Pyra- zolone deriva- tive	Thio R =	Prod- uct	Solvent	М.р., <sup>а</sup> °С.	Vield, %	Formula	Carb Caled.	on, % Found	Hydro Caled.	gen, % Found	Nitrog Calcd.	en, % Found	Sulfi Caled.	ır, % Found
IIIa	C6H4CH3-0	VIb	Alcohol	137	60	C24H22N2OS	74.61	74.58	5.69	5.60	7.25	7.30	8.29	8.31
IIIa	C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -p	VIc	Alcohol	129	78	C24H22N2OS		74 63		5.59		7.29		8.09
Шь	CoHo	VId	Alcohol	103	60	C24H22N2O2S	71.64	71.59	5.47	5.44	6.96	6.90	7.96	7.91
IIIb	CoH4CH3-0	VIe	Alcohol	96	55	C25H24N2O2S	72.11	72.06	5.76	5.59	6.73	6.79	7.69	7.61
шь	C6H4CH3-p	VIf	Alcohol	131	68	C25H24N2O2S		72.18		5.40		6.66		7.71
IIIc	C6H5	VIg	Alcohol	138	70	C24H22N2OS	74.61	74.50	5.69	5.70	7.25	7.22	8.29	8.08
IIIc	CoH4CH3-0	VIh	Benzene-petr. ether											
			(50→70°)	136	60	C26H24N2OS	75.00	75.10	6.00	5.89	7.00	6.91	8.00	8.09
IIIc	CoH4CH1-p	VIi	Alcohol	145	78	C26H24N2OS		75.09		6.03		6.88		7.98
IIId	C6H6	VIj	CHCl: in petr. ether											
			(50-70°)	156	73	C23H19N2OSC1b	67.89	67.90	4.67	4.73	6.88	6.69	7.87	7.80
IIId	C:H4CH:-0	VIk	Alcohol	140	66	C24H21N2OSC16	68.48	68.51	4.99	4.88	6.65	6.71	7.60	7,61
IIIđ	C6H4CH2-p	VII	Alcohol	158	70	C14H21N4OSCld		68.40		4.90		6.48		7.38
IIIf	CeHs	VIm	Benzene-petr. ether	125	65	C28H19N8O8S	66.18	66.00	4.55	4.40	10.07	10.29	7.67	7.49
IIIf	C6H4CH3-0	VIn	Benzene-petr. (50-											
			70°)	118	65	C24H21N2O2S	66.82	66.90	4.87	4.77	9.74	9.66	7.42	7,30
IIIf	C6H4CH3-p	VIo	Benzene-petr. (50-											
			70°)	97	73	C24H21N3O3S		66.76		4.92		9.70		7.28
ª All 1	the melting	points	are uncorrected.	<sup>b</sup> Cl, ca	lcd. 8	.73, found 8.80	. ° C1	caled	8.44,	found	8.38.	<sup>d</sup> C1,	found,	8.51.

#### TABLE III

ACTION OF AROMATIC THIOLS ON 1-PHENYL-3-METHYL-4-ARYLIDENE-5-PYRAZOLONES

All the melting points are uncorrected. Cl, calcd. 8.73, found 8.80.

gradually faded and on addition of 8 ml. of petroleum ether (b.p.  $50-70^{\circ}$ ) to the reaction mixture, colorless crystals separated, which were collected by filtration and recrystal-lized from ethyl alcohol (cf. Table II).

Thermal Decomposition of Va.—The adduct Va (1 g.) was heated at 195–200° (bath-temperature) in a test-tube-shaped vessel for 20 minutes and then allowed to cool. The bottom of the reaction vessel contained a red oily residue which solidified after being washed with petroleum ether (p.b.  $50-70^{\circ}$ ). The solid (ca. 0.6 g.) so obtained was crystallized from ethyl alcohol and identified as IIIa (m.p. and mixed m.p. determinations).

Action of Aromatic Thiols on IIIa-d, f. General Proce**dure**.—To a solution of the appropriate 5-pyrazolone deriva-tive (1 g.) in 30 ml. of dry benzene was added 1 g. of the appropriate thiol and the reaction mixture was left at room temperature overnight. The deep red color gradually faded and colorless crystals deposited, which were collected by fi-tration and recrystallized from ethyl alcohol (cf. Table III). The thiol adducts listed in Table III are colorless, soluble

in benzene and insoluble in petroleum ether (b.p. 50-70°). They are insoluble in cold aqueous sodium hydroxide solution (10%). The thiol adducts, on treating with concd. H<sub>2</sub>SO<sub>4</sub>, give a deep orange color which turns to blood-red slowly

Action of Potassium Hydroxide on VIc .- The thiol adduct (0.5 g.) was refluxed with 50 ml. of alcoholic potassium hydroxide solution (4%) for 4 hours. The reaction mixture was poured into ice-cold water, acidified with dilute hydro-chloric acid and extracted with ether. The ether extract gave, on shaking with lead acetate solution, yellow crystals of the lead salt of p-thiorresol (m.p. and mixed m.p. deter-minations). The ether solution after thorough washing with water and then evaporation, gave a red solid substance (ca. 0.2 g.) which was identified as IIIa.

Thermal Decomposition of VIc.—The pyrolysis was car-ried out as described in case of Va at 110–115° (bath temperature); IIIa was obtained in an almost quantitative yield.

GIZA, EGYPT, U.A.R.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

## The Synthesis of Carbazoles from 3-Vinylindoles with Tetracyanoethylene and Dimethyl Acetylenedicarboxylate

## BY WAYLAND E. NOLAND, WILLIAM C. KURYLA<sup>1</sup> AND RONALD F. LANGE<sup>1</sup>

RECEIVED APRIL 10, 1959

The tricyanovinylation of indole has been extended to substituted indoles, including 1-methylindole, 2-methylindole and The tricyanovinylation of indole has been extended to substituted indoles, including 1-methylindole, 2-methylindole and 1,2-dimethylindole, giving the corresponding 3-tricyanovinylindoles (Ib-Id) in good yields. Several derivatives of the latter are described. Tricyanovinylation of skatole occurred in the 1-position, giving 3-methyl-1-tricyanovinylindole (Ie) in 77% yield. 3-Tricyanovinylindole (Ia) and 1-methyl-3-tricyanovinylindole (Ib), acting as dienes, undergo Diels-Alder reactions with dimethyl acetylenedicarboxylate, resulting in the loss of hydrogen cyanide and forming the corresponding dimethyl 3,4-dicyanocarbazole-1,2-dicarboxylates (X). Saponification of the latter, followed by esterification of the resulting tetraacids with diazomethane, yielded the corresponding tetramethyl carbazole-1,2,3,4-tetracarboxylates (XI). The one derived from indole (XIa) was prepared independently, along with three minor products (XVIII-XX), by the reaction of indole with dimethyl acetylenedicarboxylate in a Diels-Alder reaction with a second molecule of dimethyl acetylenedicarboxylate in a Diels-Alder reaction with a second molecule of dimethyl acetylenedicarboxylate in a Diels-Alder reaction with a second molecule of dimethyl acetylenedicarboxylate in a Diels-Alder reaction with a second molecule of dimethyle acetylenedicarboxylate in a Diels-Alder reaction with a second molecule of dimethyle acetylenedicarboxylate in a Diels-Alder reaction with a second molecule of dimethyle acetylenedicarboxylate in a Diels-Alder reaction with a second molecule of dimethyle acetylenedicarboxylate in a Diels-Alder reaction with a second molecule of dimethyle acetylenedicarboxylate in a Diels-Alder reaction with a second molecule of dimethyle acetylenedicarboxylate in a Diels-Alder reaction with a second molecule of dimethyle acetylenedicarboxylate in a Diels-Alder reaction with a second molecule of dimethyle acetylenedicarboxylate in a Diels-Alder reaction with a second molecule of dimethyle acetylenedicarboxylenedicarboxylenedicarbox mediate 3-vinylindole (XII) which acts as a diene in a Diels-Alder reaction with a second molecule of dimethyl acetylenedi-These reactions appear to represent the first examples of the 3-vinylindole synthesis of carbazoles. Decarboxylate. carboxylation of the carbazole tetraacids by pyrolysis with soda-lime gave carbazole in both cases, N-demethylation having occurred in the N-methyl case. Since N-methylcarbazole does not demethylate under the same conditions, it is suggested that the N-demethylation occurs by intramolecular nucleophilic displacement (in a 6-membered ring transition state) of the methyl group by the neighboring 1-carboxylate anion.

The reaction of tetracyanoethylene with indole, yielding 3-tricyanovinylindole (Ia), has been de-

(1) Taken in part from the M.S. thesis of William C. Kuryla, University of Minnesota, August, 1958, and from the Ph.D. thesis of Ronald F. Lange, University of Minnesota, June, 1958. We gratefully acknowledge the financial support provided R.F.L. through academic year fellowships by the Ethyl Corporation (1956-1957) and

scribed previously.<sup>2</sup> By use of boiling benzene as solvent, containing a small amount of pyridine, the

the Monsanto Chemical Co. (1957-1958), and through summer fellowships provided by the Procter and Gamble Co. (1956) and the Hercules Powder Co. (1957).

(2) G. N. Sausen, V. A. Engelhardt and W. J. Middleton, THIS JOURNAL, 80, 2815 (1958).

TABLE	L
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ULTRAVIOLET AND INFRARED ABSORPTION MAXIMA OF 3-TRICYANOVINVLINDOLES Ia, 3-tricyanovinylindole; Ib, 1-methyl-3-tricyanovinylindole; Ic, 2-methyl-3-tricyanovinylindole; Id, 1,2-dimethyl-3tricyanovinylindole; Ie, 3-methyl-1-tricyanovinylindole: V. 2-methyl-5.6-dibromo-3-tricyanovinylindole

	uicya		ic, ic, o-m	Thtra	violet	ою, у, 2-щ	ctily1-0,0-01				frared-	
		, == w	ave lengths o are gi	of maxima and ven in $m\mu$ with	inflections (*) intensities in	in 95% etha (log ε)	nol		Fr NH	equenc C≣N	ies in c C=C	m. ⁻ı Medium
Iaª		251 (3.86)		270* (3.80)	277* (3.83)	285 (3.90)		468 (4.33)	3260	2220	1512	Nujol
Iь			262 (4.11)			280* (3.97)	357 (4.08)	465 (3.91)		2210	ь	CHCI
										2200	1507	Nujol
Ic		253* (3.70)	264 (3.72)	271 (3.99)		281* (3.70)		471 (4.22)	3410	2210	ь	CHCl.
									3290	2210	1511	KBr
									3320	2220	1527	Nujol
Id			263(4.12)		277* (4.02)	284* (3.98)	355 (3.86)	476 (3.89)		2220	ь	CHCI
										2220	1515	Nujol
Ie¢		255 <sup>b</sup> (4.03)		272** (3.83)		291°(3.76)		411° (4.08)	••	2220	1550	CHCl:
										2220	1541	Nujol
v	226 (4.57)		282 (4.03)		297 (4.04)	304 (4.05)		458 (4.22)	3320	2220	1532	Nujol

<sup>a</sup> Reported<sup>2</sup>  $\lambda_{max}$  in acetone: 453 (4.32);  $\nu_{NH}$  3280,  $\nu_{0 \equiv N}$  2220 cm.<sup>-1</sup>. <sup>b</sup> Blocked by CHCl<sub>2</sub> band. <sup>c</sup> In CHCl<sub>3</sub> solution. In 95% ethanol the initially yellow solution became colorless rapidly upon being warmed to dissolve it, or more slowly upon standing overnight at room temperature. In both cases the resulting spectra were essentially identical and indicated that a significant chemical change had occurred. With the intensities calculated on the basis of the molecular weight of 3-methyl-1-tricyanovinylindole: 228\* (4.11), 269 (4.04), 274 (4.05), 293 (3.75), 331 (3.97).

yield has been increased to 92% from the reported 76%. We have extended the synthesis of 3tricyanovinylindoles, utilizing as starting materials substituted indoles having an open 3-position, to include Ib (80% yield) from 1-methylindole, Ic (78%) from 2-methylindole, and Id (67%) from 1,2-dimethylindole. Skatole, which lacks an open 3-position, did not react with tetracyanoethylene in benzene solution at room temperature, but in boiling benzene containing pyridine, reaction occurred at the 1-position, giving 3-methyl-1-tricyanovinyl-indole (Ie) in 77% yield. Assignment of structure is based on the absence of NH absorption in the infrared spectrum. In the visible and ultraviolet spectrum the lower wave length of the 1-vinylindole band (411 m $\mu$ ), relative to the 3-vinylindole band  $(471 \text{ m}\mu)$  of the 2-methylindole derivative (Ic) is also consistent with the shorter conjugated system between nitrogen and the cyano groups in the former case (Ie). The ultraviolet spectrum of Ie was determined in chloroform solution because in ethanol solution it underwent chemical change to colorless products (Table I, note c). The ultraviolet and most significant infrared absorption maxima of all the tricyanovinylindoles are summarized in Table I.

All of the indoles which yielded 3-tricyanovinylindoles, as well as skatole, immediately form deep blue-black colored  $\pi$ -complex<sup>8</sup> solutions with tetracyanoethylene in benzene at room temperature. Subsequent 3-tricyanovinylindole formation is assumed to be preceded by the formation as an intermediate of the adduct tetracyanoethane (like II) or its anion (like III). The latter can then eliminate cyanide ion, yielding the 3-tricyanovinvlindole (I). The apparent catalytic effect of pyridine in 3-tricyanovinylindole formation may be attributed to its possible function in facilitating the removal of the proton from the 3-position of the indolenine nucleus in the primary addition product, or probably more importantly, in removing the proton from the adduct tetracyanoethane (like II), which is assumed to be a strong acid, like tetracyanoethane ( $pK_a 3.6^4$ ).

(3) R. E. Merrifield and W. D. Phillips, THIS JOURNAL, 80, 2778 (1958).

(4) W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *ibid.*, **80**, 2783 (1958).

In one case the assumed intermediate, the adduct tetracyanoethane (II), was sufficiently stable and insoluble so that it could be isolated and briefly characterized. The reaction of tetracyanoethylene



with the most reactive indole, 2-methylindole, at room temperature in the absence of pyridine, gave in quantitative yield an unstable pinkish-white crystalline solid. On the basis of its color (indicating an unconjugated side-chain), infrared spectrum (see Experimental), mode of formation and thermal decomposition to 2-methyl-3-tricyano-

Solvent and concentration in $M \times 10^4$			Wave lengths of mµ	maxima and inflect and intensities in	tions (*) are given (log ε)	in	
				CHCl₃			
5.857	a	ь	ь			ь	483 (2.89)
1.082	a	257 (4.10)	277 (3.92)	Not p	present	335 (4.00)	487(2.88)
			98	5% EtOH			
5.872	ь	ò	ь	ь	5	ь	487 (2.93)
1.161	ь	259(4.11)	278 (4.12)	289* (4.04)	306 (3.97)	336* (3.79)	487 (2.94)
0.465	220(4.51)	259*(4.09)	278(4.15)	288* (4.10)	303* (4.04)	$342^{*\circ}(3.51)$	d
0.232	220(4.52)	d	d	d	d	d	d

 TABLE II

 Ultraviolet and Visible Absorption Spectra of 2-Methyl-3-(1-hydroxy-2,2-dicyanovinyl)-indole (IV)

<sup>a</sup> CHCl<sub>3</sub> is opaque in this region. <sup>b</sup> Concentration too great for measurement. <sup>c</sup> Log  $\epsilon$  at 336 m $\mu$  is 3.54. <sup>d</sup> Concentration too low for accurate measurement.

vinylindole, this solid is assumed to be the intermediate adduct tetracyanoethane (II), from which a molecule of hydrogen cyanide has not yet been lost.

Mild alkaline hydrolysis, as has been described previously for the conversion of 1-methyl-2-tricyanovinylpyrrole to 1-methyl-2-(1-hydroxy-2, 2dicyanovinyl)-pyrrole,<sup>2</sup> was used to convert 2methyl - 3 - tricyanovinylindole (Ic) to 2 - methyl -3 - (1 - hydroxy - 2, 2 - dicyanovinyl) - indole (IV). The product is an indicator acid, turning color from pale magenta in neutral aqueous solution to red upon the addition of alkali. Also, its solutions in 95% ethanol do not obey Beer's law in the 240– 400 m $\mu$  region of the ultraviolet spectrum. The results, which are shown in Table II, indicate that dilution increases the relative concentration of a species with  $\lambda_{max}$  at 278 m $\mu$  and decreases the relative concentration of a species with  $\lambda$  inflection at 336 m $\mu$ .

The action of bromine in acetic acid converted 2-methyl-3-tricyanovinylindole to a dibromo derivative, in which all of the cyano groups were retained. The presence of the visible absorption band at 458  $\dot{m}\mu$  (see Table I), attributed to the conjugated 3-vinylindole system, indicates that bromine has not added to the side-chain or the pyrrole unsaturation; the presence of NH infrared absorption at  $3320 \text{ cm}^{-1}$  indicates that bromine substitution has not occurred at the 1-position. Consequently, bromine substitution must have occurred in the benzenoid portion of the molecule. The closest analogy appears to be the bromination of 3-indolecarboxylic acid in acetic acid solution, the product of which has been proved to be 5,6-dibromo-3-indolecarboxylic acid.<sup>5</sup> Both the tricyanovinyl and carboxyl groups are electronwithdrawing and the 2-methyl group would be expected to promote, rather than inhibit, electrophilic substitution in the 6-position. Consequently, the bromination product of 2-methyl-3tricyanovinylindole is assigned by analogy the 2-methyl-5,6-dibromo-3-tricyanovinylstructure indole (V).

3-Vinylindoles contain a diene system which we have found will undergo Diels-Alder reactions (VI) with active dienophiles, yielding carbazole derivatives, like VII or VIII.

(5) R. Majima and M. Kotake, Ber., 63, 2237 (1930).

Heating of 3-tricyanovinylindole (Ia) or 1-methyl-3-tricyanovinylindole (Ib) at 230–250° with dimethyl acetylenedicarboxylate resulted in the loss of hydrogen cyanide and gave in 30 and 44% yields the corresponding dimethyl 3,4-dicyanocarbazoledicarboxylates (Xa and Xb). The reaction is assumed to proceed through an intermediate dihydrocarbazole (IX), which subsequently aromatizes through the loss of hydrogen cyanide.



R = H or alkyl; X = electron-withdrawing group

Saponification of Xa and Xb, and then acidification and esterification with diazomethane, gave in 61 and 40% yields the corresponding tetramethyl carbazole-1,2,3,4-tetracarboxylates (XIa and XIb). The carbazole XIa was identical with a sample obtained as the major product from reaction after long standing of indole and dimethyl acetylenedicarboxylate in 1:2 molar ratio. The latter reaction is assumed to proceed through the known 3-vinylindole, dimethyl (3-indole)-fumarate<sup>6</sup> (XII), which then acts as a diene in a subsequent Diels-Alder cyclization with a second molecule of dimethyl acetylenedicarboxylate.7 The resulting dihydrocarbazole XIII must then undergo spontaneous oxidative aromatization, either by air or by an unsaturated component of the reaction mixture, to the carbazole XIa. These reactions appear to represent the first examples of the 3-vinylindole synthesis of carbazoles. Further examples will be reported later. The ultraviolet and infrared spectra of the carbazoles prepared in this work are summarized in Table III.

(6) (a) W. E. Noland, R. F. Lange, F. B. Stocker and G. L. Sauer. Paper 10 presented before the Organic Division at the 132nd National Meeting of the Am. Chem. Soc., New York, N. Y., Sept. 9, 1957, Abstracts, p. 6-P; (b) Ronald F. Lange, Ph.D. Thesis, University of Minnesota, June, 1958, pp. 128, 145.

(7) It has been shown recently (unpublished work with Robert W. Campbell) that the reaction of dimethyl (3-indole)-fumarate (XII) with dimethyl acetylenedicarboxylate yields XIa. Hence XII can serve as an intermediate in the formation of XIa from indole and dimethyl acetylenedicarboxylate. Compound XIa, m.p. 180-182°, was isolated in 26% yield after a methanol solution of equimolar portions of the reactants had been set aside at room temperature for 102 days.

### TABLE III

#### Ultraviolet and Infrared Absorption Maxima of Carbazoles and Derivatives

		Wave lengt	Ultravi s of maxima and in given in my with it	olet	ethanol	
Xa	227(4.46)				295(4.60)	360 (3,83)
Xb	232(4.50)				300(4.67)	375(3.54)
XIa	220(4.47)				284(4.63)	362 (3.70)
XIb	225(4.43)				282(4.65)	355 (3.53)
XIVª	229(4.54)	244(4.37)	284*(4.01)	288(4.08)	293(4.23)	336 (3.49)
$XV^b$	230(4.57)	244* (4.39)	284* (3,97)	288 (4.05)	293(4.25)	344(3.61)
XVIII		251 (3.81)	(* - )			350(3.87)
XIX		243(4.04)		290*(3.88)	299(4.01)	347(4.00)
XX	220 (4.94)	242* (4.47)	274(4.25)	280 (4.25)	289 (4.22)	,
	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		Inf	rared ———		
	2.11	Frequencies of max 1800–1520	cm. <sup>-1</sup> region (C=O	(*) are given in cm. , C=C, C=N, or NI	deformation)	
37	NH DODOS	intens	ities: vs, very stron;	g; s, strong; m, med	um; w, weak	Medium
ла	3330"	1732VS,	1715vs*	1500 1501		CHCI3
	3330*	1730*,	1716vs,° 1616mw	7, 1588m, 1581m		Nujol
Ab		1729vs	1616m,	1568mw		CHCI3
377		1729vs,	1718vs, 1612m,	1560m		Nujol
XIa	3440		1726vs	1623mw, 1595m	, 1577mw	CHCl <sub>3</sub>
	3360	1740s,	1721vs,° 1709s,°	1623mw, 1600m		Nujol
XIb	• •	1733vs	1625mw	7, 1580m		CHCl <sub>3</sub>
		1738vs,	1721,* 1622mw	7, 1575m		Nujol
XIV	3480					$CS_2$
	3490	1611m,	1587w			CHC13
	3440	1631mw,	1609mw*			Nujol
XV	• •	1636mw,	1608m			CHCl <sub>3</sub>
	••	1634mw,	1606m			Nujol
XVIII	••		1730 vs	1645w, 1611,*	1602 mw	CHCl <sub>3</sub>
	••	1749vs,	1725vs,° 1715,*	1649mw, 1608,*	1596m, 1532s	Nujol
XIX	3460, 3410		1736s, 1676ms	, 1643m, 1610s		CHCl <sub>3</sub>
	3380	1738,*	1723s," 1688s,	1638s, 1608m	s	Nujol
XX	3510	1723s, <sup>d</sup>	1694s,* 1629m,	1603s, 1575m		CHCl <sub>3</sub>
	3400, 3370*	1709s, <sup>4</sup>	1689s, 1634m,	1602ms, 1572m		KBr
	3390, 3360	1728s, <sup>d</sup>	1661s.º 1635m.	1601ms, 1569m	. 1543w	Nuiol

<sup>a</sup> Also bands at 234(4.60), 257(4.28), 31\*(3.43), 323(3.55). The ultraviolet spectrum of carbazole is in essential agreement with that in 95% ethanol previously published (R. A. Friedel and M. Orchin, 'Ultraviolet Spectra of Aromatic Compounds,'' John Wiley and Sons, Inc., New York, N. Y., 1951, no. 338). <sup>b</sup> Also bands at 235(4.63), 262(4.33), 320\*(3.36), 330(3.55). The ultraviolet spectrum of 9-methylcarbazole is in essential agreement with that in absolute ethanol (W. A. Schroeder, P. E. Wilcox, K. N. Trueblood and A. O. Dekker, *Anal. Chem.*, 23, 1744 (1951)) and with those of 9-ethylcarbazole zole and 9-*n*-butylcarbazole in cyclohexane (ref. *a*, no. 339 and 340). <sup>c</sup> Also C=N band at 2220 cm.<sup>-1</sup>. <sup>d</sup> Stronger band.

A Diels-Alder cyclization with 2 molecules of dimethyl acetylenedicarboxylate, analogous to that with indole, has been reported for 1-methylpyrrole, except that in the latter case the adduct (XVI) did not undergo spontaneous oxidative aromatization.<sup>8</sup> Aromatization, accomplished by the action of bromine, was reported to be accompanied by elimination of a methoxycarbonyl group, assumed to be the one *ortho* to the nitrogen. The resulting triester XVII was saponified to the insoluble potassium salt, which was acidified, and the acid decarboxylated by dry distillation with lime, giving 1-methylindole in 57% yield from the triester.<sup>8</sup>

Analogous saponification of the carbazoles Xa and Xb<sup>9</sup> and decarboxylation of the resulting salts by dry distillation with soda-lime gave carbazole (XIV) in yields of 51 and 42%, respectively. In the latter case no N-methylcarbazole (XV) but only carbazole was obtained. This N-demethylation is of interest, and particularly so because it did not occur in the N-methylindole case (XVII), in which a carboxylate group ortho to the nitrogen is assumed to be absent. Since an N-methylcarbazole derivative (XIb) was the sole product from saponification of Xb and subsequent esterification, N-demethylation could not have occurred during the saponification step but must have occurred during the decarboxylation step before all of the carboxylate groups were lost. When Nmethylcarbazole was subjected to the same decarboxylation conditions, dry distillation with soda-lime, no N-demethylation occurred and only unchanged N-methylcarbazole was recovered in 80% yield. When taken by itself, this result does not constitute a rigorous demonstration of the

<sup>(8)</sup> O. Diels, K. Alder and H. Winckler, Ann., 490, 267 (1931).

<sup>(9)</sup> As in the case of saponification of the N-methylindole derivative XVII, the potassium salt from the N-methylcarbazole derivative Xb precipitated from the saponification medium used, whereas the potassium salt from the carbazole derivative Xa did not.



necessity for a carboxylate group *ortho* to the nitrogen for N-demethylation to occur, since N-methylcarbazole might be less strongly adsorbed on the soda-lime (and thus be incapable of reacting with it) than would an N-methylcarbazole derivative (from Xb) having carboxylate groups which could serve as anionic "handles" or "solubilizing" groups, thus permitting intimate interaction with the soda-lime surface. When taken together with the lack of N-demethylation in the N-methylindole case in which "solubilizing" carboxylate groups are present elsewhere in the molecule, however, these results are suggestive of the necessity for participation of a neighboring *ortho* carboxylate group in the N-demethylation during dry distillation with soda-lime. Intramolecular nucleophilic displacement, involving a 6-membered ring transition state and leading to a resonance-stabilized carbazole anion, appears to represent a probable explanation for the observed results



The methyl group transferred from nitrogen to oxygen of the neighboring carboxylate group would then be removed as methoxide ion by hydroxide cleavage. Subsequent decarboxylation would yield carbazole.

From the reactions of one mole of indole and two moles of dimethyl acetylenedicarboxylate, besides the major product, tetramethyl carbazole-1,2,3,4-tetracarboxylate (XIa), as many as three minor products were isolated. Two of these, isolated in 7-8% yields, are 1:3 adducts of indole and dimethyl acetylenedicarboxylate. One of them (XVIII), m.p. 172-173°, has no NH stretching absorption in the infrared region, but does have a strong band at 1532 cm.<sup>-1</sup>, which may possibly be attributed to the C=N system. The ultraviolet spectrum shows the complete absence of the indole chromophore, but strong absorption bands at 251 and 350 m $\mu$  (see Table III) indicate considerable conjugation. A negative Ehrlich test indicates that both the 2- and 3-positions of the original indole nucleus are substituted. It seems possible either that this 1:3 adduct may be formed by attack of a third molecule of dimethyl acetylenedicarboxylate on the basic nitrogen of a common intermediate---the same Diels-Alder adduct (XIII) which yields tetramethyl carbazole-1,2,3,4-tetracarboxylate after dehydrogenation to the fully aromatic carbazole, or that the 1:3 adduct may contain a conjugated indolenine system.

The other 1.3 adduct (XIX), m.p. 229–230°, may also be derived from a common intermediate the Diels-Alder adduct XIII—by attack of a third molecule of dimethyl acetylenedicarboxylate at a nucleophilic center other than nitrogen. The presence of an NH stretching band in the infrared region indicates that the indole nitrogen remains unsubstituted. The ultraviolet spectrum contains strong bands at 243, 299 and 347 m $\mu$ (see Table III), indicating considerable conjugation. A negative Ehrlich test indicates that both the 2- and 3-positions of the indole nucleus are substituted.

The third minor product (XX), m.p.  $242-243^{\circ}$ , isolated in only 2% yield from the 1:2 mole ratio

employed in the present carbazole synthesis, is a 2:1 adduct of indole and dimethyl acetylenedicarboxylate. The ultraviolet spectrum shows the indole chromophore superimposed upon a long tail extending toward the visible (see Table III), with an additional inflection at 242 m $\mu$ . A positive Ehrlich test indicates that one or more of the indole nuclei have an open 2-position. The infrared spectra in KBr and Nujol suggest the presence of two different kinds of NH linkages.

During the course of this work we had occasion to prepare considerable quantities of 1-methylindole. The Fischer indole synthesis,10 starting from  $\alpha$ -methylphenylhydrazine and pyruvic acid, gives pure 1-methylindole, free from NH absorption in the infrared,<sup>11</sup> but the method is laborious and results in a low over-all yield. The methylation of sodioindole, either in organic solvents<sup>12-15</sup> or in liquid ammonia, 16,17 gives a product contaminated with the starting material, indole,14,18 and skatole, the C-methylation product of the ambident anion,<sup>19</sup> which can be isolated from the last fraction of the distilled product.<sup>12</sup> Consequently, 1-methylindole prepared by methylation invariably has NH absorption in the infrared.11 We have found that the NH absorption can be eliminated entirely by refluxing the crude 1methylindole over sodium for 48 hours and then distilling the unreacted 1-methylindole from the sodio derivatives and tarry decomposition products.

## Experimental

Melting points were determined on calibrated hot-stages. 1-Methylindole was prepared from indole by methylation with dimethyl sulfate<sup>17</sup> or methyl iodide<sup>16</sup> and sodamide in liquid ammonia. The crude distilled product, which had strong NH absorption in the infrared at 3420 cm.<sup>-1</sup>, was refluxed with molten sodium for 48 hours. Vacuum distillation of the resulting mixture yielded 1-methylindole, free of NH absorption in the infrared, as an initially colorless liquid, b.p. 72° (0.85 mm.), n<sup>26.20</sup> 1.6018, having an odor reminiscent of naphthalene; reported n<sup>20</sup> D 1.6062.<sup>11</sup>

2-Methylindole was prepared from acetyl-o-toluidine by the Madelung synthesis.<sup>20</sup>

1,2-Dimethylindole was prepared from 2-methylindole by methylation with dimethyl sulfate or methyl iodide<sup>16</sup> and sodamide in liquid ammonia.

Tetracyanoethylene<sup>21</sup> was prepared from dibromomalononitrile by debromination with precipitated copper powder in boiling benzene.<sup>22</sup> Completely anhydrous reactants are essential; contamination with moisture results in a sharply reduced yield.

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A solution of indole (10.00 g., 0.0854 mole) in benzene (50 cc.) was added rapidly to a boiling solution of tetracyanoethylene (6.00 g., 0.0468 mole) in benzene (50 cc.), forming an intense blue-black solution. A small amount of pyridine (0.5 cc.) then was added. The mixture turned deep red after a minute or two and an orange-red solid precipitated during a period of 10 minutes. The warm solution then was reheated to boiling for 5 minutes and the precipitated 3-tricyanovinylindole (9.43 g., 0.0431 mole, 92%), m.p. 268– 270° (on a preheated block), was filtered off; reported<sup>2</sup> m.p. 275-276° (on a preheated block).

A solution of equimolar portions of the reactants (0.0250 mole) in benzene (220 cc.) without pyridine gave only a 32% yield of 3-tricyanovinylindole after being set aside at room temperature for 24 hours.

1-Methyl-3-tricyanovinylindole (Ib).—Solutions of 1methylindole (3.28 g., 0.0250 mole) in benzene (20 cc.) and tetracyanoethylene (3.20 g., 0.0250 mole) in benzene (200 cc.) were mixed, forming an intense blue-black solution, which was set aside for two days at room temperature. Evaporation of the benzene left a blackish solid. Crystallization from ethanol-chloroform, with charcoal, gave a reddish-brown solid (3.44 g., 0.0148 mole, 59%), m.p. 212– 215°. Four recrystallizations, one with charcoal, from ethanol-chloroform yielded 1-methyl-3-tricyanovinylindole as glistening, matted orange needles, m.p. 218–219°.

Anal. Caled. for  $C_{14}H_{\$}N_{4}$  (232.24): C, 72.40; H, 3.47; N, 24.13. Found: C, 72.18; H, 3.34; N, 23.86.

When the reaction was carried out in hot benzene solution containing a small amount of pyridine, as previously described for the preparation of 3-tricyanovinylindole, the yield of 1-methyl-3-tricyanovinylindole was increased to over 80%.

80%. 2-Methyl-3-(1,1,2,2-tetracyanoethyl)-indole (II) and 2-Methyl-3-tricyanovinylindole (Ic).—Solutions of 2-methylindole (3.52 g., 0.0268 mole) in benzene (20 cc.) and tetracyanoethylene (3.72 g., 0.0290 mole) in benzene (200 cc.) were mixed, forming an intense blue-black solution, which was set aside at room temperature for 72 hours. The pinkish-white platelets (7.02 g., 0.0271 mole, 100%) which precipitated are believed to be 2-methyl-3-(1,1,2,2-tetracyanoethyl)-indole;  $\nu_{\rm NH}$  3450 in CHCl<sub>3</sub>, 3380 in KBr, 3390 in Nujol;  $\nu_{\rm C=N}$  2230 in CHCl<sub>3</sub>, 2210 cm.<sup>-1</sup> in KBr. The infrared spectrum in KBr also showed a sharp band of medium strong intensity at 2900 cm.<sup>-1</sup>, not present in the infrared spectrum of 2-methyl-3-tricyanovinylindole. This band is attributed to the tertiary CH stretching frequency.

Attempts to take the melting point by heating the pinkishwhite platelets, or to recrystallize them from boiling acetone, ethanol or water, resulted only in decomposition to the red 2-methyl-3-tricyanovinylindole. The pinkish-white platelets became distinctly orangish at room temperature after 24 hours. Solutions in hydroxylic solvents such as ethanol or water turned red very rapidly at room temperature.

To obtain 2-methyl-3-tricyanovinylindole, the pinkishwhite platelets (5.0 g., 0.0193 mole) were dissolved in ethanol, water and acetone were added, and the solution was boiled for 3 hours. The solution was evaporated to dryness and the residue recrystallized four times, with charcoal, from ethanol-chloroform. The resulting red needles (3.5 g., 0.0151 mole, 78%), m.p. 227-228°, were then sublimed at 180° (~40  $\mu$ ), yielding 2-methyl-3-tricyanovinylindole as deep red crystals, m.p. 228-229° (with darkening at 220°). *Anal.* Calcd. for C<sub>14</sub>H<sub>8</sub>N<sub>4</sub> (232.24): C, 72.40; H, 3.47; N, 24.13. Found: C, 72.67; H, 3.39; N, 24.34.

The product does not react further with tetracyanoethylene, and was recovered unchanged after 5 hours in refluxing benzene solution.

2-Methyl-3-(1-hydroxy-2,2-dicyanovinyl)-indole (IV).—A suspension of 2-methyl-3-tricyanovinylindole (1.00 g., 0.00430 mole) in aqueous 10% sodium hydroxide solution (25 cc.) was warmed on a steam-bath until solution was complete. The cooled solution was acidified to pH I-2 dropwise with concentrated hydrochloric acid, causing formation of a black precipitate. The precipitate was filtered off, washed several times with distilled water, dissolved in acetone-water, treated with charcoal, and concentrated to remove the acetone. The magenta solid (0.222 g., 0.000995 mole, 23%) m.p. 110–112°, which precipitated upon cooling was recrystallized twice from ethanol-water, yielding 2-methyl-3-(1-hydroxy-2,2-dicyanovinyl)-indole as magneta microcrystals, after drying at 80°, soften at 145°, sublime above 185°, m.p. 197–199°;  $\nu_{\rm OH~or~NH}$  3220,  $\nu_{\rm C=N}$  2200,  $\nu_{\rm C=O}$ ? 1711,  $\nu_{\rm C=C}$  1559 cm.<sup>-1</sup> in Nujol.

Anal. Caled. for C<sub>18</sub>H<sub>9</sub>N<sub>8</sub>O (223.23): C, 69.94; H, 4.06; N, 18.83. Found: C, 69.69; H, 4.30; N, 18.53.

2-Methyl-3-tricyanovinyl-5,6-dibromoindole (V).—Bromine was added dropwise to a solution of 2-methyl-3-tricyanovinylindole ( $\sim 0.05$  g.) in glacial acetic acid and chloroform until a deep red color persisted. The solution was refluxed gently for 5 minutes and then set aside at room temperature for 24 hours. The precipitated orange crystals, m.p. 280–284°, were recrystallized twice from ethanol, yielding 2-methyl-3-tricyanovinyl-5,6-dibromoindole as orange prisms, sublime above 255°, m.p. 288–289° dec.

Anal. Calcd. for  $C_{14}H_6N_4Br_2$  (390.07): C, 43.11; H, 1.55; N, 14.36. Found: C, 43.12; H, 1.68; N, 14.16.

1,2-Dimethyl-3-tricyanovinylindole (Id).—Solutions of 1,2-dimethylindole (3.38 g., 0.0232 mole) in benzene (20 cc.) and tetracyanoethylene (3.20 g., 0.0250 mole) in benzene (150 cc.) were mixed, forming an intense blue-black solution, which was set aside at room temperature for 20 hours. The solution was then evaporated to a volume of 50 cc. and light petroleum (b.p.  $30-60^{\circ}$ ) was added, causing precipitation of a purple-black solid. Three recrystallizations from acetone-water and two from ethanol-chloroform, once with charcoal, gave glistening red crystals (3.84 g., 0.0156 mole, 67%), m.p.  $188-189^{\circ}$ .

Anal. Calcd. for  $C_{15}H_{10}N_4$  (246.26): C, 73.15; H, 4.09; N, 22.75. Found: C, 73.31; H, 4.18; N, 22.64.

The product does not react further with 1,2-dimethylindole, and was recovered unchanged after being warmed for a week on a steam-bath.

**3.Methyl-1-tricyanovinylindole** (Ie).—A hot solution of skatole (3.27 g., 0.0249 mole) in benzene (10 cc.) was added to a boiling solution of tetracyanoethylene (3.20 g., 0.0250 mole) in benzene (50 cc.), forming an intense blue-black color immediately upon mixing. After about a minute, pyridine (2.5 cc.) was added and the solution was boiled down to a volume of about 10 cc. Chloroform (200 cc.) was added, the solution was boiled with charcoal, concentrated and cooled, causing precipitation of an orange-red solid (4.48 g., 0.0193 mole, 77%), m.p. in a sealed capillary (softens at 125°) 135-140°. Two sublimations at 130° (0.3 mm.) yielded 3-methyl-1-tricyanovinylindole as blood-red, chunky crystals, m.p. in a sealed capillary 154-155.5°. The infrared spectra in CHCl<sub>3</sub> and Nujol indicated that no chemical change was produced by sublimation. The ultraviolet spectral results indicate that the compound undergoes chemical change in ethanol solution (see Table I, note c).

Anal. Caled. for  $C_{14}H_8N_4$  (232.24): C, 72.40; H, 3.47; N, 24.13. Found: C, 72.64; H, 3.45; N, 24.14.

## Dimethyl 3,4-Dicyanocarbazole-1,2-dicarboxylate (Xa)

(a) Trifluoroacetic Acid-catalyzed Reaction.—A mixture of 3-tricyanovinylindole (4.80 g., 0.0220 mole), dimethyl acetylenedicarboxylate (10 cc., 0.081 mole) and trifluoroacetic acid (0.6 cc.) was heated under reflux at 250° for 15 minutes. After the dark tarry mixture had cooled to room temperature, benzene was added. Filtration of the benzene mixture left a brownish-yellow solid (2.18 g., 0.00655 mole, mole, 30%), m.p. 294–296°. Vacuum sublimation at 220– 260°, followed by washing with methanol yielded dimethyl 3,4-dicyanocarbazole-1,2-dicarboxylate as a yellow fluorescent solid, m.p. 294–295°.

Anal. Calcd. for  $C_{18}H_{11}N_3O_4$  (333.29): C, 64.86; H, 3.33; N, 12.61. Found: C, 64.63; H, 3.35; N, 12.83.

(b) Uncatalyzed Reaction.—A mixture of 3-tricyanovinylindole (3.17 g., 0.0145 mole) and dimethyl acetylenedicarboxylate (5.68 g., 0.0400 mole) was heated under reflux at 220-240° for 30 minutes. After the dark tarry mixture had cooled to room temperature, benzene was added. Filtration of the benzene mixture left a brownish-yellow solid (0.80 g., 0.00240 mole, 17%), m.p. 293-295°. Hydrolysis and Decarboxylation of Dimethyl 3,4-Dicyano-

Hydrolysis and Decarboxylation of Dimethyl 3,4-Dicyanocarbazole-1,2-dicarboxylate (Xa).—A mixture of dimethyl 3,4-dicyanocarbazole-1,2-dicarboxylate (0.470 g., 0.00141 mole) and a solution of methanolic 25% potassium hydroxide (5 cc.) and water (3 cc.) was refluxed for 22 hours on a steambath. The resulting homogeneous solution then was acidified to  $\rho$ H 1–2 by dropwise addition of concentrated hydrochloric acid. The methanol was boiled off and powdered soda-lime was added to the pasty residue. The alkaline pasty residue was thoroughly mixed and transferred to a 15-mm. diameter straight glass tube through which dry nitrogen was passed before and during heating of the tube with a Meker burner. The dry distillate was washed out of the receiver with methanol and the methanol was concentrated, yielding colorless platelets (0.12 g., 0.00072 mole, 51%), m.p. 237–239° in a sealed capillary. The mixed m.p. with an authentic sample of carbazole of m.p. 239–240° was undepressed, 239–240° in a sealed capillary. The infrared spectra of the two samples were identical in CS<sub>2</sub>, CHCl<sub>4</sub> and Nujol\_

Tetramethyl Carbazole-1,2,3,4-tetracarboxylate (XIa) A. From Dimethyl 3,4-Dicyanocarbazole-1,2-dicarboxyl--A mixture of dimethyl 3,4-dicyanocarbazole-1,2-dicarate.boxylate (1.00 g., 0.00300 mole) and a solution of methanolic  $25^{\circ}$ % potassium hydroxide (25 cc.) and water (5 cc.) was refluxed for 20 hours on a steam-bath. Methanol (50 cc.) was added to the resulting homogeneous solution, and it was then acidified to pH 1-2 with concentrated hydrochloric acid. The precipitated potassium chloride was collected on a filter, washed with ether (50 cc.), and the methanolic and ethereal filtrates combined. A solution of diazomethane<sup>23</sup> ( $\sim$ 1.3-1.4 g.,  $\sim$ 0.031-0.033 mole, from 5 g. of N-nitroso-N-methylurea) in ether was added to the cooled combined filtrates. After the solution had stood at room temperature for 2.5 hours, the solvents were evaporated and the yellowish residue was dissolvents were evaporated and the yellowish fest-due was dissolved in hot methanol. Cooling the solution to 0° produced matted pale yellow needles (0.734 g., 0.00184 mole, 61%), m.p. 176-177°. Four recrystallizations from methanol yielded tetramethyl carbazole-1,2,3,4-tetracar-boxylate, m.p. 181-182°, mixed m.p. with the sample pre-pared in part B, 181-182°. The infrared spectra of the two samples in CHCl<sub>3</sub> and Nujol were identical.

**B.** From Indole and Dimethyl Acetylenedicarboxylate.— (a) A mixture of indole (11.70 g., 0.100 mole) and dimethyl acetylenedicarboxylate<sup>24</sup> (28.40 g., 0.200 mole) was warmed gently on a steam-bath just long enough to cause the indole to dissolve, and the resulting pale yellow oil was set aside at room temperature for 74 days. The red glass which had formed was dissolved in warm methanol (300 cc.) and allowed to evaporate slowly, with occasional cooling and stirring. Numerous crystalline fractions were collected. As the mother liquor became more concentrated, it was occasionally necessary to add fresh methanol to induce formation of the next crop of crystals.

The first crystalline fraction (1.34 g., 0.00247 mole, 4%), m.p. 227-228°, was salmon-colored. It was the same as the higher melting 1:3 adduct (XIX) of indole and dimethyl acetylenedicarboxylate described below in part (b). The third crystalline fraction (0.02 g.), m.p. 160-170°, was bright yellowish-green. It was the same as the lower melting 1:3 adduct (XVIII) of indole and dimethyl acetylenedicarboxylate described below in part (b).

The second, and all crystalline fractions after the third (25.03 g., 0.0627 mole, 63%), ranged in color from pale yellowish-green to reddish-orange for the bulk of the material. One or two recrystallizations from methanol, with charcoal, yielded tetramethyl carbazole-1,2,3,4-tetracarboxylate as pale yellow needles, m.p. 182–182.5°.

Anal. Calcd. for  $C_{29}H_{17}NO_8$  (399.34): C, 60.15; H, 4.29; N, 3.51. Found: mol. wt. (Rast), 421; C, 60.26, 60.29; H, 4.45, 4.35; N, 3.60.

An Ehrlich test for an open 2- or 3-position of the indole nucleus was negative. The product was recovered unchanged from an attempted acetylation with acetic anhydride. It was recovered unchanged from attempted hydrogenations at 2 atm. over Raney nickel or platinic oxide catalysts, and from an attempted dehydrogenation with chloranil in refluxing xylene. It also was recovered unchanged after refluxing with methanolic sodium methoxide.

(b) In order to obtain larger quantities of the minor products, the experiment described above in part (a) was repeated, except that double quantities of reactants were used and the reaction solution was set aside for 99 days.

<sup>(23)</sup> F. Arndt in A. H. Blatt, "Organic Syntheses," Coll. Vol. 11, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

<sup>(24)</sup> E. H. Huntress, T. E. Lesslie and J. Bornstein, Org. Syntheses, 32, 55 (1952).

After the red glass had been dissolved in warm methanol (500 cc.), the first crystalline fraction (6.06 g., 0.0112 mole, 8%), m.p. 216–220°, was salmon-colored and corresponded to the higher melting crystalline fraction obtained in part (a). Four recrystallizations from methanol, with charcoal, yielded a 1:3 adduct (XIX) of indole and dimethyl acetyl-enedicarboxylate as small white crystals, m.p. 229–230°.

Anal. Calcd. for  $C_{26}H_{25}NO_{12}$  (543.47): C, 57.46; H, 4.64; N, 2.58. Found: mol. wt. (Rast) 514, in 1,2-dibromoethane  $453 \pm 90$  (because of low solubility)<sup>26</sup>; C, 57.75; H, 4.94; N, 2.64.

An Ehrlich test for an open 2- or 3-position of the indole nucleus was negative.

The second crystalline fraction (0.63 g., 0.00084 mole, 2%), m.p. 241.5-242°, was pale yellow in color. Recrystallization from methanol, with charcoal, yielded a 2:1 adduct (XX) of indole and dimethyl acetylenedicarboxylate as pale yellow crystals, m.p. 242-243°.

Anal. Calcd. for  $C_{22}H_{20}N_2O_4$  (376.40): C, 70.20; H, 5.36; N, 7.44. Found: mol. wt. in 1,2-dibromoethane, 394, 386, average 390; C, 70.34; H, 5.41; N, 7.44.

An Ehrlich test for an open 2- or 3-position of an indole nucleus was positive (red color).

The third and fifth crystalline fractions (26.43 g., 0.0662 mole, 33%), m.p. 150–178°, were pale yellowish-green in color. Four or five recrystallizations from methanol, with charcoal, gave tetramethyl carbazole-1,2,3,4-tetracarboxyl-ate, m.p. and mixed m.p. with the sample from part a, 182–182.5°.

The fourth, sixth and seventh crystalline fractions (4.79 g., 0.00881 mole, 7%), m.p. 80–172°, were bright yellowishgreen in color. Three or four recrystallizations from methanol, with charcoal, yielded another 1:3 adduct (XVIII) of indole and dimethyl acetylenedicarboxylate as bright greenish-yellow crystals, m.p. 172–173°.

Anal. Caled. for  $C_{26}H_{25}NO_{12}$  (543.47): C, 57.46; H, 4.64; N, 2.58. Found: mol. wt. (Rast) 537, in 1,2-dibromoethane  $582^{25}$ ; C, 57.46; H, 4.85; N, 2.72.

An Ehrlich test for an open 2- or 3-position of the indole nucleus was negative.

Dimethyl 3,4-Dicyano-9-methylcarbazole-1,2-dicarboxylate (Xb).—A mixture of 1-methyl-3-tricyanovinylindole(1.49 g., 0.00642 mole) and dimethyl acetylenedicarboxylate (10 cc., 0.081 mole) was refluxed at 230–235° for 20 minutes. After the dark tarry mixture had cooled to room temperature, benzene was added. Filtration and washing with benzene left a yellow solid (0.99 g., 0.00285 mole, 44%), m.p. 225–227°. Vacuum sublimation, followed by recrystallization from methanol yielded dimethyl 3,4-dicyano-9-methyl-

(25) Determined by Donald C. Johnson.

carbazole-1,2-dicarboxylate as glistening golden needles, m.p. 234–235°. The compound fluoresces with a bright yellow-green color.

Anal. Calcd. for  $C_{19}H_{13}N_3O_4$  (347.32): C, 65.70; H, 3.77; N, 12.10. Found: C, 65.58; H, 3.94; N, 12.05.

Hydrolysis and Decarboxylation of Dimethyl 3,4-Dicyano-9-methylcarbazole-1,2-dicarboxylate (Xb).—A mixture of dimethyl 3,4-dicyano-9-methylcarbazole-1,2-dicarboxylate (2.00 g., 0.00576 mole) and a solution of methanolic 25% potassium hydroxide (10 cc.) and water (3 cc.) was refluxed for 20 hours on a steam-bath. The potassium salt of 9-methylcarbazole-1,2,3,4-tetracarboxylic acid precipitated in quantitative yield. This salt then was divided into two equal portions.

To the first portion moist soda-lime was added and the mixture was decarboxylated as previously described in the degradation of dimethyl 3,4-dicyanocarbazole-1,2-dicarboxylate, yielding colorless platelets (0.20 g., 0.00120 mole, 42%), m.p. 236–238° in a sealed capillary. The mixed m.p. with an authentic sample of carbazole was undepressed and the infrared spectra of the two samples were identical in CS<sub>2</sub>, CHCl<sub>3</sub> and Nujol.

The second portion of the potassium salt was acidified to pH 1-2 with concentrated hydrochloric acid. Powdered soda-lime was added to the acid solution and the resulting pasty mixture was decarboxylated as previously described, yielding carbazole (0.15 g., 0.00090 mole, 31%), m.p. 234-236° in a sealed capillary.

yielding carbazole (0.15 g., 0.00090 mole,  $\delta_{1\%0}$ ), m.p. 204-286° in a sealed capillary. Tetramethyl 9-Methylcarbazole-1,2,3,4-tetracarboxylate (XIb).—A mixture of dimethyl 3,4-dicyano-9-methylcarbazole-1,2-dicarboxylate (1.68 g., 0.00484 mole) and a solution of methanolic 25% potassium hydroxide (40 cc.) and water (5 cc.) was refluxed for 20 hours on a steam-bath. The resulting homogeneous solution was acidified to pH 1-2 with 2.4 N hydrochloric acid. The resulting solution was extracted with ether (3  $\times$  20 cc.) and the ether extracts were cooled to 0°. A solution of diazomethane<sup>23</sup> (~1.3-1.4 g., ~0.031-0.033 mole, from 5g. of N-nitroso-N-methylurea) in ether was added slowly to the combined ether extracts. After the solution had stood at room temperature for 2.5 hours the ether was evaporated and the pale yellow residual oil was dissolved in hot methanol-water. Cooling the solution produced a yellow solid (0.80 g., 0.00194 mole, 40%), m.p. 100-110°. Four recrystallizations from methanol, once with charcoal, yielded tetramethyl 9-methylcarbazole-1,2,-3,4-tetracarboxylate as pale yellow crystals, having a pale green fluorescence, m.p. 124-125°.

Anal. Caled. for  $C_{21}H_{19}\mathrm{NO}_8$  (413.37): C, 61.01; H, 4.63; N, 3.39. Found: C, 60.98; H, 4.59; N, 3.44.

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[CONTRIBUTION FROM THE SCIENTIFIC LABORATORY, FORD MOTOR CO.]

# Condensations with 1,2-Hydrazinedicarboxamidine. 2,2'-Hydrazopyrimidines

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**RECEIVED MARCH 5, 1959** 

1,2-Hydrazinedicarboxamidine (I) reacts with  $\beta$ -diketones (II), giving rise to 2,2'-hydrazopyrimidines (III). These were characterized by the corresponding N,N'-diacetyl-2,2'-hydrazopyrimidines (IV). By condensation of I with either diethyl 1,3-dicarbethoxyglutaconate (V) or diethyl ethoxymethylenemalonate (VII), 4,4'-dihydroxy-5,5'-dicarbethoxy-2,2'-hydrazopyrimidine (VI) was obtained. With ethyl acetoacetate and I, an acyclic semi-condensation product (IX) resulted. Reaction of I with ethyl cyanoacetate and diethyl malonate led to the formation of 1,2-hydrazinedicarboxamidine dicyanoacetate (XI), respectively.

One of the most important properties of amidines is their ability to undergo condensation reactions to give cyclic amidines, *e.g.*, imidazoles and pyrimidines. Application of this principle to 1,2-hydrazinedicarboxamidine (I) should lead to formation of the corresponding heterocyclic hydrazo compounds with a lesser chance for hydrazoimi-

(1) This work was presented at the 134th National Meeting of the American Chemical Society, Chicago, Ill., September, 1958.

dazoles because of side reactions known to occur in this procedure. As a matter of fact, no hydrazoimidazole could be obtained by the reaction of I with  $\alpha$ -halo-ketones using the method of Kunckell.<sup>2</sup>

In contrast to this, the cyclization of amidines with a host of bifunctional compounds is known as the commonest pyrimidine synthesis. The interaction of an amidine with a  $\beta$ -diketone (II), to I, has

(2) F. Kunckell, Ber., 34, 647 (1901).