NOTES

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  $\alpha$ -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<sup>1</sup> and co-workers have synthesized  $\beta$ -diarylmethylmalonates by the conjugate addition of Grignard reagent to  $\beta$ -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  $\alpha$ -naphthylmagnesium bromide to ethoxymethylenemalonate and it has been found that  $\alpha$ -naphthylphenylmethylmalonate is obtained although in low yield.



<sup>(5)</sup> Kohler and Reimer, Am. Chem. J., 33, 353 (1905).

### EXPERIMENTAL

General procedure. An ethereal solution of  $\alpha,\beta$ -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<sub>2</sub>SO<sub>4</sub> and then evaporated. The products obtained were crystallized from appropriate solvents.

Diethyl 1-naphthylphenylmethylmalonate.  $\alpha$ -Naphthylmagnesium bromide was prepared from 0.533 g. of magnesium and 4.6 g. of  $\alpha$ -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<sup>4</sup> was negative after the additions were over. After hydrolysis and acidification, the ethereal layer was separated; washed free of acid, dried over Na<sub>2</sub>SO<sub>4</sub> 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°)<sup>a</sup>.

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

 $\alpha$ -Naphthylphenylmethylmalanonitrile.  $\alpha$ -Naphthylmagnesium bromide was prepared from 0.3463 g. of magnesium and 2.987 g. of  $\alpha$ -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<sup>4</sup> was negative after addition was over. After hydrolysis and acidification, the ethereal layer was separated, washed free of acid, dried over Na<sub>2</sub>SO<sub>4</sub>, 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.  $155^{\circ}$  (lit.  $155^{\circ}$ ).

Anal. Caled. for  $C_{15}H_{14}O_2$ : 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 Systems<sup>1</sup>

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

<sup>(6)</sup> Mixed melting point with phenylmethylenomalano-

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

present an extension of our earlier molecular orbital calculations (LCAO approximation)<sup>2</sup> 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  $\alpha$  is the Coulomb integral of carbon and  $\beta$  is the resonance integral of carbon.<sup>3</sup> The carbon-oxygen resonance integral was taken as  $\sqrt{2} \beta$ .<sup>3</sup> The results are summarized in Tables I-III. All delocalization energies (DE) are given in units of  $\beta$  (usually taken to be about -20kcal./mole), and the columns labeled  $\Delta DE$  show the increases in DE values between substituted and unsubstituted systems (after a correction of  $2\beta$  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,<sup>4</sup> cyclohexenylcyclobutenedione,<sup>5</sup> ben-

### TABLE I

DE VALUES FOR CYCLOBUTADIENE AND CYCLOBUTENEDIONE Systems

	DE	ΔDE
Cyclobutadiene <sup>a</sup>	0.00 T	
Phenylcyclobutadiene <sup>a</sup>	2.53 T	0.53
1,3-Diphenylcyclobutadiene	5.02 T	1.02
1,2-Diphenylcyclobutadiene	5.06 T	1.06
1-Phenyl-3-p-biphenylcyclobutadiene	7.42 T	1.07
1,3-Di-p-biphenylcyclobutadiene	9.82 T	1.12
1,2-Di-p-biphenylcyclobutadiene	9.87 T	1.17
Benzocyclobutadiene <sup>a</sup>	2.38	
1-Phenylbenzocyclobutadiene	4.84	0.46
1,2-Diphenylbenzocyclobutadiene	7.32	0.94
Dimethylenecyclobutene <sup>a</sup>	1.21	
1-Vinyldimethylenecyclobutene	1.69	0.48
1-Phenyldimethylenecyclobutene	3.47	0.26
1,2-Diphenyldimethylenecyclobutene	6.07	0.86
Cyclobutenedione <sup>b</sup>	1.24	
Vinylcyclobutenedione <sup>c</sup>	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 <sup>b</sup>	3.13	

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

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

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's<sup>9</sup> elegant preparation of stable salts of the 1,2,3-triphenylcyclopropenyl cation.

TA	₹B	L	$\mathbf{E}$	Π

DE VALUES FOR CYCLOPROPENYL CATIONS, ANIONS, AND FREE RADICALS

	Cation		Radical		Anion	
	DE	$\Delta D\overline{E}$	DE	$\Delta DE$	DE	$\Delta DE$
Cyclopro-						
penyla	2.00		1.00		0.00 T	
Phenylcyclo-						
propenvl	4.39	0.39	3.79	0.79	3.20	1.20
1.2-Diphenvl-						
cyclopro-						
penvl	6.70	0.70	6.20	1.20	5.69	1.69
1.2.3-Ťri-						
phenyl-						
cvelo-						
propenvl	9.19	1.19	8.68	1.68	8.18 T	2.18
4 D-f 0						

Table III summarizes calculations for several methylenecyclopropenes and cyclopropenones.

TABLE III

DE VALUES FOR METHYLENECYLOPROPENES 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 <sup>a</sup>	1.36	
Vinylcyclopropenone	1.79	0.43
Phenylcyclopropenone	3.75	0.39
Diphenylcyclopropenone	6.15	0.79

<sup>a</sup> 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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diene systems, and the stabilizing "push-pull" effect predicted by LCAO theory for 1,2-diphenylcyclobutadiene derivatives substituted in one phenyl ring by an electron-attracting group and in the other by an electron-donating group.<sup>10</sup>

We wish to thank Dr. Robert Nathan of the Institute Computing Center and Dr. John Christopher of the ElectroData Division of the Burroughs Corp. for their help in utilizing the institute's Datatron digital computer.

Contribution No. 2462 Gates and Crellin Laboratories of Chemistry California Institute of Technology Pasadena, Calif.

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## **Tetraphenylboron Derivatives of Amides**

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Sodium tetraphenylboron has received attention in recent years as a precipitant for potassium, ammonium, and organic nitrogen compounds.<sup>1,2</sup> Tetraphenylboron salts formed from an onium ion derived by protonation of a sufficiently basic organic nitrogen group are usually insoluble in water. Crane<sup>3</sup> suggested that an amine must have a basic dissociation constant of at least  $1 \times 10^{-11}$  to undergo qualitative precipitation as a tetraphenylboron salt. We have found that some organic acid amides, usually considered to be neutral, also give insoluble salts.

Amides are usually characterized by identification of their hydrolytic products. A limited number of amides have been identified by the direct formation of derivatives (mercury salts,<sup>4</sup> amide oxalates,<sup>5</sup> and xanthylamides).<sup>6</sup> The formation of tetraphenylboron derivatives of amides depends upon the weakly basic properties of the amide (*i.e.*, its ability to undergo protonation in an acidic medium); these salts may be used to identify amides for which suitable derivatives have been lacking. The stoichiometry of the reaction can be presented as follows:

$$\begin{array}{c} \overset{O}{\mathbb{R}_{2}} \\ \overset{H}{\mathbb{R}_{2}} + \overset{H}{\mathbb{B}} (C_{6}H_{\delta})_{4} \longrightarrow \\ \overset{O}{\mathbb{R}_{2}} \\ \overset{H}{\mathbb{R}_{3}} + \overset{O}{\mathbb{B}} (C_{6}H_{\delta})_{4} \downarrow \quad (1) \end{array}$$

where  $R_1R_2$ , or  $R_3$  may be hydrogen, alkyl, aryl, or part of a ring system.

When electron-attracting groups which reduce the availability of the nitrogen electrons are introduced, no derivatives are formed as with Nvinyl or N-allyl pyrrolidone-2, and acrylamide. In N-allyl- $\gamma$ -hydroxybutyramide the electron-attracting effect of the allyl group is balanced by the hydroxyl group operating in the opposite direction. Although the hydroxyl group exerts its effect over a greater distance, comparison of the pK value for glycolic and vinylacetic acids shows the greater effect of the hydroxyl group. Although monomeric N-vinyl pyrrolidone does not form a derivative, polyvinylpyrrolidone (mol. wt. 50,000) forms a derivative readily. The nitrogen analysis of the latter suggests that approximately 45% of the amide residues in the polymer form tetraphenylboron complexes. Polyvinylpyrrolidone structurally is more closely related to N-methyl pyrrolidone-2. This compound forms a derivative immediately whereas 5-methyl pyrrolidone-2 and the unsubstituted pyrrolidone-2 do not form derivatives. In the case of N-methyl pyrrolidone-2 the electron-release effect of the methyl group increases the electron density on the nitrogen atom and thus enhances onium ion formation as typified in Equation 1. In 5-methyl pyrrolidone-2 the methyl group is too far removed from the nitrogen to be effective.

It is noteworthy that tetraphenylboron derivatives are onium salts closely related to quaternary ammonium salts. In view of the antibacterial and antifungal activity of the latter class of compounds,

TABLE I

	M.P. <i>ª</i>	Nitrogen	
Amide	°C.	Theory	Found
Acetamide	180-182	3.69	4.08
Dimethylacetamide	119 - 120	3.44	3.09
Formamide	187 - 190	3.83	4.09
Dimethylformamide	117 - 121	3.56	3.54
N-methyl pyrrolidone-2	148 - 150	3.34	3.43
$N$ -allyl- $\gamma$ -hydroxybutyramide	127 - 130	3.02	3.10
Polyvinylpyrrolidone <sup>b</sup> (mol. wt. 50,000)	> 250	3.25	8.41

<sup>a</sup> Variations in melting points of tetraphenylboron salts have been reported previously for derivatives of simple amines. The rate of heating is very important for duplication of results. In our experiments temperatures were raised 2° per min. in the vicinity of the melting point range. <sup>b</sup> The melting point of this derivative is too high for characterization studies. The theoretical nitrogen analysis given is that for the polymer in which every vinylpyrrolidone residue is complexed. The actual value (8.41% N) shows that 45% of the available amide groups have formed tetraphenylboron salts.

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