and the times of flow measured at 33.8°. The readings in seconds were as follows: initial reading, 111.8 seconds; at 0.2 hours, 90.4 seconds; at 1.6 hours, 53.2 seconds; at 4.8 hours, 33.4 seconds; at 20.9 hours, 18.2 seconds; at 44.4 hours, 15.1 seconds; at 140.4 hours, 13.2 seconds.

Degradation of Polymer in Dimethylformamide in the Presence of Acids.—The homopolymer prepared as described previously, of intrinsic viscosity 5.30, was dissolved in dimethylformamide and the viscosity changes in the presence of acids observed. Figure 1 shows the effect of 1% sulfur dioxide and acetic anhydride in inhibiting the carbon chain scission of the homopolymer.

Degradation of Fibers in Water.—Fine filaments (diameter 2.7 × 10^{-4} inch) of polyvinylidene cyanide were spun from dimethylformamide solution, dried, and hot-stretched to a tenacity of 77,000 p.s.i., elongation of 22% at break.

FIBERS IMMERSED IN WATER AND TENACITIES OBTAINED

Time of immersion, hr.	*p*H of water	Final tenacity, p.s.i.
...	..	77,000
64.5	3.5	52,000
64.5	5.5	36,000
65.0	7.5	0
1.25	10.2	0
0.20	13.5	0
0.10	14.0	0

BRECKSVILLE, OHIO

[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

Vinylidene Cyanide. V. The Aluminum Chloride Catalyzed Reaction of Vinylidene Cyanide and Aromatic Compounds

BY J. C. WESTFAHL AND T. L. GRESHAM

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Vinylidene cyanide reacts, in the presence of two equivalents of anhydrous aluminum chloride, with certain aromatic compounds to give monosubstituted malononitriles of the type $ArCH_2CH(CN)_2$. The reaction succeeds with aromatic hydrocarbons, phenols, phenol ethers and certain aromatic heterocycles. It fails with aromatic compounds which polymerize vinylidene cyanide or which are sufficiently deactivated by electron attracting groups. The introduction of two $-CH_2CH(CN)_2$ groups can occur with suitably active aromatic compounds.

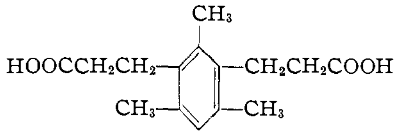
Recent communications[1,2] from this Laboratory described several syntheses of vinylidene cyanide (I). In the course of the study of this very reactive compound a new synthesis of monosubstituted malononitriles of the type Aryl $CH_2CH(CN)_2$ was developed. This paper describes the preparation of a number of monosubstituted malononitriles from I and aromatic compounds.

Reaction of I, a suitably reactive aromatic compound, and two equivalents of anhydrous aluminum chloride gave an aluminum chloride complex. The aluminum chloride complexes have been assumed to have the composition Aryl $CH_2CH(CN)_2 \cdot 2AlCl_3$. Hydrolysis of the aluminum chloride complex gave Aryl $CH_2CH(CN)_2$ (equation 1).

$$\text{Aryl-H} + CH_2{=}C(CN)_2 + 2AlCl_3 \longrightarrow \text{Aryl } CH_2CH(CN)_2 \cdot 2AlCl_3 \xrightarrow{H_2O} \text{Aryl } CH_2CH(CN)_2 \qquad (1)$$

All reactions were carried out with one mole of anhydrous aluminum chloride per mole of nitrile group unless otherwise noted. The results obtained with a number of aromatic compounds are presented in Table I. Structures of the products were established as shown in Table II.

The reaction of mesitylene with I in a molar ratio of one-to-two gave a viscous liquid which could not be crystallized. Acid hydrolysis produced a solid acid of m.p. 175–176° which gave analytical results in agreement with II.



II

Reaction of hydroquinone dimethyl ether with I in a one-to-two molar ratio gave 1,4-dimethoxy-2,5-bis-(2,2-dicyanoethyl)-benzene (III). In the preparation of 1,4-dimethoxy-2-(2,2-dicyanoethyl)-benzene (IV), III was formed as a by-product. The reaction of equimolar amounts of I and IV using four equivalents of aluminum chloride also gave III. The structure of III was established as shown in Chart I.

The 2,5-dimethoxyterephthalic acid (VII) was identified by its m.p.[3] and by conversion to its diethyl ester.[3]

No products were isolated from the action of I on *p*-nitroanisole or on 2-nitro-1,4-dimethoxybenzene. The lack of reaction with 2-nitro-1,4-dimethoxybenzene was unexpected since 2-nitroanisole has been acylated in the 4-position with acetyl chloride and aluminum chloride.[4]

Reaction of I with *p*-chloroanisole gave 2-methoxy-5-chlorobenzylmalononitrile (IX). The structure of IX was established as shown in Chart II. Since only two structures are possible for the product derived from one molecule of I and one molecule of *p*-chloroanisole, the isolation of a neutral solid XIII from the sequence of reactions in Chart II establishes the structure of the product as IX. The other possible structure would yield an acid by the sequence of reactions in Chart II.

The reaction of I with furan proceeded in an abnormal manner. Hydrolysis of the aluminum chloride complex gave practically no polymer of I thus indicating complete reaction. Distillation of the crude product gave only a small amount of volatile

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(1) A. E. Ardis, *et al.*, THIS JOURNAL, **72**, 1305 (1950).

(2) A. E. Ardis, *et al.*, *ibid.*, **72**, 3127 (1950).

(3) J. U. Nef, *Ann.*, **258**, 297, 299 (1890).

(4) F. Stockhausen and L. Gattermann, *Ber.*, **25**, 3523 (1892).

TABLE I

Aromatic component	$ArCH_2CH(CN)_2$, Ar =	Yield, % Distilled[a]	Yield, % Recrystallized (m.p., °C.)	M.p., °C. (pure)	Analyses, % Calculated C	Calculated H	Calculated N	Found C	Found H	Found N
Benzene	Phenyl	69.0[b]	60.8	90-91	76.90	5.16	17.94	76.99	5.21	17.74
			(86-90.5)					76.64	5.14	
Toluene	o-Tolyl p-Tolyl } mixt.	89.0[d] (mixture)	p-tolyl 45.1 (78-82.5)	83.5-84.3	77.62	5.92	16.46	77.18 77.26	5.72 5.75	16.47
m-Xylene	2,4-Dimethylphenyl	67.4	Liquid	Liquid[c]	78.22	6.57	15.21	See footnote[c]		
p-Xylene	2,5-Dimethylphenyl	79.4	63.2	75.3-75.8	78.22	6.57	15.21	78.30	6.57	15.23
			(75.3-76)					78.43	6.53	
Mesitylene	Mesityl	76.4	67.2	91-92	78.75	7.12	14.13	78.34	7.06	14.14
			(91-92)					78.28	6.92	
Naphthalene	2-Naphthyl	60.5[d]	37.1[e]	115.2-116.2	81.53	4.89	13.58	81.34	4.72	13.58
			(114.5-116.5)					81.26	4.71	
Thiophene	2-Thienyl	65.2	61.6	57-58	59.23	3.73	17.27	59.37	3.87	17.18
			(52.8-55.2)					59.27	3.84	
Anisole	p-Anisyl	64.1[d]	24.2[e]	88.5-89.5	70.95	5.41	15.05	70.98	5.44	15.04
			(87.5-88.5)							
1,4-Dimethoxybenzene	2,5-Dimethoxyphenyl	69.8	67.5	46.8-47.8	66.65	5.61	12.96	66.64	5.43	13.00
			(46.5-47.8)					66.53	5.38	
Phenol	2-Hydroxyphenyl 4-Hydroxyphenyl } mixt.		4-Hydroxyphenyl, 45.6 (170-173.5)	174-175	69.75	4.68	16.27	69.74	4.71	16.35 16.32

[a] Distillates completely crystalline unless otherwise noted. [b] $AlCl_3$ suspension in $CHCl_2CHCl_2$ was saturated with anhyd. HCl before adding the $CH_2{=}C(CN)_2$-benzene solution. If this preliminary treatment was omitted the yield of distilled product was 14.7%. [c] Colorless viscous liquid b.p. 101-104° (0.08 mm.), $n^{25}D$ 1.5312, d^{25}_4 1.032. Liquid did not give satisfactory analysis for C, H and N. Basic hydrolysis gave an 83% yield of crude 2,4-dimethylbenzylmalonic acid. Purified acid had m.p. 163.5° dec. See Table II. *Anal.* Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35; neut. equiv., 111. Found: C, 64.98, 64.94; H, 6.57, 6.40; neut. equiv., 112, 112. [d] Distillate was a greasy solid. [e] Low yield of recrystallized solid may be due to presence of isomer in distilled product.

TABLE II

CHARACTERIZATION OF PRODUCTS

$ArCH_2CH(CN)_2$ Ar =	$ArCH_2CH(COOH)_2$ M.p., °C.	$ArCH_2CH_2COOH$, m.p., °C. Reported	Found	$ArCH_2CH_2CONH_2$, m.p., °C. Reported	Found
Phenyl	120-121 d.[a]	For additional structural evidence, see footnote [b]			
p-Tolyl	162.5-163.5 d.	122 cor.[c]	116.5-117.5	135[d]	134-135
o-Tolyl		For structural evidence, see footnote [e]			
2,4-Dimethylphenyl	163.5 d.	108[f]	107-108	107[g]	109.3-110
2,5-Dimethylphenyl	131-132 d.	45-46[h]	44.5-45.5	For other derivative, see note[i]	
Mesityl	165.5 d.	113[j]	111.5-112.5	159-160[k]	164-165
2-Naphthyl	148 d.[l]	134-135[m]	135-136	168[m]	168-169
2-Thienyl	138.5-139 d.	43-45[n]	46.7-47.7	99-100[n]	102.5-103.4
p-Anisyl	119-120 d.	104[o]	103.8-104.6	For other derivative, see note [p]	
2,5-Dimethoxyphenyl	162 d.	65.5[q]	65.2-66	For other derivative, see note [r]	
4-Hydroxyphenyl	160.5 d.	128-129[s]	129-130	For other derivatives, see note [t]	
2-Hydroxyphenyl	For structural evidence, see footnote [u]				

[a] M. Conrad and M. Guthzeit, *Ber.*, **15**, 2846 (1882), report m.p. 121° for benzylmalonic acid. [b] M.p. 90-91° found for benzylmalononitrile. J. C. Hessler, *Am. Chem. J.*, **22**, 181 (1899), gives m.p. 91° for benzylmalononitrile. Hydration with H_2SO_4 gave benzylmalonamide m.p. 231-232°. V. H. Wallingford and A. H. Homeyer, U. S. Patent 2,367,632, gave m.p. 229-230° for benzylmalonamide. Partial hydrolysis of benzylmalonamide with 1% aq. sodium hydroxide gave benzylmalonamic acid of m.p. 138.5° dec. R. Gaudry, *Can. J. Research*, **23B**, 234 (1945), gives m.p. 140° for benzylmalonamic acid. [c] J. F. Dippy and J. E. Page, *J. Chem. Soc.*, 357 (1938). W. V. Miller and Rohde, *Ber.*, **23**, 1898 (1890), report m.p. 116°. [d] E. Buchner and P. Schulze, *Ann.*, **377**, 283 (1910). [e] o-Isomer shown to be present in filtrate from p-isomer by hydrolysis, decarboxylation and oxidation to give phthalic acid. Phthalic acid identified as its anhydride and p-bromophenacyl ester. [f] L. Gattermann, *Ann.*, **347**, 373 (1906). [g] C. Willgerodt, *J. prakt. Chem.*, **80**, 186 (1909). [h] P. A. Plattner and J. Wyes, *Helv. Chim. Acta*, **24**, 490 (1941). [i] Hydrolysis, decarboxylation and oxidation gave trimellitic acid which was identified by m.p. and by conversion to the anhydride. [j] M. J. Hoch, *Compt. rend.*, **192**, 1464 (1931). [k] R. D. Kleene, F. H. Westheimer and G. W. Wheland, THIS JOURNAL, **63**, 793 (1941). [l] F. Mayer and A. Sieglitz, *Ber.*, **55**, 1855 (1922), report m.p. 94-95° for (2-naphthylmethyl)-malonic acid. [m] F. Mayer and A. Sieglitz, *Ber.*, **55**, 1855 (1922). [n] G. Barger and A. P. Easson, *J. Chem. Soc.*, 2103 (1938). [o] G. Barger and G. S. Walpole, *ibid.*, **95**, 1723 (1909). [p] Hydration by refluxing with aq. $NaHCO_3$ solution gave p-methoxybenzylcyanoacetamide, m.p. 170.5-171.5°. R. Gaudry, *Can. J. Research*, **23B**, 234 (1945), reports m.p. 166° for p-methoxybenzylcyanoacetamide. [q] F. Fichter and E. Schlager, *Helv. Chim. Acta*, **10**, 408 (1927). [r] Hydrolysis, decarboxylation and demethylation with aq. HBr gave 6-hydroxyhydrocoumarin m.p. 162-163°. F. Fichter and E. Schlager, *Helv. Chim. Acta*, **10**, 408 (1927), report m.p. 162-163° for 6-hydroxyhydrocoumarin. [s] C. Stohr, *Ann.*, **225**, 62 (1884). [t] Bromination of $p\text{-}HOC_6H_4CH_2CH(COOH)_2$ with aq. KBr_3 gave a dibromo acid of m.p. 168.5° dec. Decarboxylation gave 3,5-dibromophloretic acid of m.p. 113-114°. T. Zincke and F. Leisse, *Ann.*, **322**, 226 (1902), report m.p. 114° for 3,5-dibromophloretic acid. [u] The liquid recovered from the recrystallization of the crude product was refluxed with hydrochloric acid to give a small amount of neutral liquid. The infrared spectrum of the neutral liquid, indicated the presence of an ester group. This liquid was probably hydrocoumarin.

liquid. This liquid was shown to contain furfurylmalononitrile by basic hydrolysis to furfurylmalonic acid[5] which was decarboxylated to β-(2-furyl)-propionic acid.[6] Since the low yield in this preparation very likely was due to cleavage of the furan ring, attempts were made to combine I with the more stable methyl furoate using aluminum chloride and using anhydrous stannic chloride. No methyl 5-(2,2-dicyanoethyl)-furoate was isolated.

None of the expected product was isolated from the simultaneous addition of equimolar amounts of I and acetanilide to three equivalents of aluminum

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[5] W. Marckwald, *Ber.*, **21**, 1083 (1888).

[6] J. J. Sudborough and J. M. Gittins, *J. Chem. Soc.*, **95**, 320 (1909).

CHART I

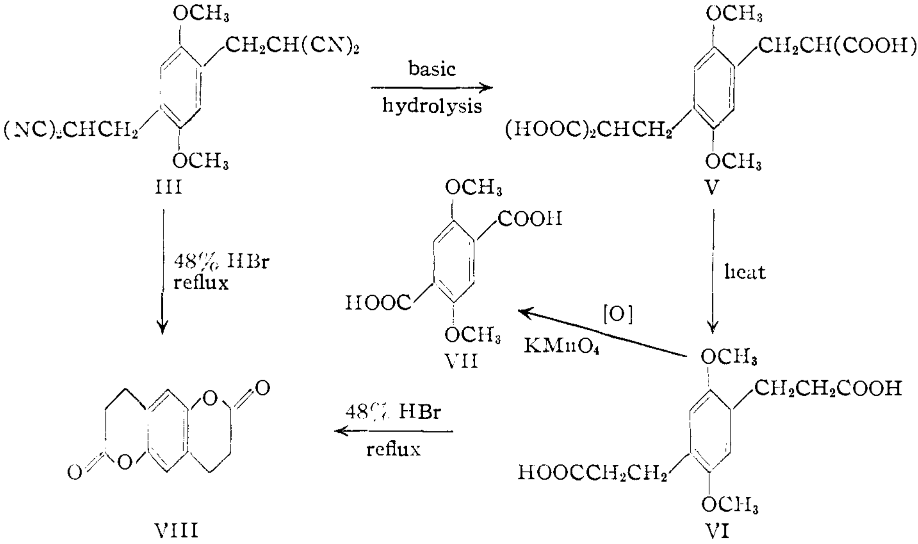
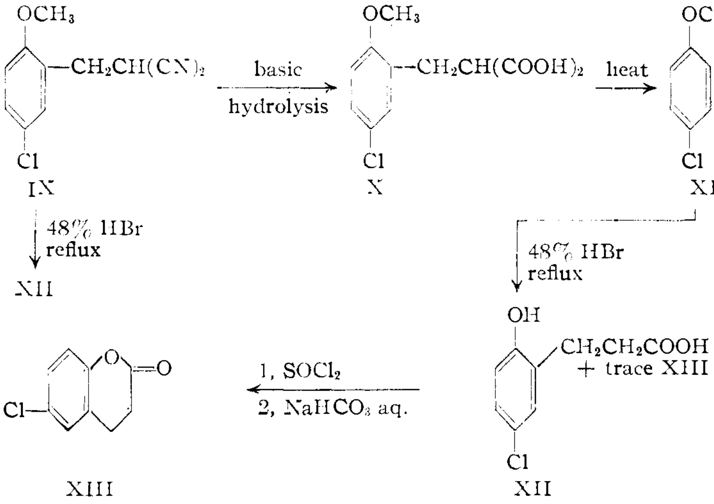


CHART II



chloride. The lack of reaction may be due to a combination of aluminum chloride with the weakly electron releasing N-acetyl group to produce an electron attracting group.

The reaction of I with benzene was unusual in that when carried out in the usual manner a 14.7% yield of distilled benzylmalononitrile was obtained. When the aluminum chloride suspension was saturated with anhydrous hydrogen chloride before adding the *s*-tetrachloroethane solution of I and benzene, a 69% yield of distilled benzylmalononitrile resulted. This observation suggests that the actual catalyst may be a combination of aluminum chloride and hydrogen chloride or that I may attack the aromatic reactant in the form $(AlCl_4)^- \overset{+}{C}H_2CH(CN)_2 \cdot 2AlCl_3$. Since reagent grade anhydrous aluminum chloride normally contains some hydrogen chloride a sufficient concentration of catalyst is available to give a fast reaction with the more reactive (nucleophilic) aromatic compounds. Benzene being the least reactive of the aromatic reactants in Table I, it gave a slow reaction and therefore a low yield in the absence of added hydrogen chloride.

The experimental observations indicate that I, in combination with anhydrous aluminum chloride and hydrogen chloride, acts as an electrophilic reagent attacking centers of high electron density in aromatic systems to produce monosubstituted malononitriles of the type Aryl-$CH_2CH(CN)_2$. The application of this reaction to aromatic compounds containing groups such as amino and alcoholic hydroxyl was not studied since these groups are known to polymerize I.[1] Phenolic hydroxyl groups, however, do not polymerize I.

Experimental[7]

Materials.—The aromatic reactants and the *sym*-tetrachloroethane were Eastman Kodak Co. White Label grade except benzene which was commercial, thiophene-free. All liquids were dried by distillation and the solids were used as received. The purity of the vinylidene cyanide was 90+%. The aluminum chloride was reagent grade, anhydrous sublimed.

Preparation of Aryl-$CH_2CH(CN)_2$.—Before introducing the reactants, a current of dry air was passed through the apparatus for 30 minutes to dry it. The use of dry apparatus and reactants is necessary because of the great tendency of water to polymerize I.[1] A solution of 0.50 mole of the aromatic compound and 0.5 mole of vinylidene cyanide (measured with pipets) in 150 ml. of *sym*-tetrachloroethane was added dropwise to a stirred suspension of 133.3 g. (1.00 mole) of anhydrous aluminum chloride in 250 ml. of *sym*-tetrachloroethane. In the preparation of benzylmalononitrile a stream of anhydrous hydrogen chloride was bubbled into the stirred suspension for 30 minutes at room temperature before adding the solution of vinylidene cyanide and benzene. The temperature was maintained with suitable heating or cooling baths during the addition and for a further 15 minutes.

Compound	Temperature, °C.
Benzene	36–39.5
Toluene	10–15
m-Xylene	20–25
p-Xylene	20–25
Mesitylene	-2– (+4.5)
Naphthalene	35–40
Furan	0–5
Thiophene	0–5
Anisole	20–25
1,4-Dimethoxybenzene	0–5
Phenol	30–35

Hydrolysis was accomplished by pouring the reaction mixture into a vigorously stirred mixture of one liter of ice and water containing 50 ml. of concentrated hydrochloric acid. After the mixture was filtered with suction through a layer of filter-aid to break any emulsion present, the *sym*-tetrachloro-

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[7] All melting points and boiling points are uncorrected.

ethane layer of the filtrate was separated and the aqueous layer was extracted with chloroform. The combined *sym*-tetrachloroethane–chloroform solution was washed with water and dried with magnesium sulfate. The chloroform was removed by distillation at atmospheric pressure (to 100°) and the *sym*-tetrachloroethane was removed at 50° (0.4 mm.) leaving a yellow to brown residue which usually crystallized. Distillation at 0.4–0.7 mm. gave colorless to yellow crystalline solids which after one recrystallization from ethanol were usually colorless.

Basic hydrolyses to the monosubstituted malonic acids were carried out by refluxing the malononitriles for 16 hours with an excess (100%) of aqueous 10% sodium hydroxide. Acidification of the cold solution followed by filtration or ether extraction gave the crude monosubstituted malonic acid.

Decarboxylation of the malonic acids was carried out by heating the acids above their melting points until the evolution of carbon dioxide stopped.

1,4-Dimethoxy-2,5-bis-(2,2-dicyanoethyl)-benzene (III).—A solution of 6.9 g. (0.05 mole) of 1,4-dimethoxybenzene and 0.1 mole of I in 30 ml. of *sym*-tetrachloroethane was added over 71 minutes to a stirred suspension of 26.7 g. (0.2 mole) of anhydrous aluminum chloride in 30 ml. of *sym*-tetrachloroethane. The temperature of the reaction was 30–35° (estimated) during the addition. After stirring for an additional 15 minutes the mixture was hydrolyzed by stirring with 300 ml. of an ice and water mixture containing 10 ml. of concentrated hydrochloric acid. Shaking the hydrolysis mixture with 150 ml. of hexane precipitated III from the *sym*-tetrachloroethane layer. Filtering the solid and recrystallizing twice from acetone–water solution gave 3.12 g. (21.2%) of colorless III, m.p. 211.5–212.5°. Further recrystallizations raised the m.p. to 212.4–213.4°.

Anal. Calcd. for $C_{16}H_{14}O_2N_2$: C, 65.29; H, 4.79; N, 19.04. Found: C, 65.11, 65.15; H, 4.75, 4.79; N, 19.01.

1,4-Dimethoxy-2,5-bis-(2,2-dicarboxyethyl)-benzene (V).—The hydrolysis was carried out as described above. The crude acid was recrystallized once from ethanol–water to give an 81.5% yield of colorless V, m.p. 226° dec.

Anal. Calcd. for $C_{14}H_{18}O_6$: C, 51.89; H, 4.90. Found: C, 51.93, 52.08; H, 4.97, 4.99.

1,4-Dimethoxy-2,5-bis-(2-carboxyethyl)-benzene (VI).—Decarboxylation of 0.44 g. (1.19 millimoles) of V was carried out by heating from 225 to 244° over a 12-minute interval to give 0.33 g. (97.6%) of crude VI. One recrystallization from water–ethanol gave 0.25 g. of VI as yellow plates, m.p. 197–199.5°.

Anal. Calcd. for $C_{14}H_{18}O_6$: C, 59.56; H, 6.43. Found: C, 59.53, 59.48; H, 6.60, 6.49.

Oxidation of VI.—A solution of 2.50 g. (8.89 millimoles) of VI as its sodium salt in 250 ml. of water and 11.20 g. (106.3 meq.) of potassium permanganate was heated to boiling with a flame. Since the permanganate color was discharged when boiling started, a further 5.60 g. (53.7 meq.) of potassium permanganate was added and refluxing was started. After 12 minutes the permanganate color was again discharged and the hot mixture was filtered with suction (filter-aid). The yellow filtrate was boiled to 38 ml., cooled and acidified. The crystals were filtered and recrystallized once from water to give 0.09 g. (4.5%) of yellow needles of m.p. 263–266°. Conversion to the diethyl ester *via* the acid chloride gave, after one recrystallization, colorless crystals of m.p. 100.5–101.5°. The reported m.p. of VII is 265° and that of the diethyl ester of VII is 101.5°.[3]

Demethylation and Cyclization of VI.—A mixture of 0.20 g. (0.71 millimole) of VI and 10 ml. (88.5 millimoles) of 48% hydrobromic acid was refluxed for 80 minutes and cooled slowly. The yellow crystals which separated were recrystallized once from alcohol (decolorizing carbon) to give colorless crystals of VIII, m.p. 292–295°.

The 3,4,8,9-Tetrahydrobenzo[1.2-b,4.5-b']dipyrone-2,7 (VIII).—A mixture of 2.94 g. (10.0 millimoles) of III and 25 ml. (221 millimoles) of 48% hydrobromic acid was refluxed for 4 hours during which III dissolved and VIII separated. The light tan solid obtained by filtering the cold mixture was suspended in water, filtered, resuspended in aqueous sodium bicarbonate, filtered and dried to give 1.495 g. (68.6%) of crude VIII. Two recrystallizations from acetone–water gave 0.955 g. (43.7%) of colorless VIII, m.p. 292–296°.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.16, 66.22; H, 4.80, 4.72.

1,3,5-Trimethyl-2,4-bis-(2-carboxyethyl)-benzene (II).—A mixture of 7.8 g. of the crude *sym*-tetrachloroethane-free liquid product from I, mesitylene and anhydrous aluminum chloride in a molar ratio of 2:1:4 was refluxed for 6 hours with a solution prepared from 25 ml. of concentrated sulfuric acid and 50 ml. of water. The insoluble viscous liquid was taken up in ether, washed with water and extracted with saturated sodium bicarbonate solution. After boiling free of ether and cooling, the bicarbonate solution was acidified. The gummy solid which precipitated was dried and then boiled with several portions of benzene. The filtered benzene solution deposited nearly colorless II on cooling. After several recrystallizations from water, colorless fine needles of m.p. 175–176° were obtained.

Anal. Calcd. for $C_{15}H_{19}O_4$: C, 68.16; H, 7.63; neut. equiv., 132. Found: C, 68.23, 68.14; H, 7.60, 7.65; neut. equiv., 134.

2-Methoxy-5-chlorobenzylmalononitrile (IX).—A solution of 14.26 g. (0.10 mole) of *p*-chloroanisole and 0.10 mole of I in 30 ml. of sym-tetrachloroethane was added over 47 minutes to a stirred suspension of 26.67 g. (0.20 mole) of anhydrous aluminum chloride in 30 ml. of *sym*-tetrachloroethane. The maximum temperature was approximately 35°. After stirring for an additional 15 minutes the mixture was hydrolyzed as given in the preparation of III. The resulting emulsion was filtered with suction to break the emulsion and remove polymer of I. The filtrate was worked up as given in the general preparation of $ArCH_2CH(CN)_2$. The liquid remaining on removing the *sym*-tetrachloroethane weighed 12.05 g. (54.6%) and crystallized completely to nearly colorless IX. One recrystallization from ethanol gave 7.46 g. (33.8%) of IX, m.p. 64.5–65.5°. Further recrystallization raised the m.p. to 65–66°.

Anal. Calcd. for $C_{11}H_9ClN_2O$: C, 59.87; H, 4.11; Cl, 16.07; N, 12.70. Found: C, 59.75; H, 3.98; Cl, 16.12; N, 12.79, 12.79.

Basic hydrolysis of IX was carried out as previously described. The crude acid isolated by ether extraction was recrystallized twice from water to give a 67.2% yield of crystalline X of m.p. 150.5° dec.

Anal. Calcd. for $C_9H_9ClO(COOH)_2$: neut. equiv., 129. Found: neut. equiv., 131, 131.

Decarboxylation of X followed by one recrystallization from hexane–benzene gave a 73.6% yield of pale yellow XI, m.p. 95–95.5°.

Anal. Calcd. for $C_9H_{10}ClO(COOH)$: C, 55.95; H, 5.17; Cl, 16.52; neut. equiv., 215. Found: C, 55.86; H, 5.26; Cl, 16.36; neut. equiv., 216.

Demethylation of XI.—A mixture of 0.50 g. (2.33 millimoles) of XI and 5 ml. (*ca.* 44 millimoles) of 48% hydrobromic acid was refluxed for four hours, cooled in ice, filtered with suction, and the product washed on the filter with cold water. The solid was stirred with a sodium bicarbonate solution and the small amount (0.02 g.) of insoluble, neutral solid was filtered. The impure neutral solid (XIII) had m.p. 94–105°. Acidification of the basic solution gave 0.38 g. (81.4%) of XII of m.p. 134.5–135.5°.

Anal. Calcd. for $C_9H_9ClO_3$: C, 53.88; H, 4.52; Cl, 17.67. Found: C, 54.04; H, 4.60; Cl, 17.70.

Acid Hydrolysis of IX.—A mixture of 2.21 g. (10.0 millimoles) of IX and 20 ml. (*ca.* 177 millimoles) of 48% hydrobromic acid was refluxed for 2.5 hours. When worked up as in the previous preparation, 0.79 g. of XII of m.p. 133–133.5° was obtained. A mixed melting point of the XII prepared by the two routes was not depressed.

6-Chlorohydrocoumarin (XIII).—When 0.50 g. (2.49 millimoles) of XII, 5.0 ml. (*ca.* 70 millimoles) of thionyl chloride and one drop of pyridine were mixed a spontaneous evolution of gas occurred with the absorption of heat. After refluxing for 40 minutes, the excess thionyl chloride was removed *in vacuo*. The yellow solid was taken up in ether and the solution was washed with saturated sodium bicarbonate solution until free of acid. After drying, the ether was removed to leave 0.43 g. (93.4%) of yellow XIII of m.p. 107–109.5° (previous softening). One recrystallization from ethanol gave 0.225 g. (48.9%) of pale yellow plates of m.p. 110–111°. Further recrystallization did not raise the melting point. A mixed melting point with the impure XIII (m.p. 94–105°) obtained in the demethylation of XI melted at 103–108°.

Anal. Calcd. for $C_9H_7ClO_2$: C, 59.19; H, 3.86; Cl, 19.42. Found: C, 59.34; H, 3.92; Cl, 19.27.

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BRECKSVILLE, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Reaction of Grignard Reagents with 4-Hydroxy- and 4-Ethoxycoumarin

BY S. WAWZONEK, R. C. NAGLER[1,2] AND L. J. CARLSON[1]

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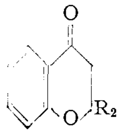
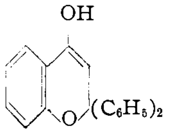
4-Ethoxycoumarin was found to react with phenylmagnesium bromide and methylmagnesium iodide and to give 2,2-diphenyl-4-chromanone and 2,2-dimethyl-4-chromanone, respectively, if the intermediate carbinol was decomposed with acid. The intermediate when decomposed with ammonium chloride gave a mixture of the corresponding chromanone and products formed by a reverse aldol reaction. 4-Hydroxycoumarin was found to be resistant to the addition reaction of Grignard reagents. The results obtained differ from those reported previously by Heilbron and Hill.

A further study of the action of Grignard reagents with 4-hydroxycoumarin and its derivatives was suggested by the conflicting reports of previous investigators on the properties of 2,2-dimethyl-4-chromanone (I, R = CH_3) and 2,2-diphenyl-4-chromanone (I, R = C_6H_5).



I



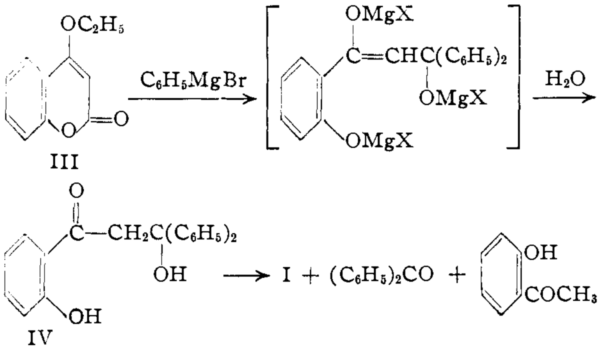
II

The former (I, R = CH_3) was found to be a neutral compound[3] while the diphenyl compound (I, R = C_6H_5), made by the addition of phenylmagnesium bromide to 4-hydroxycoumarin, was reported to be acidic[4] and to exist as the enol, 4-hydroxy-2,2-diphenyl-Δ^3-chromene (II).

Repetition of the reaction of excess phenylmagnesium bromide with 4-hydroxycoumarin gave upon decomposition of the Grignard product mainly 4-hydroxycoumarin and a small amount of tar. Similar results were obtained using methylmagnesium iodide under normal and forcing conditions.

This discrepancy in results from those reported previously[4] was partially resolved when the preparation of the chromene II from its ether was undertaken. The latter was reported to be formed by the addition of phenylmagnesium bromide to 4-methoxycoumarin.[4] The use of identical conditions to those of Heilbron and Hill's[4] with 4-ethoxycoumarin instead of 4-methoxycoumarin, gave a product with the same melting point as that reported for 4-methoxy-2,2-diphenyl-Δ^3-chromene. That this product was 2,2-diphenyl-4-chromanone (I, R = C_6H_5) and not the chromene was indicated by its insolubility in alkali, by the formation of a 2,4-dinitrophenylhydrazone, by the products isolated from the ammonium chloride hydrolysis of the Grignard addition product and by an independent synthesis.

When an ammonium chloride solution was substituted for the hydrochloric acid in the decomposition of the Grignard addition product, a mixture of 2,2-diphenyl-4-chromanone (I, R = C_6H_5), benzophenone and *o*-hydroxyacetophenone was formed. This behavior points to the formation of *o*-hydroxy-(β-hydroxy-β,β-diphenyl)-propiophenone (IV) as an intermediate, even though it was not isolated. This carbinol (IV) in weakly acid medium apparently is only slowly cyclized to 2,2-diphenyl-4-chromanone (I, R = C_6H_5) and therefore can undergo a reverse aldol to benzophenone and *o*-hydroxyacetophenone.



The cleavage of the ether by the Grignard reagent must occur after the opening of the ring, since if a limited amount of the reagent is used, a mixture of 4-ethoxycoumarin (III) and 2,2-diphenyl-4-chromanone (I, R = C_6H_5) is obtained. The ethylbenzene formed in this cleavage was isolated in a very small amount and its structure demonstrated by oxidation to benzoic acid.

The synthesis of 2,2-diphenyl-4-chromanone (I) was accomplished by condensing benzophenone with *o*-hydroxyacetophenone in the presence of sodium *t*-butoxide. The crude product obtained was converted to a mixture of 2,4-dinitrophenylhydrazones from which the golden 2,2-diphenyl-4-chromanone derivative was separated mechanically. The remaining dark red crystalline product had an elementary analysis which corresponded to the 2,4-dinitrophenylhydrazone of *o*-hydroxy-(β-hydroxy-β,β-diphenyl)-propiophenone and gave upon cyclization only trace amounts of the corresponding derivative of 2,2-diphenyl-4-chromanone (II, R = C_6H_5). The amount of red product obtained, however, was too small to be characterized further.

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(1) Abstracted in part from the Ph.D. thesis, August, 1953, of R. C. Nagler and the M.S. thesis, February, 1950, of L. J. Carlson.

(2) du Pont Fellow, 1951–1952.

(3) K. V. Auwers and W. Mauss, *Ber.*, **61**, 2545 (1928).

(4) I. Heilbron and D. J. Hill, *J. Chem. Soc.*, 2005 (1927).