as is evident from the appearance of a twin peak between 1.5–1.6 μ (6600–6300 cm.$^{-1}$) and the decrease in intensity of the 1.47 μ monomer peak. Corresponding behavior is observed in aqueous solutions (Fig. 1) except that the concentration near which aggregation becomes significant is exceedingly high. N-Methylacetamide in water shows a single absorption peak at 1.48 μ (6760 cm.$^{-1}$) with an optical density proportional to concentration until the solute becomes nearly 7–8 *M*. At this point the ratio of H_2O/amide is down to about 3. In more concentrated solutions, the 1.48 μ peak decreases in intensity and a twin peak appears in the 1.5–1.6 μ range.

A preliminary rough computation of the equilibrium constant for dimer formation by N-methylacetamide in water has been made from changes in absorption at 1.48 μ, and a $K \simeq 0.008$ obtained. From this value, as well as the spectra in Fig. 1, it is apparent that the inter-peptide hydrogen bond of small molecules in aqueous solution is exceedingly unstable. For model amides, at least, aggregation through hydrogen bonding is essentially nonexistent as long as enough water molecules are available to occupy the N–H and C=O groups.

(4) This investigation was assisted by a research grant (H-2910) from the National Heart Institute, United States Public Health Service.

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CARBOMETHOXY DERIVATIVES OF 1,2-DIMETHYLENEBENZOCYCLOBUTENE AND 1-KETO-2-METHYLENEBENZOCYCLOBUTENE

Sir:

We wish to report the synthesis of some simple derivatives of the unknown systems 1,2-dimethylenebenzocyclobutene (I) and 1-keto-2-methylenebenzocyclobutene (II). Molecular orbital calculations[1] have shown that the resonance energies of both molecules are almost identical with that of the known, stable benzocyclobutenedione (III).[2] The syntheses of 1,2-dicarbomethoxymethylenebenzocyclobutene (IV) and of 1-keto-2-carbomethoxymethylenebenzocyclobutene (VI) were achieved by the reaction of diketone III with triphenylphosphinecarbomethoxymethylene.[3]

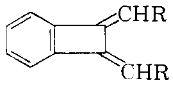
Allowing a solution of diketone III and two equivalents of triphenylphosphinecarbomethoxymethylene in methylene chloride to stand overnight at room temperature gave, in 85% yield, IV, m.p. 122–123.[4] *Anal.* Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 69.01; H, 4.95. Ultraviolet spectrum: $\lambda_{\max}^{\text{EtOH}}$ 256 mμ (log *E* 4.64), 290 mμ (log *E* 4.46), 305 mμ (log *E* 3.98) and 333 mμ (log *E* 3.98).

On catalytic hydrogenation, IV absorbed two moles of hydrogen to give 1,2-benzocyclobutenediacetic acid dimethyl ester (V). *Anal.* Calcd. for $C_{14}H_{16}O_4$: C, 67.75; H, 6.50. Found: C, 67.61; H, 6.70. The ultraviolet spectrum of V was identical with that of benzocyclobutene.[5] Significantly no reaction occurred when IV was refluxed with tetracyanoethylene[6] in toluene for twenty-four hours, and 93% of the starting material was recovered.

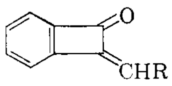
Addition of one equivalent of triphenylphosphinecarbomethoxymethylene in methylene chloride to diketone III in methylene chloride over a period of eight hours gave, in 93% yield, VI, m.p. 86–87°. *Anal.* Calcd. for $C_{11}H_8O_3$: C, 70.21; H, 4.29. Found: C, 69.91; H, 4.65. Ultraviolet spectrum: $\lambda_{\max}^{\text{EtOH}}$ 246 mμ (log *E* 4.55), 330 mμ (log *E* 4.00). The 2,4-dinitrophenylhydrazone of VI, m.p. 235° (dec.) formed readily. *Anal.* Calcd. for $C_{17}H_{12}O_6N_4$: C, 53.93; H, 3.40; N, 15.73. Found: C, 53.89; H, 3.13; N, 15.22.

A solution of VI with one mole of triphenylphosphinecarbomethoxymethylene in methylene chloride on standing overnight gave IV in 75% yield.

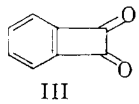
A closer study of this series of compounds is now in progress.



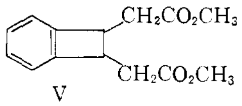
I, (R = H)
IV, (R = CO_2CH_3)



II, (R = H)
VI, (R = CO_2CH_3)



III



V

We gratefully acknowledge a grant by the National Science Foundation in support of this work.

(1) S. L. Manatt and J. D. Roberts, *J. Org. Chem.*, **24**, 1336 (1959).

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(3) O. Isler *et al.*, *Helv. Chim. Acta*, **40**, 1242 (1957).

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(6) The somewhat related 3,4-diphenyl-1,2-dimethylenecyclobutene reacts under milder conditions, a spiran rather than a cyclobutadiene being formed: A. T. Blomquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959).

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THE NON-CLASSICAL PENTAMETHYLCYCLOPENTADIENYL-CARBINYL CATION

Sir:

In considering the nature of the intensely magenta colored species obtained from hexamethylcyclopentadiene,[1] the possibility arose that the pentamethylcyclopentadienyl-carbinyl cation would have a highly stabilized non-classical structure, such as A.[2]

This was convincingly borne out by examination of the solvolysis behavior of the corresponding arenesulfonate. These are obtainable from 1,2,3,-4,5-pentamethylcyclopentadienylcarbinol(I)[3] at −10°.

Rate studies show that the *p*-toluenesulfonate acetolyses with remarkably high anchimeric acceleration and with SN1 kinetics.[4]

(1) To be published in a subsequent issue of THIS JOURNAL.

(2) This was suggested to the author by Prof. S. Winstein.

(3) L. de Vries, *J. Org. Chem.*, in press.

(4) Private communication from S. Winstein and M. Battiste.