

Physical Sciences Section

Pakistan J. Sci. Ind. Res., Vol. 20, No. 6, December 1977

SOME REACTIONS WITH ARYLIDENE MALONONITRILE, MALONIC ACID AND MALONIC ESTER

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(Received November 10, 1976; revised January 31, 1978)

Abstract. The Michael condensation of arylidene malononitrile Ia and Ib with cyclohexanone, cyclopentanone, acetylacetone, ethyl methyl ketone, ethyl phenyl acetate, ethyl cyanoacetate, nitromethane, and dimethyl phosphorus acid gave the adducts 2,3 and 5-10. Reaction of Ia with Grignard reagents gave II. The Friedel Craft's alkylation of aromatic compounds, namely *p*-xylene, *o*-xylene and benzene with Ia-d has been described.

Diethyl benzylidene malonate and its derivatives add active methylene compounds.¹⁻³ This prompted us to extend the Michael addition of other active methylene compounds to arylidene malononitrile.

Addition of cyclohexanone or cyclopentanone to Ia and Ib in the presence of sodium ethoxide gave [α - (2-oxocyclohexyl) furfuryl or piperonyl] malononitrile 2a and 2b or [α - (2-oxocyclopentyl) furfuryl or piperonyl] malononitrile 3a and 3b.

The structures of 2 and 3 were proved from the IR spectra which show strong absorption bands at (2245 cm^{-1}) attributable to $\nu \text{C}\equiv\text{N}$, (1719 cm^{-1} and 1725 cm^{-1}) due to $\nu \text{C}=\text{O}$ of cyclic ketones.

Condensation of the adduct 2a with hydrazine hydrate in boiling alcohol yielded the corresponding hydrazone 4.

The IR spectrum of 4 showed well defined absorption bands attributable for νNH at (3370 cm^{-1}), $\nu \text{C}\equiv\text{N}$ at (2240 cm^{-1}) and $\nu \text{C}=\text{N}$ at (1640 cm^{-1}).

The arylidene Ia and Ib were allowed to react with acetylacetone to give [α - (1-acetylacetyl) furfuryl or piperonyl] malononitrile 5a and 5b. The IR spectra of 5 revealed strong absorption bands at (2245 cm^{-1}) attributable to $\nu \text{C}\equiv\text{N}$ and (1675 cm^{-1}) due to $\nu \text{C}=\text{O}$.

When the arylidene Ia was allowed to react with ethyl cyanoacetate in the presence of boiling sodium ethoxide, it yielded α (cyanomethyl furfuryl) malononitrile 6. The IR spectrum of 6 showed strong absorption band at (2245 cm^{-1}) attributable to $\nu \text{C}\equiv\text{N}$.

The reaction of the arylidene Ia with ethyl methyl ketone afforded the [α - (1-methylacetyl) furfuryl] malononitrile 7. Structure 7 was proved from the following:

(i) The IR spectrum of 7 showed bands at (2240

cm^{-1} and 1700 cm^{-1}) attributable to $\nu \text{C}\equiv\text{N}$ and $\nu \text{C}=\text{O}$ respectively.

(ii) The NMR spectrum of compound 7 in CDCl_3 showed signals at 1.10 (d) ppm, 1.88 (t) ppm, 2.40 (s) ppm, 2.87 (m) ppm, 3.70 (d) ppm, 6.84 (m) ppm and 7.18 (m) ppm, corresponding to methyl protons (CH_3 -), methine proton ($\text{CH}-\text{CH}-\text{CH}$), methyl protons ($\text{CH}_3 \text{CO}$), methine proton ($-\text{CHCO}$), methine proton of ($-\text{CH}(\text{CN})_2$) β -protons of, furyl group and α -proton of furyl group, with the intensity ratio of 3:1:3:1:1:2:1, respectively.

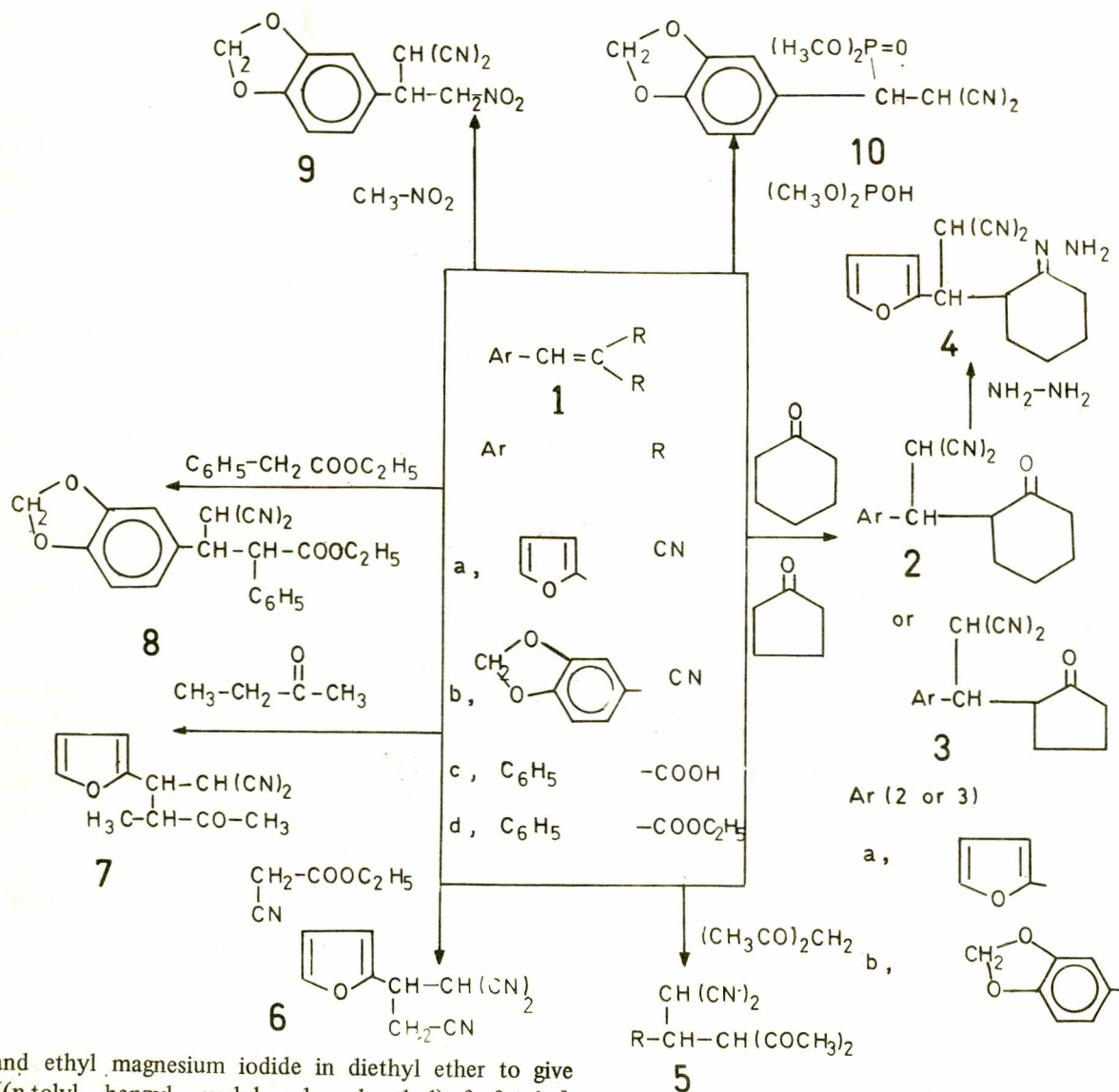
It is found that, the reaction of Ib with ethyl phenyl acetate in the presence of sodium ethoxide afforded ethyl β (dicyanomethyl)-3,4- (methylenedioxy) α - phenyl hydrocinnamate 8. The IR spectrum of 8 showed bands attributable to $\nu \text{C}=\text{O}$ of a saturated ester at (1735 cm^{-1}) and $\nu \text{C}\equiv\text{N}$ at (2260 cm^{-1}).

By analogy with the reported reaction of arylidene malonic ester with nitromethane⁴; Ib adds nitromethane in the presence of sodium ethoxide as a catalyst to give the Michael adduct 9. The IR spectrum of 9 showed α band attributable to $\nu \text{C}\equiv\text{N}$ at (2250 cm^{-1}).

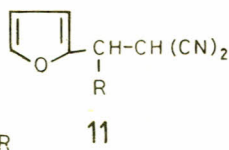
When Ib was treated with dimethyl phosphorus acid⁵; in the presence of sodium methoxide/methanol mixture it gave dimethyl [α - (dicyanomethyl) piperonyl] phosphonate 10. The structure of compound 10 was proved from its IR spectrum which showed absorption bands at (1290 cm^{-1}) due to $\nu \text{P}=\text{O}$ and at (2243 cm^{-1}) attributable to $\nu \text{C}\equiv\text{N}$. All the above Michael reactions can be represented in the following chart 1.

By analogy with the reported reaction of diethyl benzylidene malonate with methyl magnesium iodide⁶, Ia reacted with *p*-tolyl magnesium bromide, benzyl magnesium chloride, cyclohexyl magnesium bromide

CHART 1



and ethyl magnesium iodide in diethyl ether to give [(*p*-tolyl, benzyl, cyclohexyl and ethyl) furfuryl] malononitrile II.

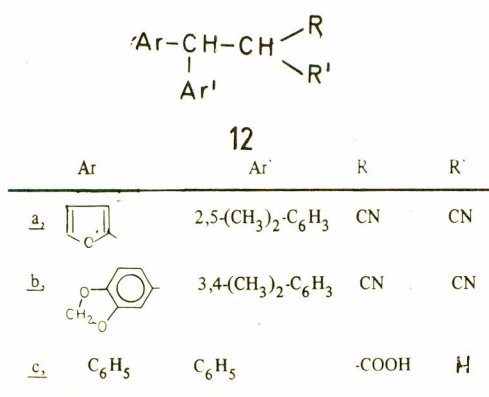


a = $p\text{-H}_3\text{C}-\text{C}_6\text{H}_4$; b = $\text{C}_6\text{H}_5\text{CH}_2$; c = C_6H_{11} ; d = C_2H_5

The IR spectra of 11 showed well defined absorption bands in the region ($2240\text{--}2245\text{ cm}^{-1}$) attributed to $\nu\text{C}\equiv\text{N}$. The NMR spectrum of compound IIa in CDCl_3 showed signals at 1.72 (d) ppm, 2.50 (s) ppm, 3.82 (d) ppm, 6.75 (m) ppm, 7.12 (m) ppm, and (7.32, 7.55) (2d), corresponding to methine proton ($-\text{CH}-\text{CH}-$), methyl protons (CH_3-), methine proton ($-\text{CH}(\text{CN})_2$), β -protons of furyl group, α -proton of furyl group and

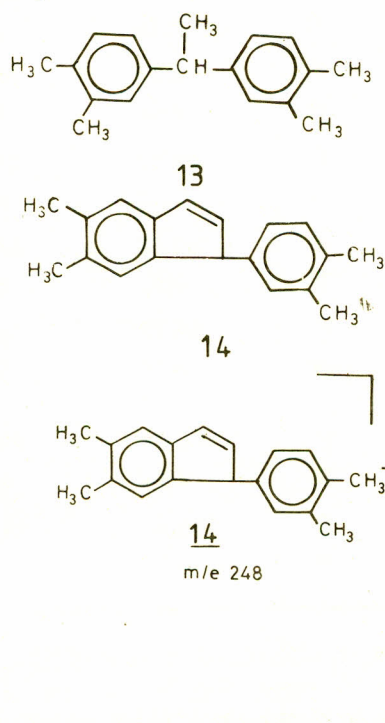
aromatic protons of the substituted phenyl group; with the intensity ratio of 1:3:1:2:1:4 respectively.

It is known that when cinnamic acid is treated with benzene and aluminium chloride, addition occurs beta to the carboxyl group⁷⁻⁹. In the present investigation this method has been applied to the arylidene malononitrile and malonic acid. The reaction of Ia with *p*-xylene, Ib with *o*-xylene and Ic with benzene afforded with the (α -2,5-xylylfurfuryl) malononitrile, (α -3,4 xylylpipe-ronyl) malononitrile and β,β -diphenylpropionic acid 12a-c respectively.



The IR spectra of 12a and 12b showed strong absorption bands at (2243 cm⁻¹) attributable to ν C≡N. However, compound 12c exhibit strong absorption band at (1700 cm⁻¹) due to ν C=O.

On the other hand, treatment of 1c with *o*-xylene and aluminium chloride under Friedel Craft's conditions gave the colourless I, I-di-3, 4-xyleneethane 13. The reaction occurred by the addition, decarboxylation and finally dearylation.



Structure of Compound 13 was proved from the following:

(i) Correct analytical data. (ii) Its IR spectrum showed ν CH of CH₃ group at (2958 and 2866 cm⁻¹) and ν CH (tertiary) at (2890 cm⁻¹) (w).

The reaction of 1d with *o*-xylene under Friedel Craft's conditions gave the same colourless product 13, which was identified by melting point and mixed melting point determinations, beside another yellowish orange 5,6-

dimethyl-1-(3,4-xyllyl) indene 14.

The formation of compound 14 can be explained by assuming initial alkylation, followed by dearylation and then cyclization. The assigned structure for compound 14 is inferred from the following:

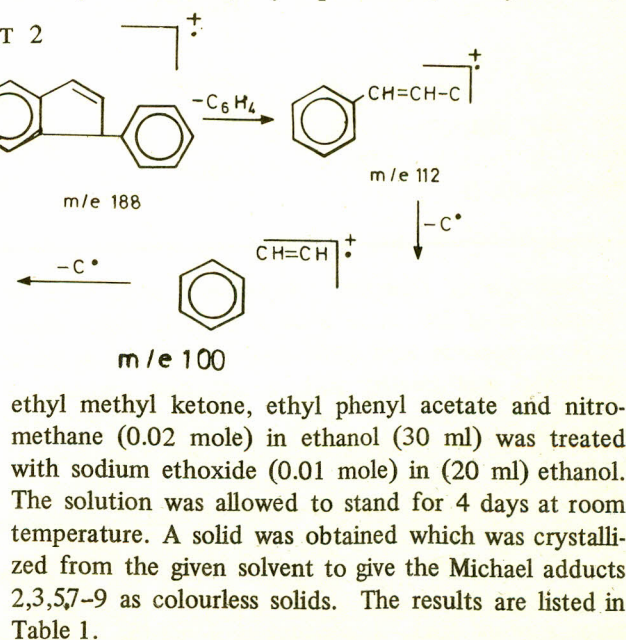
(i) Its IR spectrum shows bands at 2960-2870 cm⁻¹ due to CH₃ group., (ii) The mass spectrum of compound 14 gave rise to a peak at (*m/e* 248) which agrees with its molecular formula C₁₉H₂₀. The spectrum shows also peaks at *m/e* (233,218,203 and 188) due to loss of four methyl ions giving an ion with *m/e* 188. The latter ion upon electron impact gave the tropylium ion (C₇H₄⁺) and the spectrum shows appreciable peaks at *m/e* (112,100 and 88). The fragmentation pattern of compound 14 can be represented in the following chart 2.

(iii) The UV spectrum of 14 in ethanol showed λ_{max} (257 nm); ϵ_{max} (11850), λ_{max} (290 nm); ϵ_{max} (700) for the styrene counterpart with other two bands at λ_{max} (215 nm); ϵ_{max} (8950), and λ_{max} (265 nm); ϵ_{max} (330) for the *o*-xylene counterpart.

Experimental

The IR absorption spectra were recorded on a Unicam Sp 1200 and Sp 200-G, spectrophotometers using KBr wafer technique. For UV spectrum a Perkin-Elmer 4000 A spectro-photometer was used, and the NMR spectrum was recorded on a Varian VN 1009 (S-60 T) instrument.

Michael Reaction with Arylidene Malononitrile Ia and Ib. A mixture of arylidene malononitrile (0.01 mole) and cyclohexanone, cyclopentanone, acetylacetone,



ethyl methyl ketone, ethyl phenyl acetate and nitro-methane (0.02 mole) in ethanol (30 ml) was treated with sodium ethoxide (0.01 mole) in (20 ml) ethanol. The solution was allowed to stand for 4 days at room temperature. A solid was obtained which was crystallized from the given solvent to give the Michael adducts 2,3,5,7-9 as colourless solids. The results are listed in Table 1.

Reaction of Ethyl Cyanoacetate with Ia; Formation

of 6. A mixture of ethyl cyanoacetate (0.02 mole); Ia (0.01 mole) in ethanol (30 ml); was treated with sodium ethoxide (0.01 mole) in (20 ml) ethanol. The mixture was refluxed on a water bath for 4 hr. A solid separated upon cooling, which was then crystallized from benzene to give the product 6 as colourless crystals, m.p. 235° (yield 45 %). (Found: C, 65.03; H, 3.94 %, required for C₁₀H₇N₃O (185); C, 64.86; H, 3.78 %).

(308); C, 50.64; H, 4.22%.)

Reaction of the Michael Adduct 2a with Hydrazine Hydrate; Formation of 4. A solution of the Michael adduct 2a (0.01 mole) in ethanol (20 ml) was treated with hydrazine hydrate (0.01 mole) and the solution was refluxed for 3 hr. The solid which separated on cooling was crystallized from light petrol (b.p. 60-80°) to give the hydrazone 4 as colourless crystals of m.p. 127° (yield 66 %). (Found: C, 65.21; H, 6.53 %, required:

TABLE 1. MICHAEL ADDUCTS^{2,3,5,7-9}

Compound	m.p.	Solvent yield%	Formula (mol. wt)	Analysis		
					Found	Required
2a	140	ethanol 69	C ₁₄ H ₁₄ N ₂ O ₂ (242)	C	69.67	69.42
				H	5.43	5.48
2b	260	xylene 73	C ₁₇ H ₁₆ N ₂ O ₃ (296)	C	69.14	68.91
				H	5.12	5.40
3a	157	ethanol 55	C ₁₃ H ₁₂ N ₂ O ₂ (228)	C	68.17	68.42
				H	5.56	5.26
3b	217	toluene 63	C ₁₆ H ₁₄ N ₂ O ₃ (282)	C	68.37	68.08
				H	4.80	4.96
5a	125	pet. ether (60-80°)	C ₁₃ H ₁₂ N ₂ O ₃ (244)	C	63.82	63.93
				H	5.13	4.91
5b	146	benzene 61	C ₁₆ H ₁₄ N ₂ O ₄ (298)	C	64.58	64.42
				H	4.93	4.69
7	102	pet. ether (60-80°) 51	C ₁₂ H ₁₂ N ₂ O ₂ (216)	C	66.72	66.66
				H	5.54	5.55
8	235	methanol 68	C ₂₁ H ₁₈ N ₂ O ₄ (362)	C	69.59	69.61
				H	4.63	4.97
9	173	xylene 71	C ₁₂ H ₉ N ₃ O ₄ (259)	C	55.50	55.59
				H	3.23	3.49

Reaction of Dimethyl Phosphorus Acid with Ib; Formation of 10. A solution of Ib (0.01 mole), dimethyl phosphorus acid (0.02 mole) in 30 ml absolute methanol was treated with a saturated solution of sodium methoxide in methyl alcohol (20 ml). The temperature of the reaction mixture was maintained at 20 to 25°C. Stirring was continued for an additional 20 hr at room temperature. The whole reaction mixture was then poured in water; a solid was obtained which was then crystallized from benzene to give the Michael adduct 10 as colourless crystals m.p. 122° (yield 43 %). (Found: C, 50.25; H, 3.96 %, required: C₁₃H₁₃N₂O₅ P

ed: C₁₄H₁₆N₄O₂ (256) C, 65.62; H, 6.25 %).

Action of Grignard Reagents on the Arylidene Malononitrile Ia; Formation of II a-d. A solution of Ia (0.01 mole) in dry ether (100 ml) was added to an ethereal solution of *p*-tolylmagnesiumbromide, benzyl magnesium chloride, cyclohexyl magnesium bromide and ethyl magnesium iodide (0.03 mole) in the course of 30 min. The reaction mixture was heated under reflux for 4 hr, left over night at room temperature and then decomposed in the usual way. The viscous oils obtained were triturated with light petrol and the products were crystallized from *n*-hexane to give IIa-d as colour-

TABLE 2. (ARYL OR ALKYL) FURFURYL MALONONITRILE II a-d.

Compound	m.p.	yield%	Formula (mol. wt)	Analysis%		
				Found	Required	
11a	120	52	C ₁₅ H ₁₂ N ₂ O (236)	C	76.55	76.27
				H	5.15	5.08
11b	77	45	C ₁₅ H ₁₂ N ₂ O (236)	C	76.11	76.27
				H	5.22	5.08
11c	110	63	C ₁₄ H ₁₆ N ₂ O (228)	C	73.52	73.68
				H	7.35	7.01
11d	61	40	C ₁₀ H ₁₀ N ₂ O (174)	C	68.72	68.96
				H	5.43	5.74

TABLE 3. FRIEDEL CRAFT'S PRODUCTS 12 a-c AND 13.

Compound	m.p.	Solvent yield%	Formula (mol. wt.)	Analysis%		
				Found	Required	
12a	96	pet.ether (60-80)	C ₁₆ H ₁₄ N ₂ O (250)	C	76.51	76.80
				H	5.92	5.60
12b	240	43 xylene	C ₁₉ H ₁₆ N ₂ O ₂ (304)	C	74.67	75.00
				H	5.54	5.26
12c	150	pet. ether (100-120°)	C ₁₅ H ₁₄ O ₂ (226)	C	79.60	79.64
				H	6.30	6.19
13	282	xylene 61	C ₁₈ H ₂₂ (238)	C	90.70	90.75
				H	9.30	9.24

less crystals. The results are listed in Table 2.

Friedel Craft's Alkylation of Aromatic Hydrocarbons, with Arylidene Malononitrile, Malonic Acid and Malonic Ester; Formation of 12-14. A solution of Ia-d (0.01 mole) in the aromatic compound (*p*-xylene with Ia, *o*-xylene with Ib and Id, and benzene, *o*-xylene with Ic) was added gradually to a suspension of anhydrous aluminium chloride (about 0.04 mole) in an excess of the aromatic hydrocarbon. A vigorous evolution of hydrogen chloride took place and a brown paste precipitated. The temperature of the reaction mixture was maintained at 20-25°. Stirring was continued for an additional of 15 hr at room temperature. The whole mixture was then added to HCl/ice. The organic layer was washed with water, and the excess solvent was then removed by steam distillation. The solid that obtained was crystallized from the suitable solvent to give 12 a-c and 13. For Id with *o*-xylene; the solid formed was fractionally crystallized from light petrol (b.p 100-120°) to give the yellowish orange crystals 14, which had m.p. 180° (yield 33%). (Found: C, 91.90; H, 8.10%, required C₁₉H₂₀ (248) C,91.88; H, 128.12%).

The light petrol insoluble part was crystallized from xylene to give a colourless crystalline compound which was identified as 13 by m.p. and mixed m.p. determinations (yield 29%). The results for 12 a-c are listed in Table 3.

References

1. R. Connor and W.M.R. Mc Clellan, *J. Org. Chem.*, **3**, 570 (1938).
2. Meerwein and Co-workers, *J. Prakt. Chem.*, **2**, 116,229 (1927).
3. I.M.V. Ionescu and O.G. Popescu, *Bull. Soc. Chim. France*, **51**, 1215 (1932).
4. E.P.Kohler and S.F.Darling, *J.Am. Chem. Soc.*, **52**, 424 (1930).
5. A.N. Pudovik, *Zhur. Obshch. Khim.*, **22**, 2047 (1952); *Chem. Abstr.*, **47**, 9910(1953).
6. A.P.Kohler, *Am.Chem.J.*, **34**, 132 (1905).
7. J.F.J.Dippy and J.T.Young, *J.Chem.Soc.*, 1817 (1952).
8. J.F.Eykman, *Chem. Weekblad*, **5**, 655 (1908), *Chem. Zneti*, **2**, 100 (1908).
9. W.Wislicenus and K.Eble, *Ber.*, **50**, 250 (1917).