Substituted Benzylidenemalononitriles and Some Related Tributylphosphine Adducts

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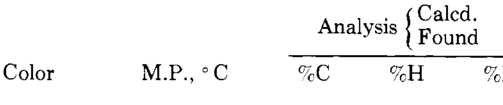
Several substituted benzylidenemalononitriles, diethyl 2-pyridylmethylenemalonate, and some related tributylphosphine adducts were synthesized and characterized. Yields, melting points, elemental analyses, and infrared data are reported.

IN A PROGRAM directed toward the development of compounds with herbicidal activity, several substituted benzylidenemalononitriles and related tributylphosphine adducts were prepared and their biological activities measured. The benzylidenemalononitriles were prepared by treatment of the substituted aromatic aldehyde with malononitrile in glacial acetic acid containing catalytic amounts of ammonium acetate and acetamide (*4*) or by azeotropic distillation of water from a benzene solution of

$$ArCHO + CH_2(CN)_2 \longrightarrow ArCH{=}C(CN)_2$$

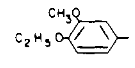
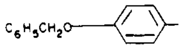
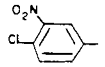
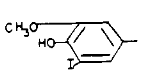
reactants and catalyst (*1, 2, 3*). The adducts were prepared by a known procedure (*4*).



$$(C_4H_9)_3P + ArCH{=}C(CN)_2 \longrightarrow (C_4H_9)_3\overset{\oplus}{P}{-}\underset{\displaystyle Ar}{CH}{-}\overset{\ominus}{C}(CN)_2$$

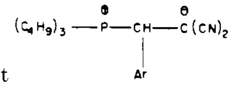
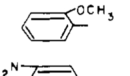
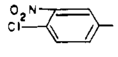
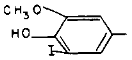
Tables I and II summarize the yields, melting points, and elemental analyses of the compounds prepared. Diethyl 2-pyridylmethylenemalonate was also synthesized by condensation of 2-pyridinecarboxaldehyde with diethyl malo-

Table I. Characterization of Some Substituted Benzylidenemalononitriles

No.	Compound	Ar	% Yield	Color	M.P., °C	Analysis {Calcd. Found} %C	%H	%N
1	4-Ethoxy-3-methoxybenzylidene-malononitrile	Ar–CH=C(CN)$_2$	40	Yellow[a]	139.5–41	68.4 68.1	5.3 5.3	12.3 12.3
2	*p*-Benzyloxybenzylidene-malononitrile		76	Pale[a] yellow	154–55	78.4 78.0	4.7 4.4	10.8 11.0
3	4-Chloro-3-nitrobenzylidene-malononitrile	 	49	Off-[a] white	139.5–41	51.4[b] 51.2	1.7 1.7	17.9 17.8
4	4-Hydroxy-3-iodo-5-methoxy-benzylidenemalononitrile		17	Bright[c] yellow	199–201	40.5 39.9	2.2 2.1	[d]

[a] Recrystallized from methanol. [b] Cl, calcd. 15.2; found, 15.1. [c] Recrystallized from benzene. [d] I, calcd., 38.9; found, 38.7.

Table II. Some Tributylphosphine Substituted Benzylidenemalononitrile Adducts

No.	Compound	Ar	% Yield	Color	M.P., °C	Analysis {Calcd. Found} %C	%H	%P
6	Tributylphosphine 2-methoxy-benzylidenemalononitrile adduct	 $(C_4H_9)_3{-}\overset{\oplus}{P}{-}\underset{\displaystyle Ar}{CH}{-}\overset{\ominus}{C}(CN)_2$	47	white	97.5–99	71.5 71.1	9.1 9.3	8.0 7.9
7	Tributylphosphine 4-chloro-3-nitrobenzylidenemalononitrile adduct		77	yellow	109–10	60.5 59.7[a]	7.1 6.7	7.1 6.5
8	Tributylphosphine 4-hydroxy-5-iodo-3-methoxybenzylidene-malononitrile adduct	 	62	tan	148–52	52.4 52.5	6.5 6.5	5.9 5.8

[a] Contaminated with 4-chloro-3-nitrobenzylidenemalononitrile, which was difficult to remove, even after repeated crystallizations.

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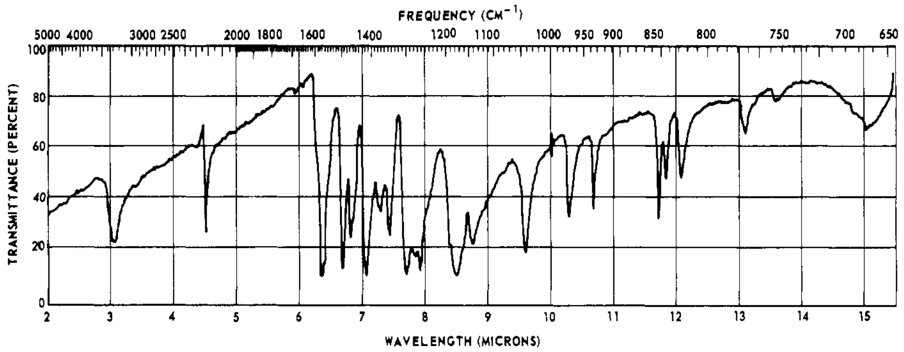

Figure 1. Infrared spectrum of 4-hydroxy-3-iodo-5-methoxybenzylidenemalononitrile

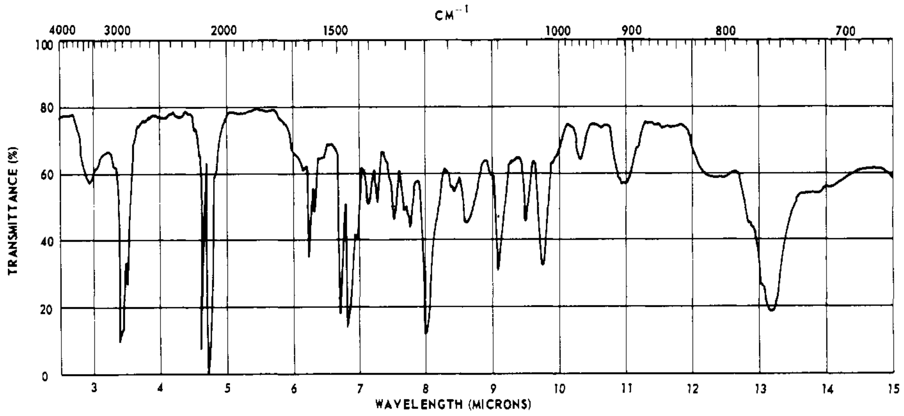

Figure 2. Infrared spectrum of tributylphosphine 2-methoxybenzylidenemalononitrile adduct

Table III. Characteristic Infrared Absorption of Some Substituted Benzylidenemalononitriles and Diethyl 2-Pyridylmethylenemalonate[a]

Compound No.	Aromatic CH Stretch, Cm^{-1}	Aliphatic CH Stretch, Cm^{-1}	C≡N Stretch, Cm^{-1}	C=C Stretch, Cm^{-1}	CH Out-of-Plane Deformations, Cm^{-1}
1	Not observed	2915	2212	1605	865
				1585	805
				1567	
				1520	
2	3040	2928	2212	1608	840
		2860		1582	810
				1515	750
					710
3	3067	. . .	2217	1595	905
	3012			1479	830
4	Not observed	2940	2222	1580	855
			2203	1500	
5	3040	2995	1742[b]	1639[c]	794
			1698[b]	1587	748
				1570	
				1475	

[a] Compound 6 is diethyl 2-pyridylmethylenemalonate. [b] These bands are due to > C=O absorption, not —C≡N. [c] High absorption due to conjugated > C=C—C=O structure.

nate by the second procedure mentioned above. Figures 1 and 2 are typical infrared spectra for a substituted benzylidenemalononitrile and a tributylphosphine substituted benzylidenemalononitrile adduct. Tables III and IV list major infrared absorption bands for the other benzylidenemalononitrile and adduct compounds, respectively. The infrared spectra were consistent in each instance with the desired structure.

EXPERIMENTAL

Tributylphosphine and reactants to prepare substituted malononitriles were obtained commercially (reagent grade) and were used without further purification. Elemental analyses were performed by Carol K. Fitz, Needham Heights, Mass. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer. All compounds were examined in a potassium bromide matrix using sodium chloride optics. Tributylphosphine substituted benzylidenemalononitrile adducts were prepared on a 0.12 scale by the method of Horner and Klupfel (*4*). 2-Methoxybenzylidenemalononitrile has been reported previously (*4*).

PREPARATION OF COMPOUNDS 1, 2, AND 3

A mixture of the aldehyde (0.50 mole) and malononitrile (0.55 mole) in glacial acetic acid (200 ml) containing

Table IV. Characteristic Infrared Absorption Bands of Some Tributylphosphine Substituted Benzylidenemalononitriles Adducts

Compound No.	C—H Stretch, Cm^{-1}	—C≡N Stretch, Cm^{-1}	P—C_6H_5 Link, Cm^{-1}	C=C Stretch, Cm^{-1}	C—H Out-of-Plane Deformations, Cm^{-1}	Specific Absorptions, Cm^{-1}
6	3030	2150	1460	1585	755	=C—O—C
	2900	2100		1480		1245
7	2930	2210	1460	1600	910	—NO_2
		2200		1480	835	1540
						1345
8	2900	2150	1450	1585	920	=C—O—C
		2080		1560		1270
				1480		

catalytic amounts of ammonium acetate (0.2 gram) and acetamide (0.2 gram) was refluxed for 2 hours (*4*). To prepare the 3,4-dichlorobenzylidene derivative (compound 3), benzene was also added and the water removed by azeotropic distillation. The cooled reaction mixture was filtered and the collected solid was washed with water, air-dried, and then recrystallized from the solvent indicated in Table I.

4-HYDROXY-3-IODO-5-METHOXYBENZYLIDENEMALONONITRILE (COMPOUND 4)

This compound was prepared by azeotropic distillation of water from a benzene solution of 5-iodovanillin (0.25 mole), malononitrile (0.26 mole), and piperidine (5 ml) (*3*). The cooled reaction mixture was filtered and the collected solid was purified by continuous extraction of red impurities with ethanol followed by recrystallization from benzene. Elemental and infrared analyses of the red impurity showed it to be the piperidine salt of the title compound.

DIETHYL 2-PYRIDYLMETHYLENEMALONATE (COMPOUND 5)

A benzene solution of 2-pyridinecarboxaldehyde (0.50 mole), diethyl malonate (0.51 mole), piperidine (5 ml), and 2-pyridinecarboxylic acid (a few crystals) was refluxed using a Dean-Stark trap until a constant quantity of water collected (*1*). The solution was concentrated in vacuo and the residue vacuum distilled to yield a bright red oil, bp 159–62° C/1.4–1.7 mm, which solidified on cooling (48 hours) to a beige solid, m.p. 45–7° C (after hexane wash). The solid was further purified by treatment of the benzene solution with charcoal. The benzene was removed in vacuo and the residue triturated in hexane to yield 22 grams (18%) of a beige solid, m.p. 46–8° C. The infrared spectrum was in accord with the assigned structure. Calcd. for $C_{13}H_{15}NO_4$: C, 62.7; H, 6.1; N, 5.6; found: C, 62.8; H, 6.1; N, 5.8.

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Synthesis of *N*-Alkyl- and *N*-Arylsulfonylphthalimides from Potassium Phthalimide and Sulfonyl Chlorides

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The facile reaction of potassium phthalimide with sulfonyl chlorides in refluxing acetonitrile to give new *N*-alkyl- and known *N*-arylsulfonylphthalimides is reported

THERE is a paucity of published information on the reaction of potassium phthalimide with sulfonyl chlorides to give *N*-alkyl- and *N*-arylsulfonylphthalimides. Attempts by Evans and Dehn (*1*) to prepare several *N*-aryl derivatives and later by Scott and Lutz (*7*) to prepare several *N*-alkyl derivatives by this reaction were unsuccessful. More recently, potassium phthalimide was reported to interact with *p*-toluenesulfonyl chloride at 140° C. (*3*) or in dimethylformamide at 5° to 40° C. (*4*) to yield *N*-(*p*-tolylsulfonyl)phthalimide.

Potassium phthalimide readily reacts with both aliphatic and aromatic sulfonyl chlorides in refluxing acetonitrile to give the corresponding *N*-substituted phthalimides. Reactions that involved aliphatic sulfonyl chlorides afforded a series of novel compounds; those that involved aromatic sulfonyl chlorides gave known compounds. The experimental results are summarized in Table I.

The yields of the *N*-alkylsulfonylphthalimides were consistently slightly lower than those of the corresponding *N*-aryl derivatives. This probably is a result of a side reaction that only the aliphatic sulfonyl chlorides can undergo—namely, attack by the phthalimido ion on the hydrogen atom α to the sulfonyl group to form phthalimide, chloride ion, and a nonisolable sulfene (*5*). Evidence in support of this supposition is that some phthalimide was isolated in several experiments only when aliphatic sulfonyl chlorides were used.

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Potassium phthalimide was prepared according to a reported method (*6*). All other reagents were Eastman Kodak Co. chemicals. Acetonitrile was distilled from phosphorus pentoxide. Except for methane- and ethanesulfonyl chlorides, which were distilled, the sulfonyl chlorides were used as received.