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Reactions of 2-Formyl-3-methoxypropionitrile Derivatives as Electrophilic Reagent[1]

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The reaction of 2-formyl-3-methoxypropionitrile derivatives (I, II, III) with benzenes (VIa—h) in the presence of an acid catalyst gave *cis* isomers of 2-methoxymethylene-3-phenylpropionitriles (VIIa—h) *via* electrophilic substitution of allyl cation (IV). The aluminum chloride-catalyzed reaction of III with the benzenes afforded 2-methoxymethyl-3,3-diphenylpropionitriles (XVa—c) *via* electrophilic substitution of oxocarbonium ion (V). The same reactions of carbomethoxy analogs of I, II, and III were carried out to provide *trans* isomers of methyl 2-methoxymethylene-3-phenylpropionates (XIa—e) and a small amount of the carbomethoxy analog (XVIc) of XVc. In these reactions indan-(VIIIa, XIIa, b), triphenylpropane-(IXa, XIIIc), and indene-(XIVa, b) derivatives were obtainable *via* successive intra- or intermolecular substitutions of benzenes at the 2-methoxymethylene groups of VII and XI. The compounds VII and XV were converted into 2-dimethoxymethyl-3-phenylpropionitriles (X) and 2-cyano-1,1-diphenyl-1-propenes (XVII), respectively, by the treatment of sodium methoxide in methanol.

Some heterocycles such as 3-cyano-2-methoxychroman (XIX), 3-cyano-2H-chromen (XXIII), and 3-cyanoquinoline (XXIV) were simply derived from I or III following the above methods.

Keywords——electrophilic substitution; allyl and oxocarbonium cations; substituted benzenes; 2-methoxymethylene-3-phenylpropionitriles; methyl 2-methoxymethylene-3-phenylpropionates; 2-cyano-1-phenylindan; 2-carbomethoxy-1H-indenes; 2-methoxymethyl-3,3-diphenylpropionitriles; 2-cyano-1,1-diphenyl-1-propenes; syntheses of heterocycles

In the preceding paper,[3] we discussed the mechanism of the acid-catalyzed interconversion among 2-formyl-3-methoxypropionitrile derivatives in methanol. The interconversion proceeds by the pathway of 2-dimethoxymethylacrylonitrile (I, X=CN)⇄2-methoxymethylene-3-methoxypropionitrile (II, X=CN)⇄2-dimethoxymethyl-3-methoxypropionitrile (III, X=CN), involving two cationic species such as allyl cation (IV, X=CN) in the path I⇄II and oxocarbonium ion (V, X=CN) in the path II⇄III as the reaction intermediates. The allyl cation IV (X=CN) was found to be so long-lived species as to attack a double bond and undergo dimerization. Hence we turned our attention to the synthetic application of these cationic intermediates as electrophilic reagents. Such synthetic approaches to heterocycles starting with II or III have been utilized in a few instances.[4] These studies include only the reaction with ureas to give 2-oxo-(or thio-)pyrimidine derivatives, but there is no report on the C-C bond formation by the electrophilic attacks of the cationic intermediates IV and/or V. This prompted us to study the acid-catalyzed alkylation of benzenes (VI) with I, II, and III. In the reactions both I and II gave only the products which should be formed by the electrophilic substitution of the allyl cation IV while III afforded another-type products attributable to the electrophilic substitution of the oxocarbonium ion V.

1) A part of this work was applied to Japanese patent 47-111841 and laid open to public, July 5, 1974, No. 49-69679.
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3) M. Tanaka, M. Kimoto, and K. Tokuyama, *Chem. Pharm. Bull.* (Tokyo), **26**, 38 (1978).
4) A. Takamizawa, K. Hirai, Y. Sato, and K. Tori, *J. Org. Chem.*, **29**, 1740 (1964); A. Takamizawa and K. Hirai, *Chem. Pharm. Bull.* (Tokyo), **12**, 804 (1964); *idem, ibid.*, **12**, 1418 (1964).

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Electrophilic Substitution of Allyl Cation IV

The reaction of I (X=CN) with a large excess of benzene in the presence of anhydrous aluminum chloride ($AlCl_3$) under a mild reaction condition gave a 1:1-adduct (VIIa), $C_{11}H_{11}NO$ (mp 81—82°), in 82% yield. The infrared (IR) spectrum of VIIa showed the absorption bands at 2200 and 1640 cm^{-1} due to an α,β-unsaturated nitrile and at 1600 cm^{-1} due to a phenyl group (Ph). The nuclear magnetic resonance (NMR) spectrum (CCl_4) exhibited signals due to a methylene group at 3.30 ppm (doublet, J=1 Hz) which coupled with an olefinic proton at 6.42 ppm (triplet), a methoxy group attached to double bond at 3.75 ppm, and five aromatic protons at 7.18 ppm, indicating the presence of $-CH_2-C(-CN)=CH-OMe$ moiety attached to the phenyl group. Therefore the structure of VIIa was established to be 2-methoxymethylene-3-phenylpropionitrile.

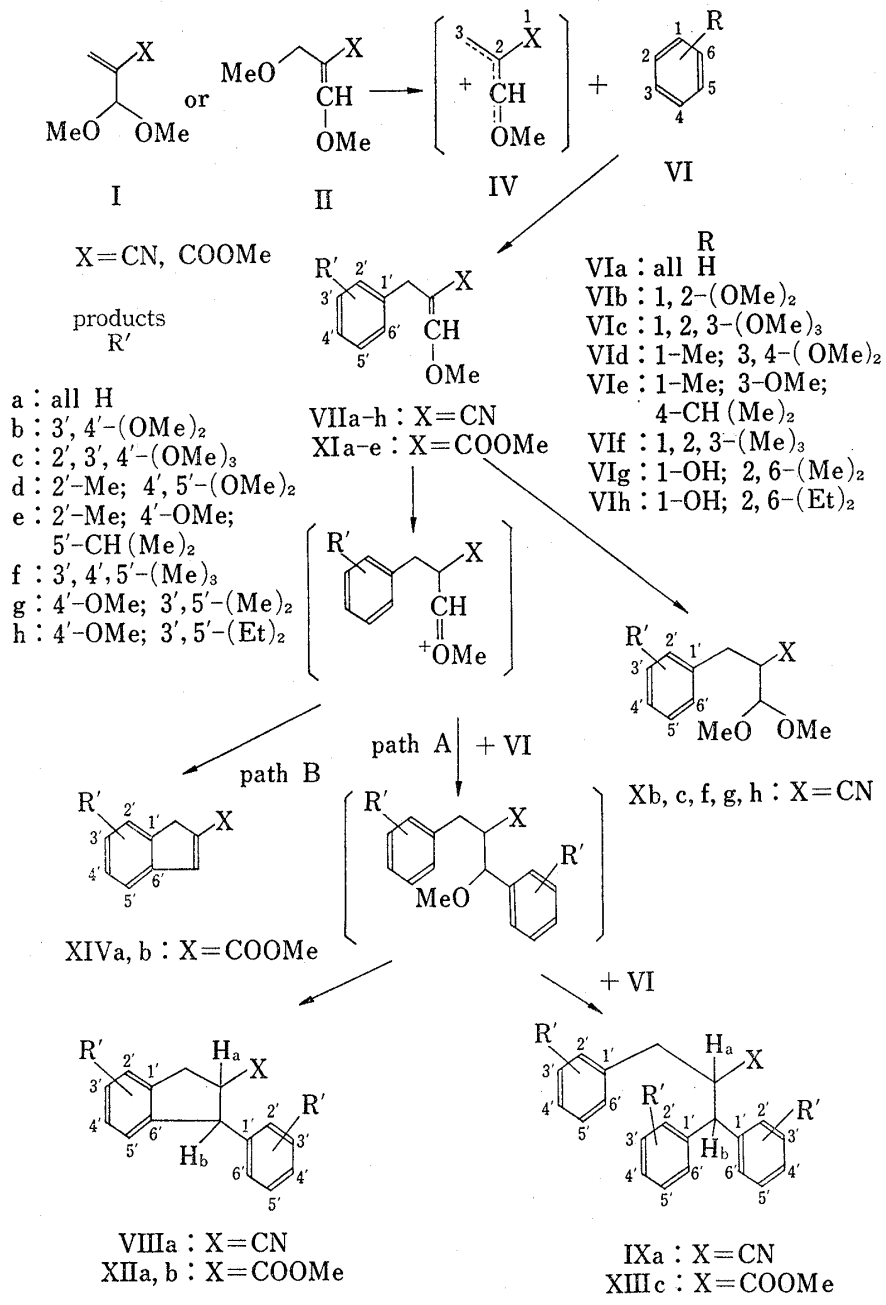

Chart 1

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When the reaction was prolonged, the 1:1-adduct (VIIa) was further converted into 1:2-(VIIIa) and 1:3-(IXa) adducts. The presence of Ph-CH_2-CH_a(-CN)-$CH_b<$ moiety in VIIIa was indicated by the IR and NMR spectra exhibiting the non-conjugated nitrile (2240 cm^{-1}) and phenyl (1600 cm^{-1}) absorption bands and an A_2BX-pattern signal. The X-part signal due to the H_b proton of the above partial structure, appearing as a doublet (J=8 Hz) at lower field (4.50 ppm), was assigned to the methine proton of a diphenylmethyl group. The presence of two phenyl groups indicated that one of them was attached to the both carbons of the methylene and $-CH_b<$ groups to form a five-membered ring. Thus the structure of VIIIa was determined as 2-cyano-1-phenylindan. Judging from the quite similar spectra, the structure of the 1:3-adduct (IXa) was assigned to 2-cyano-1,1,3-triphenylpropane.

Similar results were obtained from the $AlCl_3$-catalyzed reaction of II (X=CN) with benzene. These facts obviously indicate that the 1:1-adduct (VIIa) should be formed by the electrophilic substitution of the allyl cation IV (X=CN) at the C_3-position (see Chart 1) and that the 1:2-(VIIIa) and 1:3-(IXa) adducts should arise from VIIa *via* successive intra- and/or intermolecular substitutions of benzene at the carbon carrying the methoxy group (see path A in Chart 1).

When either I (X=CN) or II (X=CN) was reacted with a limited amount of benzenes (VIb—h) having electron-donating substituents, only the corresponding 1:1-adducts (VIIb—h) were obtained; no further reactions of VIIb—h with the benzene giving rise to the 1:2- and 1:3-adducts were observed. The results are summarized in Table I,

Table I. 2-Methoxymethylene-3-phenylpropionitriles (VII) obtained by the $AlCl_3$-Catalyzed Reaction of 2-Dimethoxymethylacrylonitrile (I, X=CN) with Benzenes (VIa—h)

Substrate (equiv.)	$AlCl_3$ (equiv.)	Solvent	Reaction Temp. (°C)	Reaction Time (hr)	Product (configuration)	Yield (%)	mp or bp (°C)	Formula	Analysis (%) Calcd. (Found) C	H	N
VIa (12.5)	4	None	7	0.5	VIIa (*cis*)	82	mp 81—82	$C_{11}H_{11}NO$	76.27 (76.51	6.40 6.52	8.09 8.13)
VIb (2.5)	4	None	r.t.	2.5	VIIb (*cis*)	50	mp 60—61.5	$C_{13}H_{15}NO_3$	66.93 (67.03	6.48 6.58	6.01 6.12)
					VIIb (*trans*)	5	Colorless oil bp 180 (2 mmHg)	$C_{13}H_{15}NO_3$	66.93 (66.65	6.48 6.71	6.01 5.91)
VIc (2.5)	4	None	r.t.	2.5	VIIc (*cis*)	64	mp 65.0	$C_{14}H_{17}NO_4$	63.86 (64.12	6.51 6.55	5.32 5.13)
					VIIc (*trans*)	6	Colorless oil bp 185 (2 mmHg)	$C_{14}H_{17}NO_4$	63.86 (64.03	6.51 6.44	5.32 5.05)
VId (2.5)	4	None	5—30	2	VIId (*cis*)	81	mp 86—88	$C_{14}H_{17}NO_3$	67.99 (68.02	6.93 6.87	5.66 5.73)
VIe (2.0)	4	None	r.t.	2	VIIe (*cis*)	56	mp 52—54	$C_{16}H_{21}NO_2$	74.10 (74.16	8.16 8.18	5.40 5.22)
VIf (0.7)	1	Cl⟨⟩Cl	r.t.	3	VIIf (*cis*)	65	mp 74—76	$C_{14}H_{17}NO$	78.10 (77.86	7.96 8.04	6.51 6.66)
VIg (1.0)	2	Cl⟨⟩Cl	70	3	VIIg (*cis*)[a]	50	mp 85—86	$C_{14}H_{17}NO_2$	72.70 (72.59	7.41 7.36	6.06 6.16)
					VIIg (*trans*)[a]	8	Colorless oil bp 170 (1 mmHg)	$C_{14}H_{17}NO_2$	72.70 (72.47	7.41 7.42	6.06 6.11)
VIh (1.5)	1.5	Cl⟨⟩Cl	50	0.75	VIIh (*cis*)[a]	57	Colorless oil bp 220 (2 mmHg)	$C_{16}H_{21}NO_2$	74.01 (74.10	8.11 8.10	5.30 5.40)
					VIIh (*trans*)[a]	3	mp 40—42	$C_{16}H_{21}NO_2$	74.01 (74.40	8.16 8.18	5.40 5.35)

a) The product was obtained by the methylation of crude reaction products with dimethyl sulfate in the presence of potassium carbonate under reflux for several hours in acetone.

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which shows that the electrophilic substitution of the allyl cation IV (X=CN) occurs selectively to give one positional isomer anticipated from the substituent effects of aromatics. The positions of substitution were indicated by the splitting pattern of the aromatic protons of products (see Table II); the *ortho*-positional protons of VIIc appeared as a double-doublet

Table II. NMR Spectra[a] of 2-Methoxymethylene-3-phenylpropionitriles

VII (configuration)	Solvent	$-CH_2-$	=CH–O	=CH–OMe	Ph–H	Substituents
VIIa (*cis*)	CCl_4	3.30(d) (J=1 Hz)	6.42(t)	3.75	7.18(br. s) (5H)	
VIIb (*cis*)	CCl_4	3.21(d) (J=1 Hz)	6.41(t)	3.80	6.64(br. s) (3H)	3.78(2×OMe)
VIIb (*trans*)	CCl_4	3.31(br. s)	6.66[b]	3.80	6.66(s) (3H)	3.76, 3.80(2×OMe)
VIIc (*cis*)	CCl_4	3.32(d) (J=1 Hz)	6.46(t)	3.87	6.54(d), 6.80(d) (each 1H, J=8 Hz)	3.80(3×OMe)
VIIc (*trans*)	CCl_4	3.34(d) (J=0.5 Hz)	6.70(t)	3.86	6.50(d), 6.76(d) (each 1H, J=8 Hz)	3.80(3×OMe)
VIId (*cis*)	CCl_4	3.23(d) (J=1 Hz)	1.21(t)	3.78	6.58(br. s) (2H)	2.20(Me), 3.78(2×OMe)
VIIe (*cis*)	CCl_4	3.23(d) (J=1 Hz)	6.21(t)	3.74	6.53(br. s), 6.86(br. s) (each 1H)	1.16(d)(J=7 Hz, CH-(Me)$_2$), 2.22(Me), 3.0—3.5 (m) (CH-(Me)$_2$)
VIIf (*cis*)	$CDCl_3$	3.38(d) (J=1 Hz)	6.33(t)	3.75	6.93(br. s) (2H)	2.22, 2.27(3×Me)
VIIg (*cis*)	$CDCl_3$	3.25(br. s)	6.58(t) (J=1 Hz)	3.80	6.83(br. s) (2H)	2.28(2×Me), 3.72(OMe)
VIIg (*trans*)	CCl_4	3.27(br. s)	6.69(t) (J=0.5 Hz)	3.78	6.77(br. s) (2H)	2.23(2×Me), 3.66(OMe)
VIIh (*cis*)	CCl_4	3.20(br. s)	6.48(t) (J=1 Hz)	3.74	6.88(br. s) (2H)	1.22(t)(J=7 Hz, 2×CH_2-Me), 2.62(q)(J=7 Hz, 2×CH_2-Me), 3.68(OMe)
VIIh (*trans*)	CCl_4	3.32(br. s)	6.70(t) (J=0.5 Hz)	3.83	6.81(br. s) (2H)	1.23(t)(J=7Hz, 2×CH_2-Me), 2.63(q)(J=7Hz, 2×CH_2-Me), 3.70(OMe)

a) Abbreviation: s=singlet, br.s=broad singlet, d=doublet, t=triplet, q=quartet, m=multiplet.
b) Overlapped with aromatic protons.

(J=8 Hz) due to the *ortho*-coupling while the *para*- and *meta*-positional protons of VIId, e and VIIf—h, respectively, appeared as single or a pair of broad-singlets. The structure of VIIb was corroborated by the experimental fact that VIIb underwent the Michael-addition of methanol upon treatment with sodium methoxide in methanol to give 2-dimethoxymethyl-3-[(3′,4′-dimethoxy)phenyl]propionitrile (Xb) which was identical with a sample synthesized by the known method.[5] The compounds VIIc,f,g,h were similarly converted into the corresponding methanol-adducts Xc,f,g,h by the Michael-addition of methanol. Analytical and NMR spectral data are shown in Table III.

From the chemical-shift values of the olefinic protons, the compounds VIIa—h thus obtained were assigned to be the *cis* configuration with respect to the nitrile group and the methoxy group of the 2-methoxymethylene moiety. In some cases, the corresponding *trans* isomers were detected as minor components in each reaction mixture and separated by chromatography (see Table I). The olefinic protons of the *cis* and *trans* isomers resonated at higher and lower fields, respectively, (see Table II), as exhibited in the NMR spectra of analogous compounds.[6] The predominant formation of the *cis* isomers should be due to

5) M. Hoffer, E. Grunberg, M. Mitrovic, and A. Brossi, *J. Med. Chem.*, **14**, 462 (1971).
6) See ref. 3). References are cited therein.

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Table III. 2-Dimethoxymethyl-3-phenylpropionitriles

	mp or bp (°C)	Formula	Analysis (%) Calcd. C	H	N	Found C	H	N
Xb	mp 50—51	$C_{14}H_{19}NO_4$	63.38	7.22	5.28	63.60	7.32	5.50
Xc	Colorless oil bp 180 (2 mmHg)	$C_{15}H_{21}NO_5$	61.00	7.17	4.74	61.23	7.23	4.64
Xf	Colorless oil bp 180 (4 mmHg)	$C_{15}H_{21}NO_2$	72.84	8.56	5.66	72.81	8.54	5.70
Xg	Colorless oil	$C_{15}H_{21}NO_3$	68.41	8.04	5.32	68.66	8.06	5.36
Xh	Colorless oil bp 210 (3 mmHg)	$C_{17}H_{25}NO_3$	70.07	8.65	4.81	69.87	8.71	4.76

	NMR spectra[a] $-CH_2-\underline{C}H-CN$	$-\underline{C}H(O)_2$	$\underline{C}H(OMe)_2$	Ph-H	Substituents
Xb	2.7—2.8(m)	4.28(m)	3.38 3.42	6.72(3H)	3.77, 3.80 (2×OMe)
Xc	2.6—3.3(m)	4.43(d) (J=5 Hz)	3.42 3.48	6.60(d)(1H) 6.92(d)(1H) (J=8 Hz)	3.83, 3.85, 3.92 (3×OMe)
Xf	2.7—3.2(m)	4.36(m)	3.40 3.42	6.87(s)(2H)	2.18, 2.22, 2.86 (3×Me)
Xg	2.6—3.2(m)	4.40(d) (J=5.5 Hz)	3.45 3.49	6.90(br. s) (2H)	2.28(2×Me) 3.72(OMe)
Xh	2.5—2.9(m)	4.32(m)	3.40 3.42	6.88(br. s) (2H)	1.32(t)(2×CH_2Me) 2.65(q)(2×CH_2Me) 3.70(OMe)

a) Xb, f, h were measured on CCl_4 solution and Xc, g on $CDCl_3$ solution.

Table IV. Methyl 2-Methoxymethylene-3-phenylpropionates

XI (configuration)	Yield (%)	Appearance mp or bp (°C)	Formula	Analysis (%) Calcd. (Found) C	H	NMR spectra[a] $-CH_2-$	=CH(O)(OMe)	COOMe	Ph-H
XIa (*trans*)	2	Colorless oil bp 150 (2 mmHg)	$C_{12}H_{14}O_3$	69.88 (70.00	6.84 6.83)	3.60(s)	7.40(s) 3.86	3.69	7.22(br.s)(5H)
XIb (*trans*)	32	Colorless oil bp 180 (2 mmHg)	$C_{14}H_{18}O_5$	63.14 (63.05	6.81 6.89)	3.52(s)	7.37(br.s) 3.86	3.69	6.78(m)(3H)
XIc (*trans*)	39	White crystals mp 65—66	$C_{15}H_{20}O_6$	60.80 (60.85	6.80 6.95)	3.55(br.s)	7.42(br.s) 3.89	3.67	6.52(d), 6.78(d) (each 1H, J=8 Hz)
XId (*trans*)	55	Colorless oil bp 180 (2 mmHg)	$C_{15}H_{20}O_5$	64.27 (64.30	7.19 7.39)	3.38(br.s)	7.24(br.s) 3.82	3.61	6.48(s)(1H) 6.57(s)(1H)
XIe (*trans*)	53	Colorless oil	$C_{17}H_{24}O_4$	69.83 (69.84	8.27 8.27)	3.37(br.s)	7.23(br.s) 3.82	3.60	6.42(s)(1H) 6.84(s)(1H)
XIe (*cis*)	2	Colorless oil	$C_{17}H_{24}O_4$	69.83 (69.62	8.27 8.28)	3.32(d) 5.85(t) (J=1 Hz)	3.78	3.62	6.50(s)(1H) 6.82(s)(1H)

a) XIa, b, c were measured on $CDCl_3$ solution and XId, e on CCl_4 solution.

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the electrophilic attack of the allyl cation IV (X=CN) having the same configuration; kinetic evidences are given in our preceding paper[3] that the cation IV (X=CN) of the *cis* configuration is more stable and more reactive than the *trans* counterpart.

The same reactions of methyl 2-dimethoxymethylacrylate (I, X=COOMe) or methyl 2-methoxymethylene-3-methoxypropionate (II, X=COOMe) with benzenes (VI) were somewhat different from the above reactions, providing the *trans* isomers of methyl 2-methoxymethylene-3-phenylpropionates (XI) and secondary reaction products. Analytical and spectral data of the products XI are shown in Table IV. The preferencial formation of the *trans* isomers of XI should be attributable to the electrophilic attack of the allyl cation IV (X=COOMe) of the *trans* configuration. This is also consistent with the greater reactivity of the cation IV (X=COOMe) having the *trans* configuration.[3] With thymol methyl ether (VIe) having bulky isopropyl substituent, the reaction afforded the corresponding *cis* isomer as a minor component of the reaction products. The olefinic-proton signal of the *cis* isomer appeared at much higher field (5.85 ppm) than those of all *trans* isomers (7.23—7.40 ppm) in the NMR spectrum (Table IV).

Secondary reaction products, indan-(XIIa, XIIb) and triphenylpropane-(XIIIc) derivatives corresponding to the 1:2- and 1:3-adducts, respectively, were also separated from these reactions by chromatography. Another-type products XIVa and XIVb were isolated from the reaction mixtures in small amounts along with XIIa and XIIb, respectively. The structures of these products were identified as 2-carbomethoxy-1H-indene (XIVa) and its 5,6-dimethoxy derivative (XIVb) by the elementary and spectral analyses. The indenes should be formed by the acid-catalyzed intramolecular cyclization of the 1:1-adducts (XI) (path B in Chart 1).

Sulfuric acid was proved to be an efficient catalyst for providing the 1:1-adducts (VII, XI) in the above reactions and also in the reactions starting with III (X=CN) and methyl 2-dimethoxymethyl-3-methoxypropionate (III, X=COOMe).

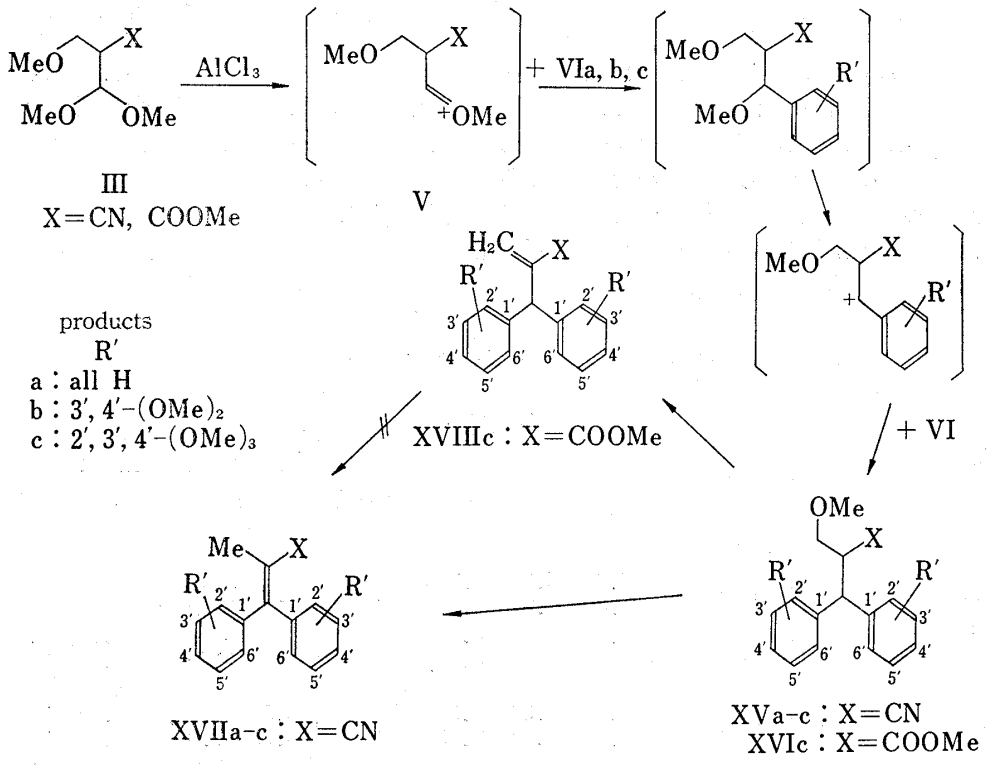

Chart 2

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Electrophilic Substitution of Oxocarbonium Ion V

When III (X=CN) was treated with anhydrous aluminum chloride in benzene at room temperature for 2.5 hr, another-type 1: 2-adduct, $C_{17}H_{17}NO$ (mp 62—64°) was obtained as a main product. This product, quite different from the 1: 2-adduct indan (VIIIa), had a moiety of CH_3O–CH_2–CH(–CN)–CH< originated from the starting material III (X=CN). A signal due to a diphenylmethyl group appeared in the NMR spectrum instead of the signal due to the acetal group of III (X=CN). Therefore the structure of the product was elucidated to be 2-methoxymethyl-3,3-diphenylpropionitrile (XVa).

The compound XVa should be formed by the electrophilic substitution of the oxocarbonium ion V (X=CN) which is generated from III (X=CN). A possible formation pathway is depicted in Chart 2 where two methoxy groups of the acetal moiety of III (X=CN) are successively substituted by two phenyl groups.

Similarly, the corresponding 1: 2-adducts XVb and XVc were obtained from the $AlCl_3$-catalyzed reaction of III (X=CN) with the benzenes VIb and VIc, respectively. Data are shown in Table V. Contrary to the above, the same reactions of III (X=COOMe) with ben-

Table V. 2-Methoxymethyl-3,3-diphenylpropionitriles

	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd. (Found) C	H	N	NMR spectra in $CDCl_3$ $-CH_2-OMe$	$O-CH_2-$ $CH-CN$	$CH(Ph)_2$	Ph–H
XVa	12	62— 64	$C_{17}H_{17}NO$	81.24 (81.52	6.82 6.92	5.57 5.71)	3.31	3.2—3.7(m)	4.34(m)	7.30(m) (10H)
XVb	33	115—116	$C_{21}H_{25}NO_5$	67.90 (67.85	6.78 6.98	3.77 3.93)	3.33	3.2—3.6(m)	4.22(m)	6.83(m) (6H)
XVc	10	128—129	$C_{23}H_{29}NO_7$	64.02 (64.06	6.77 6.80	3.25 3.25)	3.33	3.3—3.7(m)	4.93(m)	6.58, 6.65, 6.95, 7.16 (each doublet, J=8 Hz)

zenes VIa—c predominantly gave the corresponding 1: 1-adducts XIa—c. Exceptionally a small amount of the expected 1: 2-adduct, methyl 3,3-bis(2′,3′,4′-trimethoxyphenyl)-2-methoxymethylpropionate (XVIc) was obtained in the case of VIc. These results can be also explained by our previous kinetic study,[3] that is, the oxocarbonium ion V (X=COOMe) is rapidly converted into the allyl cation IV (X=COOMe).

The 1: 2-adducts XVa—c underwent elimination of methanol (retro Michael-addition) and successive allylic rearrangement to give 2-cyano-1,1-diphenyl-1-propenes XVIIa—c

Table VI. 2-Cyano-1,1-diphenyl-1-propenes

	Appearance	Formula	Analysis (%) Calcd. (Found) C	H	N	NMR spectra in CCl_4 =C–Me	Ph–H	Substituents
XVIIa	Colorless oil	$C_{16}H_{13}N$	87.64 (87.69	5.98 5.99	6.39 6.20)	2.02(s)	7.0—7.4(m)	
XVIIb	White crystals mp 96—98°	$C_{20}H_{21}NO_4$	70.78 (71.01	6.24 6.41	4.13 4.35)	2.05(s)	6.5—7.0(m)	3.73, 3.78, 3.81, 3.82 (4×OMe)
XVIIc	Colorless oil	$C_{22}H_{25}NO_6$	66.15 (66.31	6.31 6.61	3.51 3.45)	1.92(s)	6.51, 6.60, 6.72, 7.00 (each doublet, J=9 Hz)	3.49, 3.64, 3.75, 3.78, 3.80, 3.83 (6×OMe)

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when they were refluxed in methanol in the presence of sodium methoxide. The structures of XVa—c were assigned by the NMR spectra which exhibited the singlet-signals due to methyl groups attached to double bond (see Table VI). However, the compound XVIc was not converted into the expected 1-propene but 1,1-bis(2′,3′,4′-trimethoxyphenyl)-2-carbomethoxy-2-propene (XVIIIc) by the same treatment. The structure of XVIIIc was identified by the comparison of the IR and NMR spectra with those of the parent compound I (X=COOMe). The rearrangement of XVIIIc to a planar 1-propene is unlikely because of the steric interaction between the methoxycarbonyl group and the aromatic substituents.

Synthetic Application to Heterocycles

Some heterocycles could be obtained by incorporating I or III into phenol or aniline (see Chart 3). 3-Cyano-2-methoxychroman (XIX) was obtained from the reaction of III (X=CN) with an excess of phenol in the presence of sulfuric acid in a yield of 5.4%. The structure of XIX was identified by the elementary analysis and the NMR spectrum which exhibited A_2BX-pattern signal due to $-CH_2-CH(-CN)-CH<$ moiety. From the vicinal coupling constant (J=2 Hz) of the methine protons (BX part), XIX can be assigned as *trans* isomer.[7] As shown in Chart 3, the chroman XIX should be formed by the acid-catalyzed intramolecular acetalation of a 1:1-adduct (XX) which should be generated by the attack of the allyl cation IV (X=CN) at the *ortho* position to the hydroxy group of phenol.

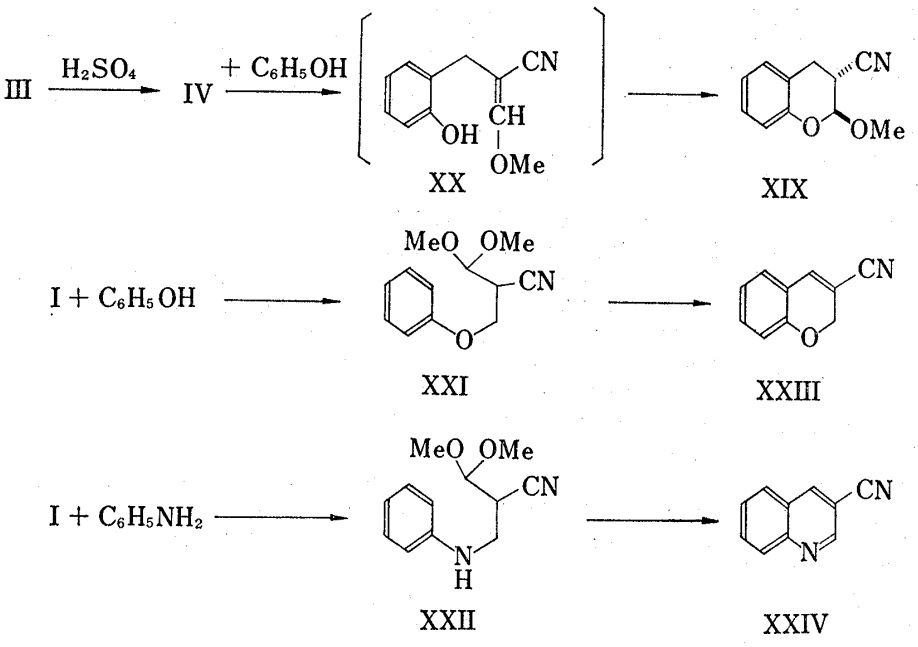

Chart 3

The Michael-type addition of phenol and aniline to I (X=CN) afforded 2-dimethoxymethyl-3-phenoxypropionitrile (XXI) (8% yield) and 3-anilino-2-dimethoxymethylpropionitrile (XXII) (17% yield), respectively, as in the early studies on the syntheses of the corresponding diethoxymethyl analogs.[8] Treatment of XXI with anhydrous aluminum chloride in dichloroethane resulted in cyclization to 3-cyano-2H-chromen (XXIII) (19% yield) which was assigned by elementary and spectral analyses. The same treatment of XXII and successive work up gave 3-cyanoquinoline (XXIV) (22% yield) which was identical with an authentic sample.[9]

7) J. Badin and G. Descotes, *Bull. Soc. Chim. Fr.*, **1970**, 1949.
8) K. Tokuyama, *Yakugaku Zasshi*, **79**, 814 (1959).
9) The sample was kindly supplied by Dr. M. Natsume, Director of Itsuu Laboratory.

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The present paper describes the synthetic usefulness of the allyl cation IV and the oxocarbonium ion V as the electrophilic reagents.

Experimental

Melting points were taken on a Yanagimoto micro melting point apparatus and are uncorrected. The spectra were recorded on the following instruments: IR, JASCO Model IRA-2 spectrophotometer; NMR, Varian A-60A spectrometer, using tetramethylsilane as an internal standard. Abbreviation used, s=singlet, d=doublet, t=triplet, m=multiplet, br.s=broad singlet, dd=double doublet. Thin-layer chromatography (TLC) were performed on silica gel (Wakogel) employing the following solvent systems: solvent a, ether: petr. ether (1: 1); solvent b, ether: petr. ether (1: 3); solvent c, ether: petr. ether (2: 1).

Reagents——The substituted benzenes (VI) used were obtained from Tokyo Kasei Co., and Kanto Kagaku Co., Ltd. They were reagent grade samples and were used without purification. Pyrogallol trimethyl ether [VIc, bp 90° (3 mmHg)], homocatechol dimethyl ether [VId, bp 90° (5 mmHg)], and thymol methyl ether [VIe, bp 79° (5 mmHg)] were obtained by the usual methylation of the corresponding phenolics with dimethyl sulfate. 2,6-Diethylphenol [VIh, bp 150° (50 mmHg)] were obtained by the acid hydrolysis of diazonium salts derived from 2,6-diethylaniline. These compounds were purified by distillation.

Preparation of 2-Methoxymethylene-3-phenylpropionitriles (VIIa—h)——General Procedure: To a mixture of anhyd. $AlCl_3$ (50 g) and benzene (60 ml) was added a benzene solution (20 ml) of I (X=CN, 12.02 g) on ice-cooling with stirring. The reaction mixture was stirred for 30 min at about 7°, poured into water (100 ml) with stirring, and acidified with 6% HCl (180 ml). The mixture was stirred for 1 hr and extracted with benzene. The extract was washed with water, dried with anhyd. $MgSO_4$, and evaporated to dryness. A residual oil was distilled to give 2-methoxymethylene-3-phenylpropionitrile (VIIa) as crystals (13.42 g, 82% yield). Recrystallization from methanol–petr. ether afforded colorless needles of mp 81—82°.

The substituted derivatives VIIb—h were obtained from the $AlCl_3$-catalyzed reactions of I (X=CN) or II (X=CN) with the substituted benzenes (VIb—h). The oily products obtained from the reactions with VIb, VIc, VIg, and VIh, were subjected to column chromatography on silica gel using solvent a. The fast eluates gave *trans* isomers of VIb, VIIc, VIIg, and VIIh which were purified by preparative TLC over silica gel using solvent a or b. The second eluates afforded the corresponding *cis* isomers. Data are summarized in Tables I and II.

2-Cyano-1-phenylindan (VIIIa) and 2-Cyano-1,1,3-triphenylpropane (IXa)——A mixture of I (X=CN, 3 g), benzene (20 ml), and anhyd. $AlCl_3$ (12.5 g) was stirred for 100 min on ice-cooling. After extraction with benzene and work up following the above procedure, the reaction mixture afforded an oil (3.49 g), which was submitted to column chromatography on silica gel (70 g) with benzene. The fast eluate gave an oil (1.66 g) and the second eluate contained VIIa mainly. A part of the oil (0.46 g) was subjected to preparative TLC on silica gel using solvent a. The upper zone on the chromatoplate gave 2-cyano-1-phenylindan (VIIIa) as white crystals (84 mg), mp 127—128° (from ether–petr. ether). *Anal.* Calcd. for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.92; H, 6.11; N, 6.53. IR ν_{max}^{Nujol} cm^{-1}: 2240 (C≡N), 1600 (Ph). NMR (CCl_4) δ: 2.85—3.45 (3H, m, Ph–C$\underline{H}_2$–C$\underline{H}$–CN), 4.50 (1H, d, J=8 Hz, Ph–C$\underline{H}$–Ph), 6.8—7.3 (9H, m, Ph). From the lower zone 2-cyano-1,1,3-triphenylpropane (IXa) was obtained as white crystals (126 mg), mp 100—105°. *Anal.* Calcd. for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.60; H, 6.55; N, 4.70. IR ν_{max}^{Nujol} cm^{-1}: 2240 (C≡N), 1600 (Ph). NMR ($CDCl_3$) δ: 2.79 (2H, d, J=7 Hz, Ph–C$\underline{H}_2$–C), 3.42 (1H, m, $CH_2C\underline{H}$–CN), 4.02 (1H, d, J=8 Hz, Ph–C$\underline{H}$–Ph), 7.20 (15H, m, Ph).

Conversion of VII into 2-Dimethoxymethyl-3-phenylpropionitriles (X)——General Procedure: A sample of VII (5 mmol) was dissolved in 2 N sodium methoxide–methanol solution (25 ml). The solution was kept overnight at room temperature, concentrated to *ca.* 5 ml under reduced pressure, and extracted with benzene. After the usual work up an oily substance was chromatographed over silica gel using solvent a, b, or c to give a methanol-adduct (X) almost quantitatively. Data are shown in Table III.

Reaction of I (X=COOMe) with Benzene in the Presence of Aluminum Chloride——A mixture of I (X=COOMe, 2.7 g), benzene (3.3 g), and anhyd. $AlCl_3$ (6.25 g) was stirred for 3 hr at room temperature. After the usual work up an oily substance was distilled to give an oil (1.45 g), bp 110—150° (1—2 mmHg), which was subjected to column chromatography on silica gel using solvent b. The first eluate contained diphenylmethane (30 mg) mainly. The second eluate gave an oil (1.24 g) which was submitted to preparative TLC over silica gel using solvent b. The upper zone on the chromatoplate gave crystals (1.0 g) of 2-carbomethoxy-1-phenylindan (XIIa), mp 66—67.5° (from ethanol) and the lower zone afforded crystals (0.2 g) of 2-carbomethoxy-1H-indene (XIVa), mp 81.5—82.5° (from ethanol). The third eluate gave methyl 2-methoxymethylene-3-phenylpropionate (XIa) as an oil (0.1 g, 2% yield) which was purified by preparative TLC. XIIa, *Anal.* Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.01; H, 6.35. IR ν_{max}^{Nujol} cm^{-1}: 1740 (C=O), 1610, 1590 (Ph). NMR ($CDCl_3$) δ: 3.30 (3H, m, Ph–C$\underline{H}_2$–C$\underline{H}$–COOMe), 3.67 (3H, s, COO$\underline{Me}$), 4.70 (1H, m, Ph–C$\underline{H}$–Ph), 6.8—7.4 (9H, m, Ph). XIVa, *Anal.* Calcd. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 76.05; H, 5.75. IR ν_{max}^{Nujol} cm^{-1}: 1710 (C=O), 1640 (C=C, very weak), 1610, 1590 (Ph). NMR ($CDCl_3$) δ: 3.67 (2H, d, J=2 Hz, Ph–C$\underline{H}_2$–C), 3.78 (3H, s, COO$\underline{Me}$), 7.1—7.5 (4H, m, Ph), 7.60 (1H, t, J=2 Hz, C=C$\underline{H}$–C).

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Reaction of I (X=COOMe) with Pyrocatechol Dimethyl Ether (VIb) in the Presence of Aluminum Chloride——A mixture of I (X=COOMe, 2.7 g), VIb (5.96 g), and anhyd. $AlCl_3$ (6.25 g) was stirred for 2.5 hr at room temperature. After the usual work up distillation of the residual oil gave an oil (1.9 g), bp 150—180° (2 mmHg), and crystals of 2-carbomethoxy-5,6-dimethoxy-1-[(3′,4′-dimethoxy)phenyl]indan (XIIb), mp 112—113° (from methanol). The oily substance was submitted to preparative TLC on silica gel using solvent a. The upper zone gave 2-carbomethoxy-5,6-dimethoxy-1H-indene (XIVb) as crystals (0.3 g), mp 124—125° (from methanol) and the lower zone afforded methyl 2-methoxymethylene-3-[(3′,4′-dimethoxy)phenyl]-propionate (XIb) as an oil (1.6 g, 32% yield). XIIb, *Anal.* Calcd. for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50. Found: C, 67.62; H, 6.57. IR ν_{max}^{Nujol} cm^{-1}: 1735 (C=O), 1600 (Ph), NMR ($CDCl_3$) δ: 3.21 (3H, m, Ph–C<u>H</u>$_2$–C<u>H</u>–COOMe), 3.69 (3H, s, COO<u>Me</u>), 3.73, 3.80, 3.87 (12H, each s, 4×OMe), 4.58 (1H, m, Ph–C<u>H</u>–Ph), 6.43—6.80 (5H, m, Ph). XIVb, *Anal.* Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.88; H, 6.17. IR ν_{max}^{Nujol} cm^{-1}: 1700 (C=O), 1600 (Ph). NMR ($CDCl_3$) δ: 3.61 (2H, d, J=1 Hz, Ph–C<u>H</u>$_2$–C), 3.83 (3H, s, COO<u>Me</u>), 3.91 (6H, s, 2×OMe), 7.03 (2H, br.s, Ph), 7.62 (1H, t, J=1 Hz, C=C<u>H</u>–C).

Reaction of I (X=COOMe) with Pyrogallol Trimethyl Ether (VIc) in the Presence of Aluminum Chloride——The same treatment of a mixture of I (X=COOMe, 2.7 g), VIc (7.35 g), and anhyd. $AlCl_3$ (6.25 g) as the above gave an oily substance (2.2 g), bp 200° (2 mmHg), which was purified by preparative TLC on silica gel using solvent a to afford methyl 2-methoxymethylene-3-[(2′,3′,4′-trimethoxy)phenyl]propionate (XIc) as white crystals (1.9 g, 39% yield), mp 65—66°. The distillation residue (3.45 g) was chromatographed over silica gel using solvent c to give methyl 2-carbomethoxy-1,1,3-tri[(2′,3′,4′-trimethoxy)phenyl]propane (XIIIc) as crystals (1.3 g), mp 125—126° (from methanol). *Anal.* Calcd. for $C_{32}H_{40}O_{11}$: C, 63.99; H, 6.71. Found: C, 64.08; H, 6.65. IR ν_{max}^{Nujol} cm^{-1}: 1730 (C=O), 1600 (Ph). NMR ($CDCl_3$) δ: 2.6—2.8 (2H, m, Ph–C<u>H</u>$_2$–CH<), 3.30 (3H, s, COO<u>Me</u>), 3.75, 3.80, 3.84, 3.90 (27H, each s, 9×OMe), 4.91 (1H, d, J=11 Hz, Ph–C<u>H</u>–Ph), 6.48, 6.58, 6.65, 6.72 (each 1H, d, J=8 Hz, Ph), 7.14 (2H, d, J=8 Hz, Ph).

Reaction of II (X=COOMe) with Thymol Methyl Ether (VIe) in the Presence of Aluminum Chloride——A mixture of II (X=COOMe, 2.7 g), VIe (6.9 g), and anhyd. $AlCl_3$ (6.25 g) was stirred for 1 hr at room temperature. After the usual work up an oily residue was chromatographed over silica gel using solvent b. The first fraction gave an oil (2.6 g) which was a complex mixture. The second fraction afforded *trans* isomer of methyl 2-methoxymethylene-3-[(2′-methyl-4′-methoxy-5′-isopropyl)phenyl]propionate (XIe) as an oil (2.6 g, 53% yield). The third fraction gave an oil (0.22 g) which was purified by preparative TLC using solvent a to afford the corresponding *cis* isomer as an oil (0.11 g).

Reaction of III (X=CN, COOMe) with Benzenes (VI) catalyzed by Sulfuric Acid——General Procedure: To a mixture of III (X=CN or COOMe) and a benzene derivative (VI) was added conc. H_2SO_4. After stirring the reaction mixture was poured into water and extracted with benzene. The extract was washed with water and evaporated. Residual oil was distilled or chromatographed to give products. The results are summarized in Table VII.

Table VII. Products obtained by the Sulfuric Acid-Catalyzed Reaction of III (X=CN, COOMe) with Benzenes (VI)

Reagents			Reaction		Products[c] (Yield, %)
III (equiv.)	VI (equiv.)	H_2SO_4 (equiv.)	Temp. (°C)	Time (hr)	
X=CN (1)	VIb (3)	1.0	50	7	VIIb (9) + Xb (45)
X=CN (1)	VIb (3)	0.5	50	0.5[a]	VIIb (48)
X=CN (1)	VIc (2.5)	0.5	r.t.	2.5	VIIc (16) + Xc (16)
X=CN (1)	VIf (0.67)	0.5	50	1	VIIf (37) + Xf (28)
X=CN (1)	VIg (0.67)	0.5	50	1.5[b]	VIIg (3) + Xg (12)
X=CN (1)	VIh (1.5)	0.5	50	0.75[b]	VIIh (9) + Xh (23)
X=COOMe (1)	VIa (2.5)	0.5	r.t.	24	XIa (0.6)
X=COOMe (1)	VIc (2.5)	0.5	r.t.	24	XIc (74)
X=COOMe (1)	VId (2.3)	0.5	r.t.	24	XId (90)

a) Carried out under reduced pressure.
b) After the reaction the crude products obtained by distillation were methylated with dimethyl sulfate by the same procedure as mentioned in Table I.
c) The products X should be formed by the acid-catalyzed addition of methanol to VII during the reaction in which methanol is released from III.

2-Methoxymethyl-3,3-diphenylpropionitrile (XVa)——To a mixture of III (X=CN, 3.76 g) and benzene (20 ml) was added anhyd. $AlCl_3$ (12.6 g). The reaction mixture was stirred for 4 hr at 0—3°. After the usual work up an oily substance (5.56 g) was chromatographed over silica gel with benzene. The first eluate

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gave an oil (2.59 g) which was a mixture of diphenylmethane and an unknown product. The second eluate afforded an oil (2.28 g) which was purified by preparative TLC over silica gel using solvent b to provide XVa as white crystals (738 mg, 12% yield), mp 62—64°.

3,3-Bis(3′,4′-dimethoxyphenyl)-2-methoxymethylpropionitrile (XVb)——A mixture of III (X=CN, 7.2 g), VIb (15.5 g), and anhyd. $AlCl_3$ (25 g) was stirred for 2.5 hr at 25—35°. After work up, ether was added to a residual oil (19 g) to give XVb as crystals (5.5 g, 33% yield), mp 115—116° (from methanol).

3,3-Bis(2′,3′,4′-trimethoxyphenyl)-2-methoxymethylpropionitrile (XVc)——A mixture of III (X=CN, 7.2 g), VIc (19 g), and anhyd. $AlCl_3$ (25 g) was stirred for 3.5 hr at room temperature. After work up, distillation of the oily residue (22 g) gave a mixture of VIIc and XVc as an oil (5.0 g) which could not be separated by chromatography. Thus the mixture was treated with 2 M sodium methoxide in methanol (50 ml) at room temperature for 2 days in order to convert VIIc into the methanol-adduct (Xc). After the usual work up the mixture of Xc and XVc was separated by column chromatography on silica gel using solvent a. The first fraction gave Xc and the second fraction afforded XVc as crystals (2.0 g, 10% yield), mp 128—129° (from ether).

Methyl 3,3-Bis(2′,3′,4′-trimethoxyphenyl)-2-methoxymethylpropionate (XVIc)——A mixture of III (X=COOMe, 3.24 g), VIc (7.09 g) and anhyd. $AlCl_3$ (6.25 g) was stirred for 3 hr at room temperature. After the usual work up an oily substance was chromatographed over silica gel with solvent a. The first eluate gave XIc (2.7 g) and the second eluate afforded XVIc as crystals (0.7 g, 9.6% yield), mp 126—128° (from methanol). *Anal.* Calcd. for $C_{24}H_{32}O_9$: C, 62.05; H, 6.94. Found: C, 61.95; H, 6.99. IR ν_{max}^{Nujol} cm^{-1}: 1730 (C=O), 1600 (Ph). NMR ($CDCl_3$) δ: 3.24 (3H, s, CH_2–OMe), 3.2—3.8 (3H, m, –CH_2–CH–CN), 3.51 (3H, s, COOMe), 3.72, 3.80, 3.82, 3.87 (6×OMe), 4.80 (1H, m, Ph–CH–Ph), 6.56, 6.60, 6.93, 7.23 (each 1H, d, J=8 Hz, Ph).

Conversion of XVa—c into 2-Cyano-1,1-diphenyl-1-propenes (XVIIa—c)——General Procedure: A sample of XV (2.6 mmol) was dissolved in 1 N sodium methoxide–methanol solution (18 ml). The solution was refluxed for 2.5 hr, concentrated, and extracted with benzene. After work up an oily substance was purified by preparative TLC using solvent a or b to give XVII (*ca.* 90% yield). Data are summarized in Table VI.

Conversion of XVIc into 1,1-Bis(2′,3′,4′-trimethoxyphenyl)-2-carbomethoxy-2-propene (XVIIIc)——The same treatment of XVIc (100 mg) as the above gave XVIIIc as an oil (57 mg, 62% yield). *Anal.* Calcd. for $C_{23}H_{28}O_8$: C, 63.88; H, 6.53. Found: C, 63.83; H, 6.74. IR ν_{max}^{film} cm^{-1}: 1725 (C=O), 1630 (C=C), 1600 (Ph). NMR ($CDCl_3$) δ: 3.69 (3H, s, COOMe), 3.80, 3.84, 3.87 (each 6H, s, 6×OMe), 5.17 (1H, t, J=1 Hz, Ph–CH–Ph), 5.90 (1H, t, J=1 Hz, H/H>=<COOMe), 6.47 (1H, t, J=1 Hz, H/H>=<COOMe), 6.58 (4H, s, Ph).

3-Cyano-2-methoxychroman (XIX)——To a stirred mixture of III (X=CN, 10 g) and phenol (6.0 g) was added conc. H_2SO_4 (3.08 g). The reaction mixture was stirred for 2 hr at room temperature and extracted with benzene. The extract was washed with dil. aq. NaOH and then with water and evaporated to give an oily residue (4.0 g). This oil was distilled to afford an oily substance (1.5 g) which was subjected to preparative TLC over silica gel using solvent a to give XIX as white needles (0.64 g, 5.4% yield), mp 96—97.5°. *Anal.* Calcd. for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.72; H, 5.84; N, 7.14. IR ν_{max}^{Nujol} cm^{-1}: 2250 (C≡N), 1610, 1590 (Ph). NMR ($CDCl_3$) δ: 2.80—3.43 (3H, m, Ph–CH_2–CH–CN), 3.55 (3H, s, O–CH–OMe), 5.26 (1H, d, J=2 Hz, –O–CH–OMe), 6.75—7.30 (4H, m, Ph).

3-Cyano-2H-chromen (XXIII)——A benzene solution of I (X=CN, 10 g), phenol (15 g), and triethylamine (24 g) was refluxed for 11 hr. After removal of excess reagents under reduced pressure, the reaction mixture was extracted with ether. The extract was washed with water and evaporated to give an oily residue which was distilled to afford 2-dimethoxymethyl-3-phenoxypropionitrile (XXI) as a colorless oil (1.4 g, 8% yield), bp 164° (5 mmHg). *Anal.* Calcd. for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.19; H, 6.86; N, 6.16. IR ν_{max}^{film} cm^{-1}: 2250 (C≡N), 1600 (Ph), 1130, 1080 (acetal). NMR (CCl_4) δ: 3.10 (1H, q, J=5.5 Hz, CH_2–CH–CN), 3.41, 3.48 (each 3H, s, MeO–CH–OMe), 4.13 (2H, d, J=5.5 Hz, –CH_2–CHCN), 4.62 (1H, d, J=5.5 Hz, MeO–CH–OMe), 6.7—7.4 (5H, m, Ph). To a 1,2-dichloroethane solution (50 ml) of XXI (0.95 g) was added anhyd. $AlCl_3$ (1.14 g). The reaction mixture was refluxed for 2 hr. After work up a residual oil (0.8 g) was submitted to preparative TLC over silica gel using solvent a to give XXIII as white crystals (0.13 g, 19% yield), mp 48—49°. *Anal.* Calcd. for $C_{10}H_7NO$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.45; H, 4.67; N, 8.79. IR ν_{max}^{Nujol} cm^{-1}: 2200 (C≡N), 1640 (C=C), 1600 (Ph). NMR ($CDCl_3$) δ: 4.81 (2H, d, J=1.5 Hz, O–CH_2–C), 6.75—7.60 (5H, m, Ph–CH=C).

3-Cyanoquinoline (XXIV)——A mixture of I (X=CN, 5 g) and aniline (36.7 g) was refluxed for 5 hr. After removal of excess aniline under reduced pressure, a residual oil was distilled to give 3-anilino-2-dimethoxymethylpropionitrile (XXII) as a yellow-green oil (1.5 g, 17% yield), bp 150° (4 mmHg), which was purified by preparative TLC under the same conditions as the above to afford a colorless oil (1.3 g). *Anal.* Calcd. for $C_{12}H_{16}N_2O_2$: C, 65.43; H, 7.32; N, 12.72. Found: C, 65.31; H, 7.37; N, 12.93. IR ν_{max}^{film} cm^{-1}: 3400 (NH), 2250 (C≡N), 1600 (Ph), 1120, 1080 (acetal). NMR ($CDCl_3$) δ: 3.13 (1H, quartet-like, J=5 Hz, CH_2–CH–CN), 3.47, 3.49 (each 3H, s, MeO–CH–OMe), 3.50—3.60 (2H, overlapping with acetal-group signal, NH–CH_2–C), 3.68 (1H, br.s, NH, changeable with D_2O), 4.54 (1H, d, J=5 Hz, MeO–CH–OMe), 6.55—7.35 (5H, m, Ph). To a 1,2-dichloroethane solution (50 ml) of XXII (1.3 g) was added anhyd. $AlCl_3$ (2.36 g). The reaction mixture was refluxed for 3 hr. After cooling, 48% aq. NaOH was added to the mixture. The

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alkaline solution was extracted with 1,2-dichloroethane. The extract was washed with water and evaporated to give an oil (0.75 g), which was purified by preparative TLC over silica gel using solvent a to afford crude crystals of XXIV (0.2 g, 22% yield). Recrystallization from methanol gave white crystals (0.15 g), mp 108—109°. *Anal.* Calcd. for $C_{10}H_6N_2$: C, 77.90; H, 3.92; N, 18.17. Found: C, 77.81; H, 4.03; N, 18.26. The compound XXIV thus obtained was identified with an authentic sample[9] by the comparison of the melting point and IR and NMR spectra.

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