, series (II); C, series (III); D, polyenes.<sup>2, 3</sup>

methanol; indeed, even when 1-methylpyrrolid-2-one was used the salt was clearly not pure, having an apparent molar extinction coefficient lower than that of its analogue (III;  $n = 3$ ). It was characterised as the benzoate (IV;  $n = 4$ ).

When condensed with methoxybutenyne, the compounds (VI;  $n = 3$  and 4) yielded acetylenic aldehydes (VII;  $n = 3$  and 4), which, being crystalline, were easier to isolate than the lower homologue. Hydrogenation and conversion into the cyanines (I;  $n = 5$  and 6) proceeded satisfactorily, although for (I;  $n = 6$ ) the reaction was impracticably slow

at 0°, perhaps because an intermediate was too insoluble. Hydrolysis to the merocyanines (II;  $n = 5$  and 6) was effected in aqueous 1-methylpyrrolid-2-one, in good yield. The potassium salt of the oxonol (III;  $n = 5$ ) could not, however, be obtained; some of the black precipitates formed from compound (II;  $n = 5$ ) and potassium hydroxide in aqueous 1-methylpyrrolid-2-one gave unstable solutions with maxima at 6440 Å, as expected, but intensities were very low. The analogous reaction with the higher homologue (II;  $n = 6$ ) was not attempted.

*Electronic Spectra.*—The absorption spectra of the oxonol potassium salts ( $n = 2-4$ ) (Fig. 1) were most conveniently determined in dimethylformamide, a little triethylamine being added to maintain alkalinity. The cyanine (I;  $n = 0-6$ ) perchlorates were most conveniently examined in methylene chloride (Fig. 2); these solvents were chosen for their ability to dissolve all members of the series at room temperature, but trials with the compounds where  $n = 2$  revealed that, as expected, the solvent effects were almost negligible. Sodium formate showed no significant absorption above 1900 Å, and the sodium salt of compound (III;  $n = 1$ ) was examined in water. The merocyanines (II;  $n = 5$  and 6) were relatively insoluble and could be examined only in methylene dichloride, (Fig. 3) but the lower homologues showed the expected very large solvent effects.

The cyanine cations obey the Lewis-Calvin rule,  $\lambda = kn$ , fairly accurately (Fig. 4), except that the tetramethylformamidinium cation absorbs at an unexpectedly long wavelength. As its intensity of absorption is also low ( $\epsilon = 14,500$ ) some steric hindrance may be responsible. The severe test of plotting  $(\lambda_{n+1} - \lambda_n)$  against  $n$  (Fig. 5) shows that the closest fit would be given by a wavelength equation of the type  $\lambda = kn^x$  with  $x$  slightly greater than 1.

The limited range of oxonol anions also obeyed the Lewis-Calvin equation,  $\lambda = kn$ , accurately, although the increment between the successive members of the series was perceptibly smaller than for the cyanines.

These results agree with the available data for symmetrical heterocyclic cyanines, where a fairly constant increment of *ca.* 1000  $\text{cm}^{-1}$  is usually observed. The series (I) provides a clear example of the difference between "convergent" and "non-convergent" behaviour; with, formally speaking, only seven unsaturated linkages, compound (I;  $n = 6$ ) absorbs maximally in the near-infrared region, whereas in the polyene field a similar chain-length barely brings the absorption maximum into the visible region.<sup>2,3</sup>

The high intensity of absorption shown by series (I) has already received comment;<sup>5</sup> the extinction coefficients are now seen to be approximately  $60,000n$ , though the result for the last homologue (I;  $n = 6$ ) is low, owing (presumably) to photo-decomposition despite the precautions taken [photo-decomposition was difficult to avoid for compounds (I;  $n > 3$ )]. The oxonol salts, on the other hand, may have been impure even before dissolution, so that  $\epsilon = 25,000n$  or  $30,000n$  is a minimum value. These figures are higher than that ( $25,000n$ ) which characterises the dimethylpolyene series<sup>2</sup> and approach the values of 70,000—80,000  $n$  characteristic of the polyynes.<sup>18</sup>

The cyanines (I) behaved as basic dyes, giving clear colours when applied to silk, rapidly fading on exposure to light. The oxonol salts dyed wool after use of an aluminium mordant, fading again being rapid.

The spectra of the merocyanines (II) differed from those of the charged molecules (I) and (III) in showing much less sharply defined main maxima, though without any sign of vibrational fine structure. As  $n$  increases, the wavelength of maximal absorption for series (II) falls far behind those of the charged analogues, and indeed the behaviour of this series, initially reminiscent of (I) and (III), becomes much more like that of the simple polyenes (Fig. 6). The clue to the change is provided by the dipole moments of members of series (II), which have recently been reported.<sup>19</sup> Although as  $n$  increases, the moment

<sup>18</sup> Cook, Jones, and Whiting, *J.*, 1952, 2883; Bohlmann, *Chem. Ber.*, 1953, **86**, 63, 657.

<sup>19</sup> Hely-Hutchinson and Sutton, *J.*, 1958, 4382.

of a compound (II) also increases, it does so much less than would be expected if the charge distribution remained constant. It is indeed probable that the moment approaches a limiting value of *ca.* 8.6 D (in benzene; no doubt dependent on the solvent used). This implies that the degree of mesomeric charge-transfer from the nitrogen lone-pair to the oxygen atom falls off as *n* increases, because of the work that would be needed to increase the distance between the opposite charges at a constant degree of polarisation. This result in turn explains why the rate of addition of dimethylamine to the aldehydes  $\text{HC}\equiv\text{C}\cdot[\text{CH}=\text{CH}]_n\cdot\text{CHO}$  diminishes rapidly with increasing values of *n*, while addition to  $\text{HC}\equiv\text{C}\cdot[\text{CH}=\text{CH}]_n\cdot\text{CH}=\text{NMe}_2^+$  (the assumed first products in solutions rich in the amine salt) remains little affected by chain length. In the first reaction, the charge separation in the transition state, approaching  $^+\text{R}_2\text{NH}\cdot\text{CH}=\text{C}=[\text{CH}\cdot\text{CH}=\text{C}]_n\text{CH}\cdot\text{O}^-$ , increases with *n*; whereas in the second, approaching  $^+\text{R}_2\text{NH}\cdot\text{CH}=\text{C}=[\text{CH}\cdot\text{CH}=\text{C}]_n\text{CH}\cdot\text{NR}_2$ , the charge is more widely dispersed the larger *n* becomes.

*Vibrational Spectra.*—These were studied only for structure confirmation, but it is noteworthy that even in series (II) the C=O stretching frequency falls only to 1678  $\text{cm}^{-1}$ , this band becoming weaker, relative to one at *ca.* 1600  $\text{cm}^{-1}$ , as *n* increases. The bands at *ca.* 970 and 1005  $\text{cm}^{-1}$  in the region typical of conjugated *trans*-CH=CH- out-of-plane deformation modes are quite weak.

The cyanine perchlorates (I) absorb intensely at 1560  $\text{cm}^{-1}$ .

*Note Added in Proof.*—Since preparing this manuscript we have learnt that Arnold and Šorm (*Coll. Czech. Chem. Comm.*, 1958, **23**, 452) have reported the chloride and picrate, and Arnold (*Coll. Czech. Chem. Comm.*, 1959, **24**, 760) the perchlorate, of the cation (I; *n* = 0); no spectroscopic data were recorded, but the conversion of (III; *n* = 1) into (I; *n* = 1) was observed. McGlynn and Simpson (*J. Chem. Phys.*, 1958, **28**, 297) have reported an absorption maximum for the cation [I; *n* = 3], without stating how this dye was prepared.

## EXPERIMENTAL

The precautions usual in work with highly unsaturated substances were taken, and, in addition, great care was necessary with the cyanines (I; *n* > 2) to protect solutions from light, notably by the use of dark brown glassware. Even diffused daylight decolorised dilute solutions and led to losses in recrystallisation; on the other hand, the compounds of series (I—III) and their aromatic analogues showed little of the sensitivity to oxidation in solution typical of the polyenes. In the solid state these compounds were more stable toward light.

*Dimethylamine Perchlorate.*—A 25% solution (370 g.) of dimethylamine and 60% perchloric acid (300 g.) were mixed with cooling and evaporated under reduced pressure, giving the *salt* as hygroscopic needles, m. p. 180—182° (Found: C, 16.6; H, 5.5; N, 9.7.  $\text{C}_2\text{H}_8\text{ClNO}_4$  requires C, 16.5; H, 5.5; N, 9.9%).

*Tetramethylformamidinium Perchlorate.*—A solution of anhydrous dimethylamine (4.5 g.), dimethylamine perchlorate (14.5 g.), and ethyl orthoformate (14.8 g.) in ethanol (10 c.c.) was heated under reflux for 4 hr., cooled, and kept overnight at -5°. The separated *salt* was collected, washed with ice-cold ethanol, and recrystallised from ethanol, giving colourless plates (8 g.), m. p. 136° (Found: C, 30.4; H, 6.5; N, 13.6; Cl, 17.5.  $\text{C}_5\text{H}_{13}\text{ClN}_2\text{O}_4$  requires C, 29.9; H, 13.9; Cl, 17.7%).

*3-Dimethylaminopropenal.*—Propynal (8 g.) and methanol (20 c.c.) were cooled to -8° while a solution of anhydrous dimethylamine (8 g.) in methanol (20 c.c.) was added during 30 min. After 18 hr. at -5° the solution was evaporated and distilled *in vacuo*, giving light yellow 3-dimethylaminopropenal (10.2 g., 68%), b. p. 72—74°/0.05 mm.,  $n_D^{19}$  1.5789 (Found: C, 60.1; H, 9.2; N, 13.8.  $\text{C}_5\text{H}_9\text{NO}$  requires C, 60.6; H, 9.2; N, 14.1%).

*3-Dimethylaminopropenylylidenedimethylammonium Perchlorate.*—The preceding compound (1.5 g.) and dimethylamine perchlorate (2.3 g.) in ethanol (5 c.c.) were heated under reflux for 4 hr. The product which crystallised on cooling was recrystallised from ethanol, giving the *salt* (2.5 g., 85%) as pale cream needles, m. p. 120° (Found: C, 37.2; H, 6.7; N, 12.2; Cl, 15.1.  $\text{C}_7\text{H}_{15}\text{ClN}_2\text{O}_4$  requires C, 37.1; H, 6.6; N, 12.3; Cl, 15.6%).

*Sodium Salt of 3-Hydroxyprop-2-en-1-al* ("Malonic Dialdehyde").—A solution of sodium hydroxide (1.5 g.) in water (7.5 c.c.) was added to 3-dimethylaminoprop-2-enal (1.5 g.) and methanol (7.5 c.c.), and the mixture was warmed on the water-bath for 4 min.; dimethylamine was evolved. On cooling to  $-8^{\circ}$  the salt (1.1 g., 95%) separated as almost colourless needles, which after recrystallisation from ethanol were indefinitely stable.

*5-Dimethylaminopenta-2,4-dienal*.—1-(2,4-Dinitrophenyl)pyridinium chloride (100 g.) in ethanol (1 l.) was treated with 25% aqueous dimethylamine (120 c.c.). The mixture was heated to  $60-70^{\circ}$  for 30 min., largely evaporated under reduced pressure, and treated with cold water (600 c.c.). The separated 2,4-dinitroaniline was collected and the filtrate was made alkaline with sodium hydroxide (20 g.) in water (100 c.c.) and extracted with methylene dichloride ( $4 \times 150$  c.c.). Evaporation of the dried extract left a hygroscopic solid, m. p.  $30-32^{\circ}$  (34 g.), which from analytical data appeared to be an unstable hydrate. After distillation at  $118-125^{\circ}/0.15$  mm. the aldehyde had m. p.  $59^{\circ}$  (Found: C, 67.3; H, 8.9; N, 11.1.  $C_7H_{11}NO$  requires C, 67.2; H, 8.8; N, 11.2%), but it was reconverted into the hydrate, m. p.  $30^{\circ}$ , on storage.

*5-Dimethylaminopenta-2,4-dienyldenedimethylammonium Perchlorate*.—(a) The foregoing compound (2.5 g.), dimethylamine perchlorate (3.5 g.), and ethanol (8 c.c.) were heated under reflux for 2 hr. The salt (4.4 g., 87%) separated on cooling and, after crystallisation from ethanol, formed yellow plates with a violet iridescence, m. p.  $167^{\circ}$  (König and Regner<sup>20</sup> give m. p.  $165^{\circ}$ ).

(b) Methyl-5-*N*-methylanilinopenta-2,4-dienyldeneanilinium perchlorate (1.8 g.), dimethylamine (3 c.c.), and dimethylamine perchlorate (3 g.) in methanol (10 c.c.) similarly gave the bisdimethylamino-salt (1.1 g., 90%), m. p.  $167^{\circ}$ .

(c) The sodium salt of 5-hydroxypenta-2,4-dienal (4 g.; see below), dimethylamine (5 c.c.), dimethylamine perchlorate (6 g.), and methanol (20 c.c.) were heated under reflux for 1 hr. On cooling, the bisdimethylamino-salt (7.5 g., 90%), m. p.  $167^{\circ}$ , separated.

*5-N-Methylanilinopenta-2,4-dienal*.—Methyl-5-*N*-methylanilinopenta-2,4-dienyldeneanilinium chloride<sup>21</sup> (535 g.) was suspended in water (1.8 l.) and cooled to  $5^{\circ}$  while a solution of sodium hydroxide (180 g.) in water (1.8 l.), also cooled to  $5^{\circ}$ , was added with shaking during 30 min. The mixture was kept at  $2-5^{\circ}$  with occasional shaking for 2 hr., then extracted with ether ( $7 \times 1$  l.). Concentration of the dried ( $MgSO_4$ ) extract to 700 c.c. and keeping it overnight at  $-5^{\circ}$  gave the aldehyde (270 g., 70%) as yellow needles, m. p.  $78-80^{\circ}$  (Zinke and Wurker<sup>19</sup> give m. p.  $78-80^{\circ}$ ). The semicarbazone separated from 2-methoxyethanol as yellow needles, m. p.  $188^{\circ}$  (Found: C, 63.6; H, 6.8; N, 22.7.  $C_{13}H_{16}N_4O$  requires C, 63.9; H, 6.6; N, 22.9%).

*Methyl-5-N-methylanilinopenta-2,4-dienyldeneanilinium perchlorate* was prepared as above from 5-methylanilinopenta-2,4-dienal (3.7 g.), methylaniline (2.2 c.c.), 60% perchloric acid (2.2 c.c.), and ethanol, in 87% yield. It formed red needles, m. p.  $102^{\circ}$ , from ethanol (Found: C, 59.9; H, 6.0.  $C_{19}H_{21}ClN_2O_4$  requires C, 60.4; H, 5.6%).

*Sodium Salt of 5-Hydroxypenta-2,4-dienal*.—Methyl-5-*N*-methylanilinopenta-2,4-dienyldeneanilinium chloride (32 g.) was dissolved in methanol (200 c.c.), and a solution of sodium hydroxide (40 g.) in water (200 c.c.) was added. The mixture was heated at  $60-70^{\circ}$  for 2-5 min. and cooled, and the separated salt (11.2 g., 90%) collected as stable yellow needles.

From *N*-methylanilinopenta-2,4-dienal and from the corresponding dimethylamino-compound the salt was similarly obtained in yields of 90% and 95%, respectively. The latter gave a particularly pale specimen; in no case was the darker polymorph<sup>11</sup> (?) encountered. The potassium salt (also pale yellow) was readily obtained by the same method. Either salt could be characterised as 5-acetoxypenta-2,4-dienal, m. p.  $75^{\circ}$  (Baumgarten<sup>11</sup> gives m. p.  $75^{\circ}$ ), or as below.

*5-Benzoyloxy-penta-2,4-dienal*.—The above sodium salt (6 g.) was dissolved in pyridine (12 c.c.), and benzoyl chloride (8 g.) was added with shaking. On addition of water the benzoyl compound separated at once as cream needles (8.9 g., 94%), m. p.  $120-121^{\circ}$  (Baumgarten<sup>11</sup> records m. p.  $116-118^{\circ}$  after crystallisation from alcohol, but observed some decomposition during this operation; we confirm this).

*Hepta-2,4-dien-6-ynal*.—A solution of ethynylmagnesium bromide was prepared<sup>15</sup> from magnesium (20 g.) in tetrahydrofuran (500 c.c.). It was added during 1 hr. to a solution of

<sup>20</sup> König and Regner, *Ber.*, 1930, **63**, 2823.

<sup>21</sup> Zinke and Wurker, *Annalen*, 1905, **338**, 121.



5-*N*-methylaminopenta-2,4-dienal (60 g.) in tetrahydrofuran (300 c.c.) at  $-10^{\circ}$  to  $-5^{\circ}$ ; after 2 hours' stirring at this temperature, ether (1 l.) and ice-cold 4*N*-sulphuric acid (400 c.c.) were added, and the mixture was shaken. The aqueous layer was extracted with ether ( $3 \times 500$  c.c.), and the combined extracts were washed with aqueous sodium hydrogen carbonate, dried ( $\text{MgSO}_4$ ), and evaporated under reduced pressure. The residue was dissolved in benzene (1 l.) and light petroleum (1 l.), then passed down a column of alumina (Peter Spence Grade 0, deactivated with 5% acetic acid) (250 g.), which was then washed with the same solvent mixture. Evaporation of the pale yellow filtrate left a brown solid (21.4 g.), m. p.  $45-50^{\circ}$ , which remained brown after repeated crystallisation. A small sample (20 mg.) was sublimed *in vacuo* and then crystallised from light petroleum as almost colourless needles, m. p.  $51^{\circ}$  (Found: C, 79.3; H, 5.9.  $\text{C}_7\text{H}_8\text{O}$  requires C, 79.3; H, 5.7%), which in ethanol had  $\lambda_{\text{max}}$ , 2075 Å ( $\epsilon$  8500) and 2895 Å ( $\epsilon$  33,500). Larger quantities decomposed explosively on sublimation, and the solid, m. p.  $45-50^{\circ}$ , was therefore used as such; by spectrophotometry it was 86% pure.

*7-Dimethylaminohepta-2,4,6-trienylidenedimethylammonium Perchlorate*.—The above aldehyde (1 g.; 86% pure) in ethanol (10 c.c.) was treated with a solution of dimethylamine (1.5 c.c.) and dimethylamine perchlorate (1.5 g.) in ethanol with shaking. After 4 hr. at  $20^{\circ}$  the product was collected; from ethanol, it formed needles (0.95 g., 38%), m. p.  $180^{\circ}$ , green by reflected and magenta by transmitted light (Found: C, 47.5; H, 7.1; N, 9.7; Cl, 12.4.  $\text{C}_{11}\text{H}_{19}\text{ClN}_2\text{O}_4$  requires C, 47.4; H, 6.8; N, 10.0; Cl, 12.7%).

*Methyl-7-N-methylaminiohepta-2,4,6-trienylideneanilinium Perchlorate*.—An ice-cold solution of *N*-methylaniline (45 g.) and 60% perchloric acid (22.2 c.c.) in ethanol (200 c.c.) was added to heptadienylnal (20 g., 86% pure) in ethanol (200 c.c.) at  $-5^{\circ}$  to  $0^{\circ}$  with shaking. After 4 hr. at  $-5^{\circ}$  the salt (60.5 g., 93%) formed blue-violet needles, m. p.  $207^{\circ}$ , unchanged after crystallisation from ethanol (Found: C, 62.5; H, 5.7; N, 6.7; Cl, 8.5.  $\text{C}_{21}\text{H}_{23}\text{ClN}_2\text{O}_4$  requires C, 62.6; H, 5.7; N, 6.9; Cl, 8.8%).

*7-Dimethylaminohepta-2,4,6-trienal*.—7-Dimethylaminohepta-2,4,6-trienylidenedimethylammonium perchlorate (0.5 g.) in water (20 c.c.) was treated with sodium hydroxide (0.5 g.) in water (5 c.c.) at  $20^{\circ}$ . After 4 hours' stirring the product was collected; crystallisation gave the aldehyde (0.2 g., 75%) as red-brown flakes, m. p.  $144^{\circ}$  (Found: C, 71.7; H, 8.7; N, 8.9.  $\text{C}_8\text{H}_{13}\text{NO}$  requires C, 71.5; H, 8.6; N, 9.3%).

*7-N-Methylaminiohepta-2,4,6-dienal*.—The corresponding cyanine perchlorate (60 g.) and sodium hydroxide (30 g.) in water (600 c.c.) were stirred for 1 hr. at  $20^{\circ}$ , then extracted with ether ( $4 \times 600$  c.c.; any unchanged salt remained undissolved at this stage and could be recycled). The extracts were dried, evaporated to *ca.* 100 c.c., and cooled to  $-8^{\circ}$ ; then the aldehyde (22.4 g., 70%) separated. It formed brown needles from ether or orange flakes from methanol or ethanol, both polymorphs having m. p.  $124^{\circ}$  (Found: C, 78.9; H, 6.9; N, 6.5.  $\text{C}_{14}\text{H}_{15}\text{NO}$  requires C, 78.9; H, 7.0; N, 6.7%).

*Potassium Salt of 7-Hydroxyhepta-2,4,6-trienal*.—7-*N*-Methylaminioheptatrienal (1 g.) in 1-methylpyrrolid-2-one (5 c.c.) was treated with potassium hydroxide (1 g.) in water (5 c.c.). The mixture was warmed to  $60-70^{\circ}$  for 5 min. and cooled, the salt forming red-brown needles. The sodium salt obtained in 50% methanol in the same way or from the dimethylamino-aldehyde was less pure and could be purified only by lyophilisation in cold methanol. These salts were characterised as 7-benzoyloxyhepta-2,4,6-trienal, prepared in pyridine (see above), as pale yellow needles, m. p.  $145^{\circ}$  (Found: C, 73.7; H, 5.4.  $\text{C}_{14}\text{H}_{12}\text{O}_3$  requires C, 73.7; H, 5.3%).

*9-Methoxynona-2,4,8-trien-6-ynal*.—Redistilled 1-methoxybut-1-en-3-yne (87.6 g.) in tetrahydrofuran (150 c.c.) was added during 30 min. at  $40^{\circ}$  to a solution of ethylmagnesium bromide, prepared from magnesium (19.2 g.) in tetrahydrofuran (550 c.c.). The mixture was stirred for 1 hr. at  $20^{\circ}$  and cooled to  $0^{\circ}$ ; a solution of 5-*N*-methylaminopenta-2,4-dienal (93.5 g.) in tetrahydrofuran (400 c.c.) was added during 30 min. After a further 3 hr. at  $0^{\circ}$ , tartaric acid (250 g.) in water (900 c.c.) was added, followed by ether (1 l.), with shaking. The aqueous layer was extracted with ether ( $3 \times 500$  c.c.), and the combined organic layers were washed with aqueous sodium hydrogen carbonate, dried ( $\text{MgSO}_4$ ), and evaporated below  $35^{\circ}$ . The dark residue was dissolved in benzene (1.5 l.), treated with light petroleum (b. p.  $40-60^{\circ}$ ), and filtered from polymeric material; the filtrate was passed through a short column of alumina (200 g.; deactivated), evaporated under reduced pressure, and dissolved in ether (100 c.c.), methylaminopentadienal (7.5 g.) separating. As much amino-aldehyde remained present, the filtrate was evaporated and the residue dissolved in the 1 : 1 benzene-light petroleum (2 l.)

and chromatographed on deactivated alumina (1200 g.). The colourless fore-run contained methoxybutenyne and was discarded; later yellow fractions contained the desired product (43.5 g., undistilled); finally a little of the orange *amino-aldehyde* was collected. An analytical specimen was prepared by distillation at 95–100°/5 × 10<sup>-3</sup> mm., with decomposition (Found: C, 73.3; H, 6.7. C<sub>10</sub>H<sub>10</sub>O<sub>2</sub> requires C, 74.0; H, 6.2%). It could be stored as a glass at -40°, but darkened rapidly at room temperature even *in vacuo*.

*9-Methoxynona-2,4,6,8-tetraenal*.—Hydrogenation of the foregoing compound in ethanol over a partially poisoned catalyst until the absorption amounted to 1 mol. gave a solution of the tetraenal (possibly a mono-*cis*-form) which decomposed rapidly to deeply coloured products on attempted isolation but could be stored for several days at -40°.

*9-Dimethylaminonona-2,4,6,8-tetraenylienedimethylammonium Perchlorate*.—A solution of dimethylamine (2 c.c.) and dimethylamine perchlorate (3.8 g.) in ethanol (10 c.c.) was cooled to 0° and added with shaking to a cooled solution of methoxynonatetraenal (from the undistilled acetylenic aldehyde; 4.1 g.). After 8 hr. at 0° the product was collected and recrystallised from ethanol, giving the *salt* (3.9 g., 51%) as blue-green needles, m. p. 145° (Found: C, 51.2; H, 7.0; N, 8.9; Cl, 12.2. C<sub>13</sub>H<sub>21</sub>ClN<sub>2</sub>O<sub>4</sub> requires C, 51.2; H, 6.9; N, 9.2; Cl, 11.7%).

*Methyl-9-N-methylanilinonona-2,4,6,8-tetraenylienedeanilinium Perchlorate*.—Similarly prepared from the acetylenic aldehyde (22 g.), *N*-methylaniline (30 c.c.), 60% perchloric acid (15 c.c.), and alcohol (75 c.c.), the *salt* (35 g., 61%) formed deep green needles, m. p. 108° (decomp.) (Found: C, 64.6; H, 6.2; N, 6.7; Cl, 8.0. C<sub>23</sub>H<sub>25</sub>ClN<sub>2</sub>O<sub>4</sub> requires C, 64.4; H, 5.8; N, 6.5; Cl, 8.2%).

*9-Dimethylaminonona-2,4,6,8-tetraenal*.—To a solution of 9-dimethylaminonona-2,4,6,8-tetraenylienedimethylammonium perchlorate (3 g.) in 1-methylpyrrolid-2-one (15 c.c.), sodium hydroxide (2 g.) in water (20 c.c.) was added. After 4 hr. at 20° the product was collected; crystallisation from ethanol gave the *aldehyde* (2.1 g., 75%) as deep brown plates, m. p. 192° (decomp.) (Found: C, 74.6; H, 8.2. C<sub>11</sub>H<sub>13</sub>NO requires C, 74.5; H, 8.5%). When 50% alcohol was used in a similar experiment much of the cyanine was recovered; after recycling the yield was 50%.

*9-N-Methylanilinonona-2,4,6,8-tetraenal*.—(a) This was prepared similarly from the corresponding cyanine (25 g.), 1-methylpyrrolid-2-one (125 c.c.), sodium hydroxide (8 g.), and water (80 c.c.). A sharp colour change (blue → red) indicated completion after 30 min. After crystallisation from ethanol the *aldehyde* (10 g., 77%) formed violet-brown flakes, m. p. 143° (decomp.) (Found: C, 80.4; H, 7.1; N, 5.9. C<sub>16</sub>H<sub>17</sub>NO requires C, 80.3; H, 7.2; N, 5.9%).

(b) A solution of ethylmagnesium bromide [from magnesium (1.6 g.)] in tetrahydrofuran (50 c.c.) was treated with 4-methoxybut-3-en-1-yne (7.3 g.). 5-*N*-Methylanilinopenta-2,4-dial (12.4 g.) was added during 20 min. with ice-cooling. After 2 hours' stirring at 0°, ethanol (2.5 c.c.), and lithium aluminium hydride (2 g.) were added, and stirring was continued for 3 hr. at 20°. Ethyl acetate (3 c.c.), water (15 c.c.), 4*N*-sulphuric acid (75 c.c.), and ether (100 c.c.) were added successively, and after some bluish insoluble material had been separated the aqueous layer was extracted with ether (3 × 400 c.c.). The combined organic layers were washed with sodium hydrogen carbonate solution, dried (MgSO<sub>4</sub>) and evaporated, the residue was dissolved in benzene (320 c.c.) and treated with light petroleum (80 c.c.), and the solution was filtered and passed down a column of alumina (200 g., deactivated). Evaporation and addition of ether gave the *aldehyde* (0.29 g., 2%), m. p. 143°, undepressed on admixture with a specimen prepared by method (a).

*Potassium Salt of 9-Hydroxynona-2,4,6,8-tetraenal*.—Potassium hydroxide (1 g.) in water (5 c.c.) was added to a solution of 9-*N*-methylanilinononatetraenal (1 g.) in 1-methylpyrrolid-2-one (5 c.c.). A solid separated but redissolved on heating to 75° for 5–10 min.; on cooling, the violet-brown salt separated and was washed with ice-cold water and ethanol. It was characterised by its absorption spectrum—which indicated a purity of *ca.* 60%—and by conversion into 9-*benzoyloxy*nona-2,4,6,8-tetraenal, which formed golden-yellow flakes, m. p. 160°, from ethanol (Found: C, 75.5; H, 5.7. C<sub>16</sub>H<sub>14</sub>O<sub>3</sub> requires C, 75.6; H, 5.5%).

*11-Methoxyundeca-2,4,6,10-tetraen-8-ynal*.—7-*N*-Methylanilinohepta-2,4,6-trienal (16 g.) in tetrahydrofuran (200 c.c.) was added to a Grignard reagent prepared from magnesium (3.2 g.) and methoxybutenyne (14.6 g.) in tetrahydrofuran, as described above. After decomposition with tartaric acid the neutral fraction was passed through 150 g. of deactivated alumina in 1:1 benzene–light petroleum (1 l.). Evaporation under reduced pressure left a residue which

was triturated with ether (250 c.c.), some of the starting material remaining undissolved. Chromatography on deactivated alumina (800 g.) in the 1:1 solvent mixture gave, after a colourless fore-run, a yellow band, then an orange band containing more of the starting material (4.0 g. recovered in all). Evaporation of the solvent from the yellow band and crystallisation from light petroleum gave the desired *aldehyde* (3.4 g., 24%) as pale-yellow plates, m. p. 80—81° (Found: C, 76.2; H, 6.5.  $C_{12}H_{12}O_2$  requires C, 76.5; H, 6.4%).

11 - *Dimethylaminoundeca-2,4,6,8,10-pentaenylidenedimethylammonium Perchlorate*.—A solution of the foregoing aldehyde (1.06 g.) in ethanol (20 c.c.) was hydrogenated over a partially poisoned palladium catalyst, as described above. A cooled solution of dimethylamine perchlorate (1 g.) and dimethylamine (1 c.c.) in ethanol (5 c.c.) was added, and the mixture was kept at 0—5° with occasional shaking for 12 hr. Crystallisation of the separated *product* from alcohol, with care to minimise heating, gave green needles, m. p. 164° (0.88 g., 50%) (Found: C, 54.5; H, 6.8; N, 8.4; Cl, 10.9.  $C_{15}H_{23}ClN_2O_4$  requires C, 54.5; H, 7.0; N, 8.5; Cl, 10.7%).

11-*Dimethylaminoundeca-2,4,6,8,10-pentaenal*.—The preceding salt (330 mg.) in 1-methylpyrrolid-2-one (5 c.c.) was treated with sodium hydroxide (200 mg.) in water (5 c.c.) with shaking. After 2 hr. at 20° water was added in excess and the product was collected and recrystallised from a large volume of ethanol or methylene dichloride by dissolution at 20° and cooling. The *aldehyde* (100 mg., 50%) formed deep-brown flakes, m. p. 218—220° (decomp.) (Found: C, 77.2; H, 8.6; N, 7.1.  $C_{13}H_{17}NO$  requires C, 76.8; H, 8.4; N, 6.9%).

13-*Methoxytrideca-2,4,6,8,12-pentaen-10-ynal*.—9-*N*-Methylanilino-2,4,6,8-tetraenal (10 g.) in tetrahydrofuran (200 c.c.) was condensed with the Grignard reagent from magnesium (1.6 g.) and methoxybutenyne (7.3 g.), the resultant complex was decomposed, and after filtration through alumina (150 g.) in 1:1 benzene-light petroleum (1 l.) and evaporation a brown residue was obtained. This was treated with boiling ether (400 c.c.), and separated from unchanged methylanilinononatetraenal (1.8 g., almost pure). Chromatography in benzene-light petroleum (1 l.) on deactivated alumina (900 g.) gave an orange-yellow and a red band, which for complete separation required a second chromatogram. Evaporation of the former band below 30° and recrystallisation from ether at -8° gave the *aldehyde* (2.4 g., 25%) as yellow plates, m. p. 147° with some previous softening (Found: C, 78.2; H, 6.9.  $C_{14}H_{14}O_2$  requires C, 78.5; H, 6.5%).

13 - *Dimethylaminotrideca-2,4,6,8,10,12-hexaenylidenedimethylammonium Perchlorate*.—A solution of the above aldehyde (1.0 g.) in ethanol (70 c.c.) and ethyl acetate (20 c.c.) was hydrogenated until 1 mol. had been absorbed, as described above. The hexaene-aldehyde separated partly, and it was necessary to warm slightly before filtering off the catalyst. The solution was cooled to 0° and treated with a solution of dimethylamine perchlorate (1 g.) and dimethylamine (0.5 g.) in ethanol, and the mixture was kept at -5° to 0° for 2 hr., then at 15—20° for 18 hr., with exclusion of light. The *salt* (1.05 g., 60%) separated from methanol as greenish-grey needles, m. p. 183° (decomp.); neither m. p. nor intensity of absorption at the main maximum altered on recrystallisation, best carried out by brief gentle warming in methanol followed by strong cooling (Found: C, 57.9; H, 7.0; N, 7.4; Cl, 9.7.  $C_{17}H_{25}ClN_2O_4$  requires C, 57.2; H, 7.0; N, 7.8; Cl, 9.9%).

13-*Dimethylaminotrideca-2,4,6,8,10,12-hexaenal* was prepared in 63% yield from the foregoing salt exactly as described for the lower homologue. It formed almost black plates, m. p. 247—248°, from acetonitrile (Found: N, 5.7.  $C_{15}H_{19}NO$  requires N, 6.1%).

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