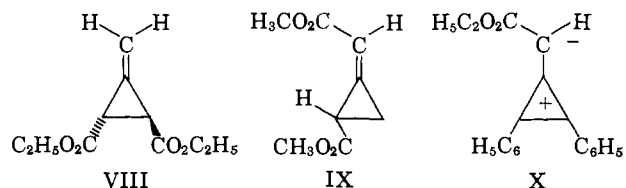
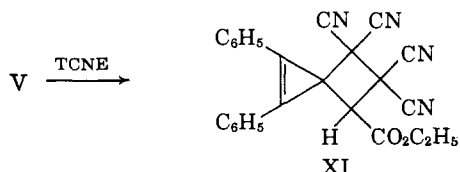


polar form X to the resonance hybrid. The effect of solvent on the long wave length absorption band of V in the ultraviolet likewise supports the view of a highly polar ground state. Further studies to check this point are currently in progress including dipole moment measurements of V and similar systems.



Preliminary observations on the stability and chemical reactivity of V suggest that the chemistry of methylenecyclopropenes may not be too unlike that of their reactive seven-membered ring counterparts, the heptafulvenes. Unless V is isolated and carefully stored in a highly pure solid form, it will resinify within a few weeks at normal room temperature conditions. Although no apparent reaction of V with dimethyl acetylenedicarboxylate is observed at room temperature,<sup>13</sup> an immediate reaction with tetracyanoethylene (TCNE) in acetonitrile solvent is noted by disappearance of the long wave length band at 371 m $\mu$  and appearance of a new peak at 322 m $\mu$ . The retention of the typical absorption pattern of the covalent diphenylcyclopropenes in the 300 m $\mu$  region of this spectrum suggests the possible formation of the interesting spirohexene derivative XI. Our investigations of this and other reactions of V are continuing.



The application of the Wittig olefin synthesis to the preparation of other methylenecyclopropenes, and, similarly, to the preparation of heptafulvenes from tropone and tropolone derivatives is apparent. It is further apparent that the stability of and the nature of substituents on the methylenephosphorane and the method of its generation should have an important bearing on the success of the synthesis. The establishment of the relevant significance of these factors requires further investigation.

(13) For the pertinent reaction of dimethyl acetylenedicarboxylate with heptafulvene, see W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1980).

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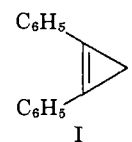
### Attempts to Generate a Cyclopropenylidene. I. An Unexpected Synthesis of a Methylenecyclopropene

Sir:

As a continuation of our investigations on small ring carbenes,<sup>1</sup> we have attempted to generate 2,3-diphenylcyclopropenylidene (I). We felt that this would be a particularly interesting species since its chemical properties would probably be more nucleophilic<sup>2</sup> in character than a typical alkylidene because of conjugation

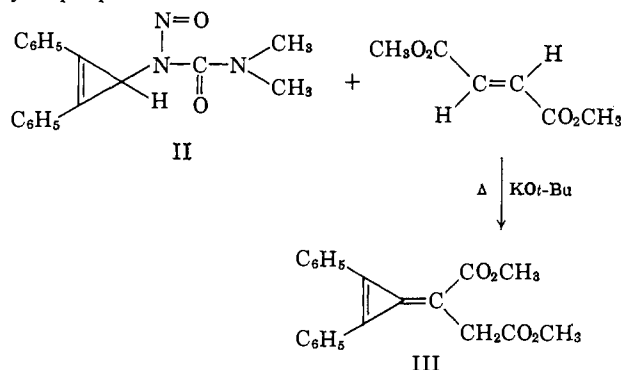
(1) Cf. W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Am. Chem. Soc.*, **85**, 2754 (1963).

(2) For a review dealing with nucleophilic carbenes, see H. W. Wanzlick, *Angew. Chem. Intern. Ed. Engl.*, **1**, 75 (1962).



of the double-bond electrons with the vacant orbital of the carbene.

In this communication we wish to report the synthesis of one potential cyclopropenylidene progenitor, N,N-dimethyl-N'-nitroso-N'-(2,3-diphenyl-2-cyclopropenyl)urea (II). Furthermore, we wish to report that the reaction of this material with dimethyl fumarate and potassium *t*-butoxide at 98° gives rise to a good yield (48%) of an adduct that corresponds to the addition of 2,3-diphenylcyclopropenylidene to dimethyl fumarate and has the structure of the methylenecyclopropene III.



This result constitutes an unexpected synthesis of a rather elusive<sup>3</sup> and inherently very interesting type of compound.

N,N-Dimethyl-N'-(2,3-diphenyl-2-cyclopropenyl)urea was synthesized from 1,2-diphenylcyclopropene-3-carboxylic acid<sup>4</sup> via the acid chloride, the acid azide, the isocyanate, and the dimethylurea in the same manner as we have reported for the synthesis of N-(2,2-diphenylcyclopropyl)urea.<sup>1</sup> Under typical nitrosating conditions, the nitrosourea (II) is quite unstable. For this reason, a variation of White's method<sup>5</sup> was used to effect the nitrosation of the urea. In a typical run, 0.9 g. of the urea was treated with an equimolar amount of dinitrogen tetroxide in 25 ml. of ether in the presence of an equimolar amount of sodium acetate at -55°. The mixture was stirred for 2 hr. at this temperature, an equal volume of cold pentane was added, and the mixture filtered. The residue of yellow solid was washed rapidly with very dilute sodium bicarbonate solution and water and dried. Recrystallization from benzene-pentane gave 73% of beautiful yellow crystals of the nitrosourea,<sup>6</sup> m.p. 96-97° dec., analytical sample, m.p. 102° dec. The nitrosourea is stable for months in the refrigerator but is remarkably unstable to protonic acids (even as weak as methanol).

Thermal decomposition of this material in the presence of dimethyl fumarate has been carried out under a variety of conditions. The conditions that we have found to be most effective for producing the adduct III are as follows. To 200 ml. of degassed (with argon) heptane was added 0.5 g. of the nitrosourea and 3.0 g. of dimethyl fumarate. The mixture was refluxed for 30 min., cooled to room temperature, 0.250 g. of potassium *t*-butoxide added, and the mixture re-

(3) Cf. A. S. Kende, *J. Am. Chem. Soc.*, **85**, 1882 (1963), and references cited therein. For a very straightforward synthesis of this type of compound, see M. A. Battiste, *ibid.*, **86**, 942 (1964).

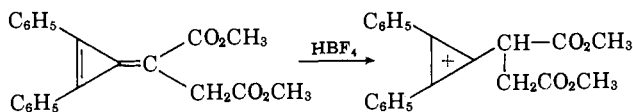
(4) R. Breslow, R. Winter, and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959).

(5) See E. H. White, *J. Am. Chem. Soc.*, **77**, 6008 (1955).

(6) All new compounds gave correct elemental analyses.

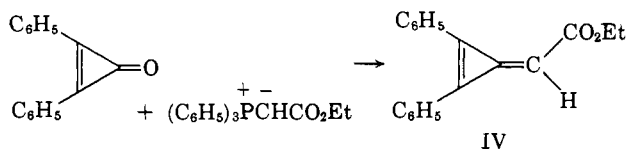
fluxed again for 17 hr. The reaction mixture was cooled and washed with dilute acid. The almost colorless heptane solution was then extracted with concentrated hydrochloric acid and the acid layer diluted with water to give the bright yellow adduct. Traces of dimethyl fumarate were removed by chromatographing the crude product over a short column of acid-washed alumina (or silica gel). This gave 0.264 g. (48.5%)<sup>7</sup> of III, m.p. 126–127.5°. Recrystallization from methanol gave an analytical sample.

The methylenecyclopropene is a stable yellow solid, m.p. 127.0–127.5°. *Anal.* C, 75.39; H, 5.66; mol. wt., 350. The infrared spectrum (KBr) shows strong peaks at 5.4  $\mu$  (cyclopropene) and at 5.75 and 5.98  $\mu$  (unconjugated and conjugated ester). Its ultraviolet spectrum (acetonitrile) shows maxima at 244 m $\mu$  ( $\epsilon$  21,600), 252 (22,000), 268 (18,200), 298 (19,600), and at 378 (6850). In the presence of fluoroboric acid, the spectrum shows absorptions at 249 m $\mu$  ( $\epsilon$  16,600), 294 (29,800), and at 308 (31,000). This spectrum is strikingly similar to the reported spectra of the diphenylcyclopropenyl cation<sup>8</sup> and 1,2-diphenyl-3-propylcyclopropenyl fluoroborate<sup>9</sup> and suggests the following reaction.



The n.m.r. spectrum of the methylenecyclopropene is also interesting. The phenyl resonances appear as three peaks, each of which appears to have some fine structure. These peaks appear at  $\tau$  1.65, 2.08, and 2.44 (from tetramethylsilane) and have relative areas of 1.97:2.47:5.85 (the latter two are not completely resolved). The methyl hydrogens and the methylene hydrogens could not be completely resolved although they could be very easily assigned resonance values, the two methyls appearing at  $\tau$  6.18 and 6.28 and the methylene at  $\tau$  6.34.

Final evidence for the suggested methylenecyclopropene structure resides in the alternate synthesis of a similar compound by Battiste<sup>10</sup> according to the following reaction.<sup>11</sup> The ultraviolet spectra of III and IV are virtually identical. In the phenyl region, the



n.m.r. spectra are also strikingly similar.<sup>12</sup>

We are presently engaged in experiments that we

(7) It is interesting that low yields (6–7%) of adduct III can be obtained by thermally decomposing the nitrosourea in the presence of dimethyl fumarate but in the absence of the base. This reaction, as well as the details of the reaction with potassium *t*-butoxide, will be discussed in detail in a forthcoming publication.

(8) D. G. Farnum and M. Burr, *J. Am. Chem. Soc.*, **82**, 2651 (1960); R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961).

(9) R. Breslow, H. Hover, and H. W. Chang, *ibid.*, **84**, 3168 (1962).

(10) M. A. Battiste, *ibid.*, **86**, 942 (1964).

(11) Preliminary attempts to alternately synthesize adduct III by reaction of the appropriate ylide with diphenylcyclopropenone according to the method of Battiste<sup>10</sup> were met with only limited success. Thus, for example, reaction of the ylide with the ketone in refluxing heptane for 2 weeks followed by column chromatography and by thin layer chromatography gave a trace of yellow material, which showed an ultraviolet spectrum that had all of the peaks of the adduct contaminated with an appreciable amount of some other material.

(12) See ref. 10 for details.

hope will shed some light on the mechanism of this reaction.

**Acknowledgment.**—The authors are most grateful to the U. S. Army Research Office (Durham) for its generous support of this work.

(13) Alfred P. Sloan Fellow.

(14) National Science Foundation summer research participant, 1963.

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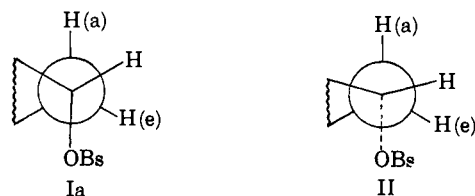
### The Conformational Dependence of Secondary Deuterium Isotope Effects in Solvolytic Reactions<sup>1</sup>

Sir:

$\beta$ -Deuterium effects on the rates of a large number of carbonium ion solvolyses can be satisfactorily correlated by the postulate that the governing mode of interaction between the sites of reaction and isotopic substitution is hyperconjugation.<sup>2</sup> This postulate requires that the maximum rate retardation be observed when the  $\beta$  C–D bond axis is parallel to the axis of the developing vacant p-orbital. We now wish to report the first *direct* observation of such an effect in the aqueous ethanolysis of a conformationally homogeneous system,<sup>3,4</sup> *cis*-4-*t*-butylcyclohexyl bromobenzenesulfonate (brosylate), I.

A comparison of the isotope effect caused by a single axial  $\beta$ -deuterium atom with that caused by *four*  $\beta$ -deuterium atoms on the rate of solvolysis of ester I was presented earlier.<sup>1</sup> We now wish to present a more valid comparison: The isotope effects on the rate of solvolysis of *cis*-4-*t*-butylcyclohexyl brosylate-*trans*-2-*d* (single axial  $\beta$ -deuterium) and *cis*-4-*t*-butylcyclohexyl brosylate-*cis*-2-*d* (single equatorial  $\beta$ -deuterium.)

The conformations of the initial and transition states for this reaction may be represented as Ia and II in which the dihedral angle between the carbon-leaving



group axis and the  $\beta$ -carbon–hydrogen bond axis is 180° for an axial (a) hydrogen atom and 60° for an equatorial (e) hydrogen atom in both the initial and transition states. It is possible that some change in the extent of ring puckering accompanies transition state formation; if the ring flattens, 1,3 steric interactions involving the leaving group would be reduced, the dihedral angle with the axial hydrogen would become less than 180°, and that with the equatorial hydrogen less than 60°.

*cis*- and *trans*-4-*t*-butylcyclohexanol-1-*d* were prepared by lithium aluminum deuteride reduction of 4-*t*-butylcyclohexanone and separated by elution chromatography on activated alumina. *cis*-4-*t*-Butylcyclohexanol-*trans*-2-*d* was prepared by lithium aluminum deuteride reduction of a mixture of *cis*- and *trans*-4-*t*-butylcyclohexene oxide followed by separation of the desired alcohol by fractional crystallization of the *p*-nitrobenzoates. *cis*-4-*t*-Butylcyclohexanol-*cis*-2-*d* was

(1) Presented in part at 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) V. J. Shiner, Jr., and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **85**, 2416 (1963).

(3) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

(4) E. L. Eliel and C. A. Lukach, *ibid.*, **79**, 5986 (1957).