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 non-existent as long as enough water molecules are available to occupy the N–H and C=O groups.

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

(5) Postdoctoral Fellow, United States Public Health Service.

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RECEIVED AUGUST 3, 1960

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]

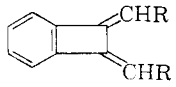
Allowing a solution of diketone III and two equivalents of triphenylphosphinecarbomethoxymethylene in methylene chloride to stand overnight at room temperature gave, in 85% yield, IV, m.p. 122–123.[4] *Anal.* Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 69.01; H, 4.95. Ultraviolet spectrum: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

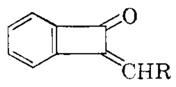
Addition of one equivalent of triphenylphosphinecarbomethoxymethylene in methylene chloride to diketone III in methylene chloride over a period of eight hours gave, in 93% yield, VI, m.p. 86–87°. *Anal.* Calcd. for $C_{11}H_8O_3$: C, 70.21; H, 4.29. Found: C, 69.91; H, 4.65. Ultraviolet spectrum: $\lambda_{\max}^{\mathrm{EtOH}}$ 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.

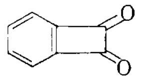
A closer study of this series of compounds is now in progress.



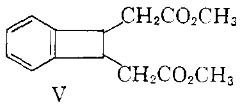
I, (R = H)
IV, (R = CO_2CH_3)



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.

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

(2) M. P. Cava and D. R. Napier, THIS JOURNAL, **79**, 3606 (1957).

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

(4) All melting points are uncorrected.

(5) M. P. Cava and D. R. Napier, THIS JOURNAL, **80**, 2256 (1958).

(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]

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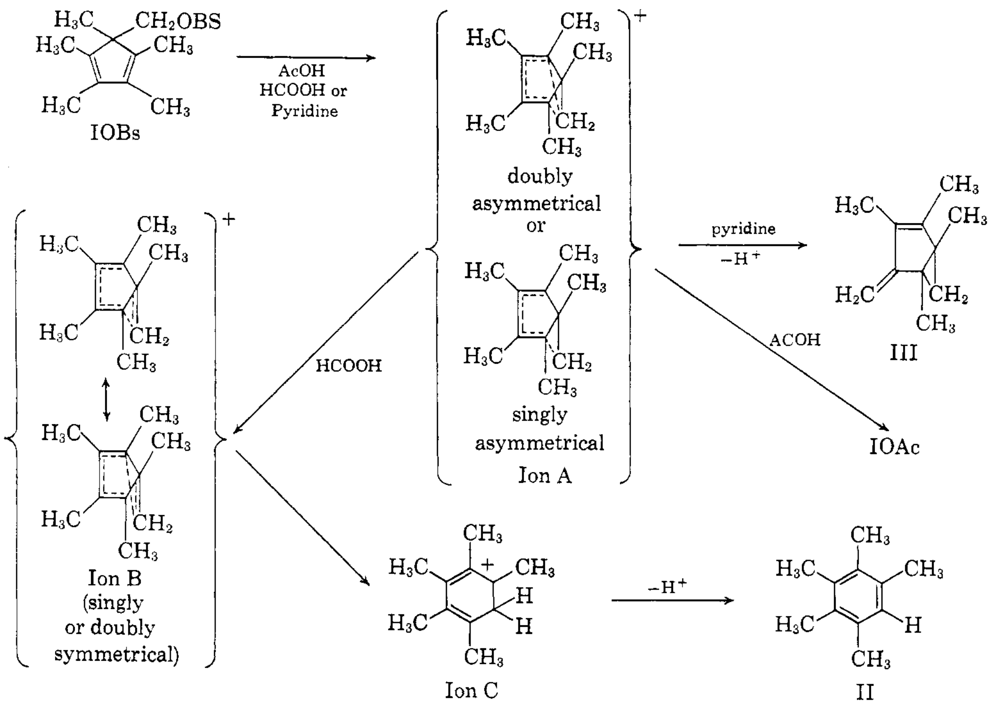
(1) To be published in a subsequent issue of THIS JOURNAL.

(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.



Product studies, using the *p*-bromobenzenesulfonate (IOBs) prove that this is not due to a simple Wagner-Meerwein rearrangement, which through ring enlargement and proton elimination would give pentamethylbenzene (II).

The unusual nature of the intermediates involved in ionization is indicated clearly by the observation that in pyridine at room temperature, IOBs loses HOBs to give a new hydrocarbon, 1,3,4,5-tetramethyl-2-methylenebicyclo[3.1.0]hex-3-ene (III), $n^{20}\mathrm{D}$ 1.5005, b.p. 40.6° (2.5 mm), mass spec. mol. wt. 148. *Anal.* C, 89.01; H, 10.76. The structure assignment is based on these data:

(a) Infrared bands: $\tilde{\nu}(>C{=}CH_2)$ 3085 cm.$^{-1}$ (m.), 854 cm.$^{-1}$ (v.s.); $\tilde{\nu}(C{=}C{-}C{=}CH_2)$ 1260 cm.$^{-1}$ (s.); $\tilde{\nu}$(cycloprop. CH_2) 3055 cm.$^{-1}$ (m.),[5] 1020 cm.$^{-1}$ (m.).[6]

(b) λ isoöctane 252 mμ; ε 10,000. The high value of ε indicates an extended dienic system, unlike the cyclopentadiene system in I.

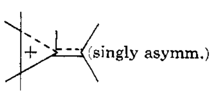
(c) The n.m.r. spectrum (40 Mc.) indicates six types of C–H. In c.p.s. rel. to internal $Si(CH_3)_4$ capillary: −189.5, rel. area 2 ($>C{=}CH_2$); −69.2, −63.1, each rel. area 3 (CH_3-C-C-CH_3); −20.7 rel. area 2 (cycloprop. CH_2). A peak at so high a field virtually constitutes proof for a methylene group in a cyclopropane ring.[7]

$LiAlH_4$ reduction of the product of acetolysis of IOBs in the presence of 1.5 equivalents of sodium acetate at room temperature for 20 hours affords essentially pure I; from the product of formolysis in the presence of 1.5 equivalents of sodium formate at room temperature for 45 minutes I (42%), II (17%), as well as unidentified orange colored products, probably mostly polymeric in nature, are obtained (separation by chromatography. Identification by infrared, ultraviolet spectra and melting point).

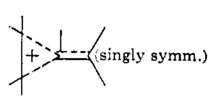
IOBs decomposes at 60° in a vacuum sublimation apparatus to give a high yield of II (45%).

Although the evidence is insufficient to establish the exact nature or number of the intermediates involved, the high yield of IOAc and the absence of II in acetolysis precludes ring expansion as a primary process and suggests that a doubly asymmetrical[8a,b] ion A is involved. In pyridine, this ion or a singly asymmetrical analog loses a proton to give III. In formic acid or in thermal decomposition of IOBs where the ion is long-lived or may be reformed from primary products, partial rearrangement may occur to a singly or doubly symmetrical[8a,c] ion B. This species, which may be an actual intermediate or merely a transition state can rearrange further to the "classical" pentamethylcyclohexadienyl Cation C, which eliminates a proton to give II.

8(b)



(c)



With pure IOBs color phenomena are absent in acetolysis; in formolysis a magenta color slowly develops well after the HOBs elimination is complete. Ion A should be obtainable directly by protonation of III. In $CH_3COOHCH_3SO_3H$ (0.1 %) an initial yellow flash, presumably due to Ion A is followed immediately by color discharge, presumably due to solvent attack; eventually a magenta color develops slowly. Since the purple colored species is quite stable in acetic or formic

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(5) A. R. H. Cole, *J. Chem. Soc.*, 3807 (1954).

(6) L. M. Derfer, E. E. Pickett and C. E. Boord, THIS JOURNAL **71**, 2482 (1949); V. A. Slabey, *ibid.*, **76**, 3604 (1954).

(7) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 237.

(8) (a) S. Winstein, *et al.*, THIS JOURNAL, **76**, 18 (1954); **74**, 1140 (1952).

acid, it is not one of the intermediates in acetolysis or formolysis.

Acknowledgment.—I am indebted to Professor S. Winstein for invaluable discussions and suggestions.

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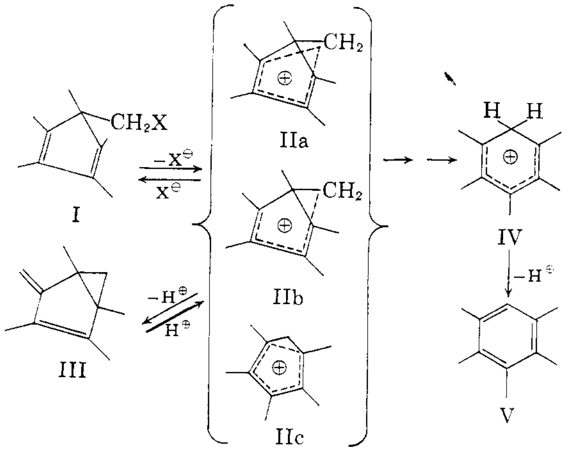
RECEIVED JULY 11, 1960

CYCLOPENTADIENYLMETHYL DERIVATIVES AS HOMOALLYLIC SYSTEMS[1,2]

Sir:

Pentamethylcyclopentadienylmethanol (I-OH), very recently prepared by de Vries,[3] appeared to be of considerable interest as a homoallylic[4] system with a conjugated diene group uniquely disposed toward the developing cationic center in ionization of derivatives such as the toluenesulfonate I-OTs. Carbonium ions from ionization of I-OTs were of interest as possibly unique non-classical species and as an example of a possible type of intermediate in isomerization and cracking of aromatic hydrocarbons.[5] Examination of the behavior of pentamethylcyclopentadienylmethyl *p*-toluenesulfonate (I-OTs) in solvolysis does indeed show that uniquely stabilized non-classical carbonium ion intermediates are involved.



As is clear from the observed rate constant, acetolysis of I-OTs is anchimerically accelerated. For I-OTs, m.p. 63.0–63.5° (dec.) (correct C, H analysis), derived from I-OH, which was in turn prepared by the method of de Vries,[3] the observed acetolysis rate constant at 25° is $1.83 \pm 0.04 \times 10^{-3}$ sec.$^{-1}$. This is larger than the value for neopentyl toluenesulfonate[6] by a factor of *ca.* 10^8. Allowing a power of ten per olefinic group for inductive retardation of anchimerically unassisted ionization,[4b] we see that ionization of I-OTs must be anchimerically accelerated by a factor of at least 10^{10}.

From acetolysis of 0.04–0.08 *M* I-OTs at room temperature under nitrogen in acetic acid containing 0.11 *M* sodium acetate, there is isolated after 1.2 hours (11 half-lives of I-OTs) an 80% yield of a mixture of a hydrocarbon and the acetate of the parent alcohol, I-OAc. The hydrocarbon is the main component, vapor phase chromatographic analysis giving an 18:1 hydrocarbon:acetate ratio. From infrared and ultraviolet spectra, the hydrocarbon is the interesting compound III prepared by de Vries[7] by decomposition of the bromobenzenesulfonate I-OBs in pyridine. A specimen of III which we prepared from I-OTs by this method displayed identical vapor phase chromatographic behavior as that of the hydrocarbon fraction from acetolysis of I-OTs. Hydrocarbon III is also very predominantly the product from solvolysis of I-OTs in 70% aqueous acetone, 0.16 *N* in sodium carbonate. No pentamethylbenzene (V) was detectable in these solvolysis products.

When the acetolysis of I-OTs in acetic acid containing sodium acetate was allowed to proceed for 20 hours, the acetate I-OAc was now the main component of the hydrocarbon–acetate product mixture, the acetate:hydrocarbon ratio being 5.5. However, no pentamethylbenzene was observed. When acetolysis of 0.04 *M* I-OTs was carried out at room temperature for 1.2 hours in the absence of sodium acetate, the product was now mainly acetate I-OAc, together with some pentamethylbenzene (*ca.* 9%). A similar mixture of acetate I-OAc and pentamethylbenzene is obtained from hydrocarbon III after 1.2 hours in acetic acid containing 0.05 *M* toluenesulfonic acid. No pentamethylbenzene was produced from acetate I-OAc under the same conditions, however. On addition of alcohol I-OH to ethanesulfonic acid or heating I-OTs above its melting point, large amounts of pentamethylbenzene are formed.

While it is clear that anchimerically assisted ionization of I-OTs leads to non-classical[4] homoallylic ions such as II, it is not clear exactly how to represent the electron delocalization, nor how many such discrete species need to be written. This is illustrated with ions IIa, doubly homoallylic, IIb, singly homoallylic, and IIc, monohomocyclopentadienyl.[8] Even more delocalized structures are conceivable. Kinetic control of products in basic acetic acid or aqueous acetone solvents leads very predominantly to hydrocarbon III by proton loss. However, this hydrocarbon re-adds a proton even in basic acetic acid solvent and the carbonium ion II leads to some acetate I-OAc, so that acetate I-OAc can become the predominant product from more thermodynamic control.

Carbonium ions of the II-variety do not lead to pentamethylbenzene, prior rearrangement to ion IV through an unspecified number of stages pre-

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[1] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] Research sponsored by the Office of Ordnance Research, U. S. Army.

[3] L. de Vries, *J. Org. Chem.*, in press.

[4] S. Winstein, *et al.*, THIS JOURNAL, (a) **70**, 838, 3528 (1948); (b) **72**, 5795 (1950); (c) **76**, 18 (1954); (d) **77**, 4183 (1955); (e) **78**, 592 (1956); (f) **78**, 4347, 4354 (1956); (g) **81**, 4399 (1959); (h) **82**, 2084 (1960).

[5] R. F. Sullivan, C. J. Egan, G. E. Langlois and R. P. Sieg, "A New Reaction that Occurs in the Hydrocracking of Certain Aromatics," Petroleum Division, American Chemical Society, New York, N. Y., Sept. 11–16, 1960.

[6] S. Winstein and H. Marshall, THIS JOURNAL, **74**, 1120 (1952).

[7] L. de Vries, *ibid.*, **82**, 5242 (1960).

[8] (a) S. Winstein, J. Sonnenberg and L. de Vries, *ibid.*, **81**, 6523 (1959); (b) S. Winstein, *ibid.*, **81**, 6524 (1959).