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REACTION OF DIPHENYLCYCLOPROPENONE WITH ACTIVATED ISOCYANATES.
A FACILE SYNTHESIS OF SELECTED IMINOCYCLOPROPENES

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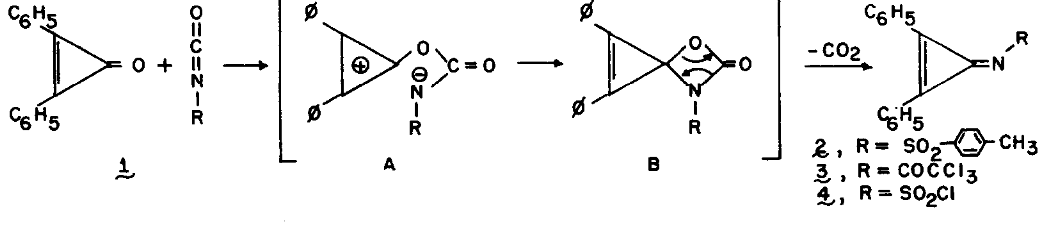
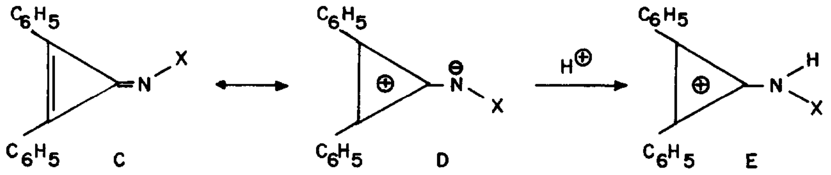
Since its independent synthesis by two research groups in 1959,[3,4] 1,2-diphenylcyclopropenone (**1**) has commanded considerable interest because of its strained, highly polar, and pseudoaromatic nature.[5] Despite the fact that iminocyclopropenes can be expected to possess equally interesting physical and chemical characteristics, only one recent report has disclosed a multistep preparation of derivatives of this class of compounds.[6] In this note, we wish to describe an unusually facile one-step conversion of **1** to selected imino derivatives and the interesting electronic spectra of these novel molecules.

Dropwise addition of *p*-toluenesulfonyl isocyanate to an equimolar quantity of **1** in methylene chloride solution at room temperature proceeded readily with the gradual evolution of carbon dioxide. Subsequent removal of the solvent *in vacuo* and recrystallization of the colorless crystalline residue from CH_2Cl_2-hexane gave **2**, mp $151-152.5^{\circ}$,[7] in 88% yield. Reaction of **1** with trichloroacetyl isocyanate proceeded in similar fashion to afford **3** as white crystals, mp $169-171^{\circ}$ (from CH_2Cl_2-ether),[7] in 83% yield. Exposure of **1** to chlorosulfonyl isocyanate in chloroform solution eventuated in immediate gas evolution and ultimate isolation of **4** as white crystals, mp $183.5-184^{\circ}$ (from $CHCl_3$),[7] in 52% yield.[8] When the latter two reagents were mixed neat at room temperature, there resulted an extremely exothermic reaction which was accompanied by copious CO_2 evolution. All three iminocyclopropenes displayed infrared bands ($CHCl_3$) at 3010, 1840, 1600, 1580, 1530, 1480, 1445, 1080, and 680cm.$^{-1}$; in addition, the spectrum of **3** exhibited prominent carbonyl absorption at 1680cm.$^{-1}$, whereas those of **2** and **4** also featured typical sulfonamide bands.



The reaction is most logically formulated as involving nucleophilic attack of the cyclopropenone oxygen atom at the isocyanate carbon to produce a dipolar species (A) which subsequently (or concomitantly) cyclizes to a 1,3-oxazetidin-2-one (B). Rapid expulsion of carbon dioxide from B is expected in view of the well-established instability of this heterocyclic system.[9] The requirement that the R group in A be capable of substantial stabilization of negative charge for the success of the process has been demonstrated by the lack of reaction between benzoyl and phenyl isocyanates with 1 in refluxing benzene solution for 10-24 hrs. Therefore there exists a limitation as to the types of iminocyclopropenes that may be prepared in this fashion.

The ultraviolet spectra of the three iminocyclopropenes are listed in Table I. Although variation of the solvent from isooctane to the more polar acetonitrile produced distinct differences in the spectra of 1 and 3, a very dramatic change was observed in the case of 4. In fact, the spectrum of 4 in CH_3CN is quite similar to that of the diphenylcyclopropenium cation (see Table I).[10-12] Acidification of the acetonitrile solutions of 2 and 3 afforded spectra that were indicative of cyclopropenium cation formation; under these conditions, the spectrum of 4 was unaltered. On the basis of these electronic spectra, we conclude that in isooctane solution the spectra reflect the presence of non-polarized iminocyclopropenes (C). Dipolar forms (D) are sufficiently stabilized in acetonitrile solvent that their contribution to the resonance hybrid gains importance which is significant with 2 and 3 and complete in the chlorosulfonyl example (4). The fact that the spectrum of 4 is unaltered upon acidification while those of 2 and 3 shift essentially to that of 4 in neutral CH_3CN strengthens these conclusions. In other words, protonation of 2 and 3 is required to observe them as cyclopropenium cations (E), whereas the large negative inductive effect of the chlorosulfonyl group permits the attainment of maximum dipolar contribution in 4 merely by dissolution in polar solvents.



Since there is no evidence that 4 is protonated upon acidification, the possibility of an ionic structure such as F for acetonitrile solutions of 4 cannot be overlooked. Stabili-
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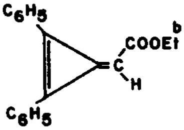
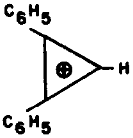
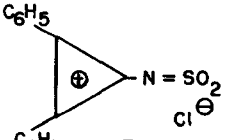
TABLE I
Electronic Spectra

Compound	Solvent	λmax,mμ	(log ε)	λmax	(log ε)	λmax	(log ε)
2	Isooctane[a]	325 (sh)	4.06	289 (sh)	4.12	223	4.35
		316	4.16	280	4.06		
		297	4.20	243	4.34		
	CH_3CN	310	4.37	246	4.39	221	4.40
		297	4.38	225	4.40		
	0.1N $HClO_4$ in CH_3CN	310 (sh)	4.46	300	4.55	250	4.46
						221	4.50
3	Isooctane[a]	323 (sh)	3.98	278	4.22	220 (sh)	4.02
		312	4.09	250	3.95	214	4.06
		286 (sh)	4.21	229	3.98		
	CH_3CN	328(infl)	4.13	288	4.41	239	3.98
		315 (sh)	4.32	248	3.97		
	0.1N $HClO_4$ in CH_3CN	315	4.40	301	4.46	255 (sh)	4.14
4	Isooctane[a]	327 (sh)	4.39	256 (sh)	4.38	220	4.34
		313	4.57	247	4.49		
		303 (sh)	4.52	226 (sh)	4.34		
	CH_3CN	320	4.33	305	4.46	256	4.24
	0.1N $HClO_4$ in CH_3CN	320	4.34	305	4.46	256	4.25
 [b]	Isooctane	452 (sh)	3.23	312	4.12	268	4.33
		423 (sh)	3.71	299	4.26	252	4.43
		400	3.87	286	4.24	244	4.42
		382	3.89				
	CH_3CN	371	3.95	286 (sh)	4.30	242	4.39
		308	4.24	267	4.34		
		295	4.35	250	4.39		
	HBF_4/CH_3CN	307	4.53	293	4.51	247	4.22
 [c]	CH_3CN-10%EtOH 0.1N $HClO_4$	305	4.52	292	4.50	246	4.03

[a] Extinction coefficients for isooctane spectra are given only to present a relative picture of band magnitudes. The insolubility of the iminocyclopropenes in this solvent prevented certainty of absolute concentrations. [b] M. A. Battiste, J. Am. Chem. Soc., **86**, 942 (1964). [c] See reference 10.

zation of the reactive[13] N-sulfonylamine moiety by the diphenylcyclopropenium substituent



F

can be expected in this instance, and addition of acid would have little effect on the spectral results obtained in neutral solution.

The extension of this reaction to tropones is apparent and is presently under investigation.

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FOOTNOTES AND REFERENCES

(1) Alfred P. Sloan Foundation Research Fellow.

(2) National Institutes of Health Postdoctoral Fellow, 1967.

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(4) M. E. Vol'pin, Y. D. Koreshkov, and D. N. Kursanov, Izv. Akad. Nauk SSSR, Otd. Khim Nauk, 560 (1959); Chem. Abstr., **53**, 21799 (1959).

(5) For recent reviews of cyclopropenone chemistry, see (a) G. L. Closs, Advances in Alicyclic Chemistry, **1**, 53 (1966); (b) A. W. Krebs, Angew. Chem. Intern. Ed. (English), **4**, 10 (1965).

(6) T. Eicher and G. Frenzel, Z. Naturforschg., **20b**, 274 (1965).

(7) Acceptable elemental analyses (± 0.30%) were obtained on all new compounds.

(8) A quantity of an unidentified high melting and insoluble by-product accompanied the production of **4**.

(9) H. Ulrich, ''Cycloaddition Reactions of Heterocumulenes,'' Academic Press, New York, 1967, Chapters I and IV.

(10) D. G. Farnum and M. Burr, J. Am. Chem. Soc., **82**, 2651 (1960).

(11) R. Breslow, J. Lockhart, and H. W. Chang, ibid., **83**, 2375 (1961).

(12) It should be noted that the solvent effects and basic spectral patterns given in Table I appear to be quite similar to those obtained with diphenylcyclopropenone also, as would be expected. A referee has stated that the spectra of protonated **2** and **3** are almost identical to that of protonated diphenylcyclopropenone (H_2SO_4 solution; unpublished results from his laboratory).

(13) The generation of N-sulfonylamines by the dehydrohalogenation of sulfamoyl chlorides with triethylamine has recently been reported: G. M. Atkins, Jr., and E. M. Burgess, J. Am. Chem. Soc., **89**, 2502 (1967).