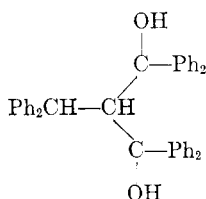


The structure of diphenylmethylmalanonitrile was confirmed by 1:4 addition of phenylmagnesium bromide to phenylmethylenomalononitrile which was obtained by the reaction of malononitrile with benzaldehyde.

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 ethoxymethylenemalonate 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.

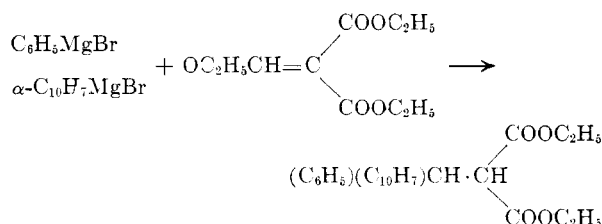


which is formed both by 1:2 as well as 1:4 addition of more reactive phenyllithium.

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 phenylmethylenomalononitrile.

Newman¹ 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.



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

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

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

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 test⁴ 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°)⁵.

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

α -Naphthylphenylmethylmalononitrile. 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 phenylmethylenomalononitrile 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 test⁴ 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 $\text{C}_{15}\text{H}_{14}\text{O}_2$: C, 79.68; H, 6.19. Found: C, 79.7; H, 6.1.

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Small Ring Compounds. XXIV. Molecular Orbital Calculations of the Delocalization Energies of Some Small-Ring Systems¹

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

present an extension of our earlier molecular orbital calculations (LCAO approximation)² which includes these compounds and also a number of other small-ring systems which have not yet been synthesized, but which are predicted to have substantial electron delocalization energies.

All of the calculations were made by the simple molecular orbital method (LCAO) with neglect of resonance integrals between nonadjacent atoms and of the nonorthogonality of the atomic orbitals on different atoms. Group theory procedures were used to factor the secular determinants where possible. In the systems containing carbonyl groups, the oxygen Coulomb integral was taken as $\alpha + 2\beta$ where α is the Coulomb integral of carbon and β is the resonance integral of carbon.³ The carbon-oxygen resonance integral was taken as $\sqrt{2} \beta$.³ The results are summarized in Tables I-III. All delocalization energies (DE) are given in units of β (usually taken to be about -20 kcal./mole), and the columns labeled ΔDE show the increases in DE values between substituted and unsubstituted systems (after a correction of 2β for each phenyl group present). A *T* is placed after the DE value if the lowest state is predicted to be a triplet.

Of the substances listed in Table I, phenylcyclobutenedione,⁴ cyclohexenylcyclobutenedione,⁵ ben-

zocyclobutenedione,⁶ 1,2-diphenyldimethylenecyclobutene^{7a} and diphenylcyclopropenone^{7b} have been isolated as stable substances. Formation of benzocyclobutadiene as an unstable reaction intermediate has been demonstrated.⁸

Computations for some cyclopropenyl cations, radicals, and anions are given in Table II. The predicted extra stabilizing influence of phenyl groups on the cyclopropenyl cation has been verified by Breslow's⁹ elegant preparation of stable salts of the 1,2,3-triphenylcyclopropenyl cation.

TABLE II
DE VALUES FOR CYCLOPROPENYL CATIONS, ANIONS, AND FREE RADICALS

	Cation		Radical		Anion	
	DE	ΔDE	DE	ΔDE	DE	ΔDE
Cyclopropenyl ^a	2.00		1.00		0.00	<i>T</i>
Phenylcyclopropenyl	4.39	0.39	3.79	0.79	3.20	1.20
1,2-Diphenylcyclopropenyl	6.70	0.70	6.20	1.20	5.69	1.69
1,2,3-Triphenylcyclopropenyl	9.19	1.19	8.68	1.68	8.18	<i>T</i> 2.18

^a Ref. 2.

TABLE I

DE VALUES FOR CYCLOBUTADIENE AND CYCLOBUTENEDIONE SYSTEMS

	DE	ΔDE
Cyclobutadiene ^a	0.00	<i>T</i> ...
Phenylcyclobutadiene ^a	2.53	<i>T</i> 0.53
1,3-Diphenylcyclobutadiene	5.02	<i>T</i> 1.02
1,2-Diphenylcyclobutadiene	5.06	<i>T</i> 1.06
1-Phenyl-3- <i>p</i> -biphenylcyclobutadiene	7.42	<i>T</i> 1.07
1,3-Di- <i>p</i> -biphenylcyclobutadiene	9.82	<i>T</i> 1.12
1,2-Di- <i>p</i> -biphenylcyclobutadiene	9.87	<i>T</i> 1.17
Benzocyclobutadiene ^a	2.38	
1-Phenylbenzocyclobutadiene	4.84	0.46
1,2-Diphenylbenzocyclobutadiene	7.32	0.94
Dimethylenecyclobutene ^a	1.21	
1-Vinyldimethylenecyclobutene	1.69	0.48
1-Phenyldimethylenecyclobutene	3.47	0.26
1,2-Diphenyldimethylenecyclobutene	6.07	0.86
Cyclobutenedione ^b	1.24	
Vinylcyclobutenedione ^c	1.74	0.50
Phenylcyclobutenedione	3.68	0.44
Diphenylcyclobutenedione	6.03	0.79
1,2-Dimethylenebenzocyclobutene	3.15	
1-Keto-2-methylenebenzocyclobutene	3.17	
Benzocyclobutenedione ^b	3.13	

^a Data from Ref. 2. ^b Unpublished results of Dr. E. J. Smutny. ^c Cyclohexenylcyclobutenedione would be calculated to have the same energy.

(1) Supported in part by the National Science Foundation.

(2) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

(3) R. D. Brown, *Quart. Revs.*, **6**, 63 (1952).

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Table III summarizes calculations for several methylenecyclopropenes and cyclopropenones.

TABLE III

DE VALUES FOR METHYLENECYCLOPROPENES AND CYCLOPROPENONES

	DE	ΔDE
Methylenecyclopropene	0.96	
1-Vinylmethylenecyclopropene	1.42	0.45
1-Phenylmethylenecyclopropene	3.37	0.41
1,2-Diphenylmethylenecyclopropene	5.79	0.83
Cyclopropenone ^a	1.36	
Vinylcyclopropenone	1.79	0.43
Phenylcyclopropenone	3.75	0.39
Diphenylcyclopropenone	6.15	0.79

^a Unpublished results of Dr. E. J. Smutny.

Further theoretical work is being done on estimation of the importance of 1,3-interaction in cyclobutenone, cyclobutenedione, and cyclobuta-

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(6) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 3606 (1957).

(7) (a) A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **79**, 5317 (1957); (b) R. Breslow, R. Haynie, and J. Mirra, *J. Am. Chem. Soc.*, **81**, 247 (1959).

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