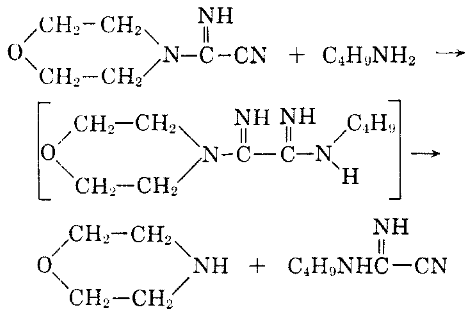

After the reaction had occurred the three heterocycles were identified in the filtrate by forming their picrates.

EXPERIMENTAL

In the experimental details which follow only general procedures are outlined. There was only slight variation in yield with each compound studied.

Reaction of a heterocyclic cyanoformamidine (free base) with aniline. Two g. of the cyanoformamidine was heated with an excess of aniline at 100° for 6 hr. The hot solution was cooled, poured into 10 ml. of 95% ethanol, and diluted with water until aniline began to separate. Sufficient ethanol was then added to bring it back into solution. After standing at room temperature for 12 hr., a small amount of crystalline material was collected and dried in air. The melting point after recrystallization was 209–210°. Mixed with a known sample of *sym*-diphenyloxamidine the melting point remained the same.

Reaction of a heterocyclic cyanoformamidine hydrochloride with n-butyl amine. One g. of the hydrochloride was refluxed with an excess of *n*-butyl amine for 3 hr. The reaction mixture was allowed to cool and diluted to about 200 ml. with water. After standing for several hours a quantity of white crystals had formed. These were collected, washed with water, and dried. The yield was about 0.2 g. After recrystallization from petroleum ether the crystals melted at 85.5–86°. Admixture with *sym*-tetra-*n*-butyloxamidine[4] resulted in no depression of the melting point.

Reaction of a heterocyclic cyanoformamidine (free base) with n-butyl amine. Two g. of the cyanoformamidine was refluxed with an excess of *n*-butyl amine for 6–8 hr. The reaction mixture was poured over crushed ice and the mixture diluted to approximately 200 ml. with water. After 48 hr. in the ice chest an oil gradually separated and crystallized. The solid product was washed several times with cold water and dried in a vacuum desiccator kept in the ice chest. Yields of crude product ranged from 0.5 to 0.75 g. Recrystallized from petroleum ether, the material became almost white and melted at 33–34°.

Anal. Calcd. for $C_6H_{11}N_3$: C, 57.6; H, 8.8; N, 33.6. Found: C, 57.5; H, 8.9; N, 33.2.

The three heterocycles were proved to be present in the filtrates from the reaction mixtures by isolating their picrates.

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Synthesis of Diarylmethylmalonates and Analogous Compounds

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In connection with the synthesis of polynuclear compounds, β-arylacrylates and diarylmethylmalonates were required. One of the convenient ways for their preparation was thought to be the stepwise reaction of organometallics with α-carbethoxy-β-ethoxyacrylate (diethyl ethoxymethylenemalonate). A recent report regarding the synthesis of diarylmethylmalonates and diarylmethylcyanoacetates[1,2] by alternate procedures prompts us to publish our preliminary results.

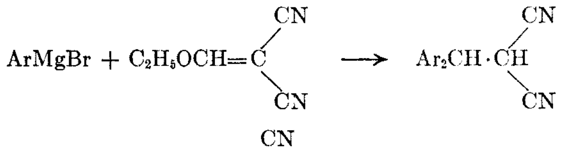
The only reference in the literature to the reaction of an organometallic compound with the acrylate is that of Reynolds[3] who, by carrying out a normal addition, *i.e.*, addition of ester to phenylmagnesium bromide, has obtained diphenylmethylmalonate.

Since we were interested in the preparation of β-acrylates it was of interest to see whether these compounds could be obtained by reverse addition and following the reaction by color tests.[4] However, the products obtained by the above procedure, in all cases, were intractable oils. The reaction of the organometallic compounds with the acrylate carried out by normal addition, *i.e.*, addition of ester to Grignard reagent in equimolar proportions gave in all cases diarylmethylmalonates; formed by the nucleophilic displacement of ethoxide group followed by the conjugate addition of Grignard reagent to β-arylacrylate:

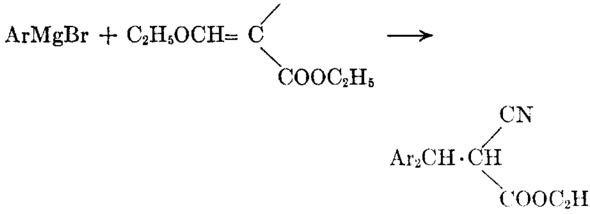
$$\mathrm{ArMg\ Br} + \mathrm{C_2H_5OCH{=}C(COOC_2H_5)_2} \longrightarrow \mathrm{Ar_2CH\cdot CH(COOC_2H_5)}$$

For structural confirmation of the above products, diphenylmethylmalonate was hydrolyzed with alcoholic potash and the resulting dicarboxylic acid was converted to the known β,β-dipheylpropionic acid by partial decarboxylation with acetic acid.

Next, reactions were carried out with ethoxymethylenemalononitrile and ethoxymethylenecyanoacetate. In these cases also the corresponding diarylmethylmalononitrile and diarylmethylcyanoacetate were obtained.



$$\mathrm{ArMgBr} + \mathrm{C_2H_5OCH{=}C(CN)_2} \longrightarrow \mathrm{Ar_2CH\cdot CH(CN)_2}$$



$$\mathrm{ArMgBr} + \mathrm{C_2H_5OCH{=}C(CN)(COOC_2H_5)} \longrightarrow \mathrm{Ar_2CH\cdot CH(CN)(COOC_2H_5)}$$

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(1) (a) M. S. Newman and H. R. Flanagan, *J. Org. Chem.*, **23**, 796 (1958). (b) M. S. Newman and D. Lednicer, *J. Am. Chem. Soc.*, **78**, 4765 (1956).

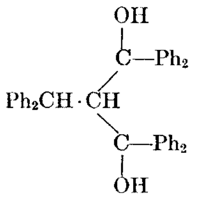
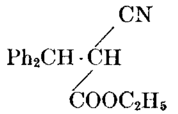
(2) E. Clar, W. Kemp, and D. G. Steward, *Tetrahedron*, **3**, 325 (1958).

(3) Reynolds, *Am. Chem. J.*, **44**, 305–31 (1910).

(4) H. Gilman and Schulz, *J. Am. Chem. Soc.*, **47**, 2002–5 (1925).

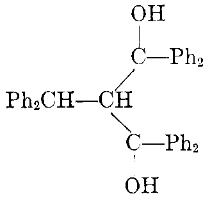
TABLE I

Reactions of Organometallics with Ethoxymethylenemalonate and Analogous Compounds

No.	Organometallic Compound	α-β-Unsaturated Ester or Nitrile	Product	Molecular Formula	Color and Crystalline Nature	Solvent for Crystallization	Yield, %	Melting Point	Found, %			Required, %		
									C	H	N	C	H	N
I	C_6H_5MgBr	Ethoxymethylenemalonate	$Ph_2CH\cdot CH(COOC_2H_5)_2$	$C_{20}H_{22}O_4$	Colorless needles	Aqueous methanol	67	53	74.3	6.5	...	73.6	6.79	...
II	α-$C_{10}H_7MgBr$	Ethoxymethylenemalonate	$(\alpha\text{-}C_{10}H_7)_2CH\cdot CH(COOC_2H_5)_2$	$C_{28}H_{26}O_4$	Pale yellow needles	Aqueous methanol	76	110[1b]	78.5	5.9	...	78.85	6.14	...
III	C_6H_5MgBr α-$C_{10}H_7MgBr$	Ethoxymethylenemalonate	$\alpha\text{-}C_{10}H_7Ph\cdot CH\cdot CH\cdot(COOC_2H_5)_2$	$C_{24}H_{24}O_4$	Colorless needles	Petroleum ether (60–80°)	32	97[1a]	...	...	...	...	...	...
IV	C_6H_5MgBr	Ethoxymethylene cyanoacetate	$Ph_2CH\cdot CH\cdot(CN)(COOC_2H_5)$	$C_{18}H_{17}O_2N$	Colorless needles	Petroleum ether (60–80°)	57	76[5]	...	...	...	...	...	...
V	α-$C_{10}OH_7MgBr$	Ethoxymethylene cyanoacetate	$(\alpha\text{-}C_{10}H_7)_2CH\cdot CH(CN)(COOC_2H_5)$	$C_{26}H_{21}O_2N$	Colorless needles	Ethanol 95%	62	191[1a]	...	...	...	...	...	...
VI	C_6H_5MgBr	Ethoxymethylenemalanonitrile	$Ph_2CH\cdot CH\cdot(CN)_2$	$C_{16}H_{12}N_2$	Colorless needles	Petroleum ether (60–80°)	57	87	82.9	5.0	11.9	82.7	5.21	12.05
VII	C_6H_5MgBr	Phenylmethylenomalanonitrile	$Ph_2CH\cdot CH\cdot(CN)_2$	$C_{16}H_{12}N_2$	Colorless needles	Petroleum ether (60–80°)	82	87	...	...	...	...	...	...
VIII	α-$C_{10}H_7MgBr$	Phenylmethylenomalanonitrile	$(\alpha\text{-}C_{10}H_7)Ph\cdot CH\cdot CH(CN)_2$	$C_{20}H_{14}N_2$	Colorless prisms	Petroleum ether (90–100°)	84	156	85.0	4.9	9.7	85.08	5.00	9.92
IX	C_6H_5Li	Ethoxymethylenemalonate		$C_{40}H_{32}O_2$	Colorless prisms	Petroleum ether (90–100°)	7	210	87.3	6.3	...	87.88	6.27	...
X	C_6H_5Li	Ethoxymethylenemalanonitrile	$Ph\cdot CH{=}C(CN)_2$	$C_{10}H_6N_2$	Pale yellow needles	Petroleum ether (60–80°)	14	86[6]	78.4	4.1	...	77.9	3.92	...
XI	C_6H_5Li	Ethoxymethylene cyanoacetate		$C_{18}H_{17}O_2N$	Colorless needles	Petroleum ether (60–80°)	3	76[7]	77.5	5.2	...	77.4	6.09	...

The structure of diphenylmethylmalanonitrile was confirmed by 1:4 addition of phenylmagnesium bromide to phenylmethylenomalononitrile which was obtained by the reaction of malononitrile with benzaldehyde.

In order to compare the mode of reaction of organolithium compounds, we studied the reaction of phenyllithium and α-naphthyllithium with the above esters. The reverse addition in the case of ethyoxymethylenemalonate gave intractable oils whereas the normal addition of ester to phenyllithium gave a compound (m.p. 210°) which was found, from the elemental analysis and infrared spectrum, to be a derivative of 1,3-propanediol.

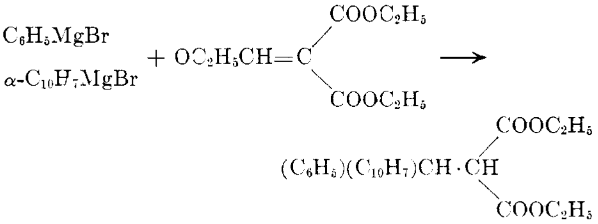


which is formed both by 1:2 as well as 1:4 addition of more reactive phenyllithium.

In the case of ethoxymethylenecyanoacetate the normal addition of phenyllithium gave diphenylmethylcyanoacetate in very poor yield. In the case of ethoxymethylenemalononitrile, however, the phenyllithium gave two products, one of which was identified as phenylmethylenomalonotrile.

Newman[1] and co-workers have synthesized β-diarylmethylmalonates by the conjugate addition of Grignard reagent to β-arylmethylenomalonates, which are prepared by the reaction of sodio derivative of malonates, with the corresponding aldehydes. As compared to this the present method is simpler, involves only one step and gives good yield. Moreover, the esters used in the present work are now commercially available.

We have tried to investigate whether unsymmetrical diarylmethylmalonates can be prepared by the simultaneous addition of phenylmagnesium bromide and α-naphthylmagnesium bromide to ethoxymethylenemalonate and it has been found that α-naphthylphenylmethylmalonate is obtained although in low yield.



EXPERIMENTAL

General procedure. An ethereal solution of α,β-unsaturated esters were added dropwise to well stirred solution of Grignard compounds and phenyllithium; rate of addition being just sufficient to maintain ether reflux. The reaction in all cases was instantaneous and complete after the esters were added. After stirring for 0.5 hr. the products were hydrolyzed and acidified. The ethereal layer was separated and washed free of acid, dried over Na_2SO_4 and then evaporated. The products obtained were crystallized from appropriate solvents.

Diethyl 1-naphthylphenylmethylmalonate. α-Naphthylmagnesium bromide was prepared from 0.533 g. of magnesium and 4.6 g. of α-bromonaphthalene and phenylmagnesium bromide was prepared from 0.533 g. of magnesium and 2.42 ml. of bromobenzene. These two Grignards were simultaneously added to 4.32 g. of diethyl ethoxymethylenemalonate in 20 ml. of dry ether. There was immediate formation of yellow precipitate. The color test[4] was negative after the additions were over. After hydrolysis and acidification, the ethereal layer was separated; washed free of acid, dried over Na_2SO_4 and evaporated. Pale yellow oil (5.00 g.) on distillation gave yellow viscous oil (b.p. 150–180°/0.04 mm.) yield 2.42 g. (32%). It was crystallized from petroleum ether (60–80°) in colorless needles melting at 96° (lit. 93–96°)[a].

The yields, and analysis of the compounds are given in Table I.

α-Naphthylphenylmethylmalanonitrile. α-Naphthylmagnesium bromide was prepared from 0.3463 g. of magnesium and 2.987 g. of α-bromonaphthalene. To this Grignard, 2.0 g. of phenylmethylenomalnonitrile in 20 ml. of ether benzene mixture was added dropwise. There was immediate formation of yellow precipitate which then changed to reddish brown oil. The color test[4] was negative after addition was over. After hydrolysis and acidification, the ethereal layer was separated, washed free of acid, dried over Na_2SO_4, and evaporated. Reddish viscous oil (5.0 g.) after crystallization from benzene and petroleum ether (60–80°) gave colorless compound (3.1 g.) yield 84% melting at 148–50°. The analytical sample after crystallizing from petroleum ether (90–100°) melted at 156°.

Saponification of I. Diphenylmethylmalonate (2 g.) was refluxed for 6 hr. with 30 ml. of 15% alcoholic potash; after which most of the alcohol was distilled off. To the solid mass was added 20 ml. of water and then acidified with concd. HCl. The acid separated, was filtered, and crystallized from glacial acetic acid; yield 0.650 g., m.p. 155° (lit. 155°).

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.68; H, 6.19. Found: C, 79.7; H, 6.1.

Acknowledgment. We are grateful to Messrs. Kay-Fries Chemicals, Inc., West Haverstraw, N. Y. (U.S.A.) for a generous gift of ethoxymethylenemalonate and other chemicals used in this work.

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(5) Kohler and Reimer, *Am. Chem. J.*, **33**, 353 (1905).

(6) Mixed melting point with phenylmethylenomalanonitrile shows no depression.

(7) Mixed melting point with product from IV shows no depression.

Small Ring Compounds. XXIV. Molecular Orbital Calculations of the Delocalization Energies of Some Small-Ring Systems[1]

Stanley L. Manatt and John D. Roberts

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The recently reported syntheses of several interesting small-ring compounds prompt us to