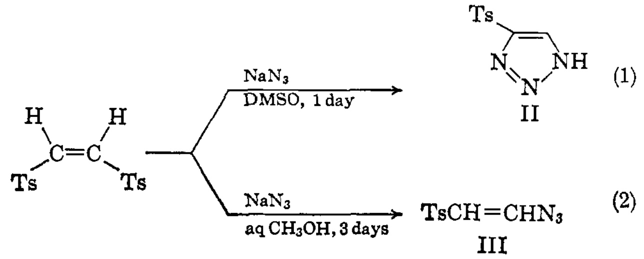
The Isomerization of a Vinyl Azide to a Triazole

Sir:

The conversion of a vinyl azide to a triazole was first attempted in 1910;[1] in 1962 further unsuccessful attempts to carry out this isomerization were made,[2] and a recent text calls attention to the fact that this is still an unknown reaction.[3]

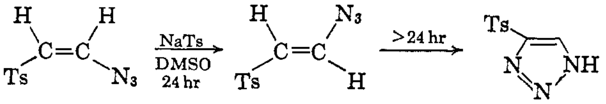
In our studies on addition–elimination reactions of 1,2-di-*p*-toluenesulfonylethene (I), we have observed that the reaction of I with sodium azide in dimethyl sulfoxide proceeded to give 4(5)-*p*-toluenesulfonyltriazole (II) in 45% yield, and not *β*-azidovinyl *p*-tolyl sulfone (III) as expected.



Since I reacted with sodium azide in aqueous methanol to yield a mixture of the *cis* and *trans* isomers of III, we were led to investigate the possible intermediacy of III in the formation of II.

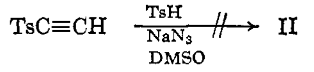
When reaction 1 was shortened to 5 min, a small amount of III was isolated. When reaction 1 was observed from its initiation by use of nmr, the formation and disappearance of III could be followed. When the *trans* isomer of III was isolated, it did not isomerize in dimethyl sulfoxide unless a base, such as sodium azide, sodium *p*-toluenesulfinate, or potassium *t*-butoxide, was present. Sodium *p*-toluenesulfinate in DMSO was the most effective in carrying out the isomerization since with both sodium azide and potassium *t*-butoxide nitrogen loss from the vinyl azide occurred.

When the *cis* isomer of III was allowed to stand in DMSO with sodium *p*-toluenesulfinate for 1 day it was partially converted to the *trans* isomer. If allowed to stand longer, the triazole could be detected by nmr.



(3)

The possibility that triazole formation is occurring through elimination of *p*-toluenesulfinic acid to yield *p*-toluenesulfonylacetylene (IV) followed by cycloaddition of hydrazoic acid to IV (4) is very unlikely since the addition of sodium azide and *p*-toluenesulfinic acid to a cold solution of IV in DMSO results in decomposition with gas evolution.

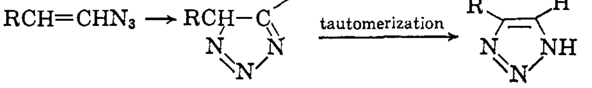


$$\text{TsC}{\equiv}\text{CH} \xrightarrow[\text{NaN}_3\ \text{DMSO}]{\text{TsH}}\!\!\!\!\!\!\!\!/\ \ \ \text{II} \qquad (4)$$

IV

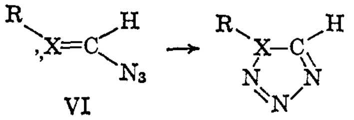
In contrast with the previous observations that many vinyl azides do not cyclize to triazoles is the observation of the very facile cyclization of imidoyl azides to tetrazoles[4] and of thioacyl azides to thiatriazoles.[5] It has been postulated[3] that electronic structure VI is necessary for cyclization.

The cyclization of a vinyl azide would involve the intermediate triazolenine, V, which would have to tautomerize in order to gain aromatic stabilization.

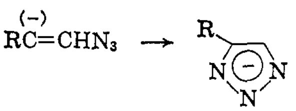


V (5)

However, when a heteroatom such as nitrogen or sulfur is *β* to the azido group, cyclization to an aromatic species is possible. It can be seen that a carbanion


VI (6)

would also possess the electronic requirement for cyclization. Nesmeyanov and Rybinskaya have sug-


(7)

gested that such a carbanion is formed in the reaction of phenyl ethynyl ketone with sodium azide in dimethylformamide to produce 4-benzoyl-1,2,3-triazole.[6]

The acidity of vinyl protons *α* to sulfonyl groups has been demonstrated[7] recently, and the conversion of III to II is consistent with the formation of a carbanion which then cyclizes.

The triazole II was acidic and, after recrystallization from water, melted at 158°; the nmr spectrum in deuteriochloroform showed signals at δ 2.40 (3 H, singlet), 7.66 (4 H, A_2B_2 quartet), and 8.48 (1 H, singlet). *Anal.* Calcd for $C_9H_9N_3O_2S$: C, 48.42; H, 4.06; N, 18.82. Found: C, 48.44; H, 3.95; N, 18.87. The structure of II was supported by an independent synthesis using *p*-toluenesulfonylacetylene and trimethylsilyl azide patterned after the method of Birkofer and Wegner.[8]

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(1) M. S. Forster and S. H. Newman, *J. Chem. Soc.*, **97**, 2570 (1910).

(2) A. N. Nesmeyanov and M. I. Rybinskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **5**, 816 (1962).

(3) P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin Inc., New York, N. Y., 1966, p 243.

(4) E. Lieber, E. Oftedahl, and C. N. R. Rao, *J. Org. Chem.*, **28**, 194 (1963).

(5) P. A. S. Smith, *J. Am. Chem. Soc.*, **76**, 436 (1954).

(6) A. N. Nesmeyanov and M. I. Rybinskaya, *Dokl. Akad. Nauk SSSR*, **166**, 1362 (1966).

(7) C. D. Broaddus, *J. Am. Chem. Soc.*, **88**, 3863 (1966).

(8) L. Birkofer and P. Wegner, *Chem. Ber.*, **99**, 2512 (1966).

(9) National Institutes of Health Predoctoral Fellow, 1966–1967.

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Received February 23, 1967

Photofragmentation of Epoxides. IV. Precursors for Phenylcyanocarbene[1a]

Sir:

Recently we have described photofragmentation reactions of simple aryl- and alkylaryl-substituted

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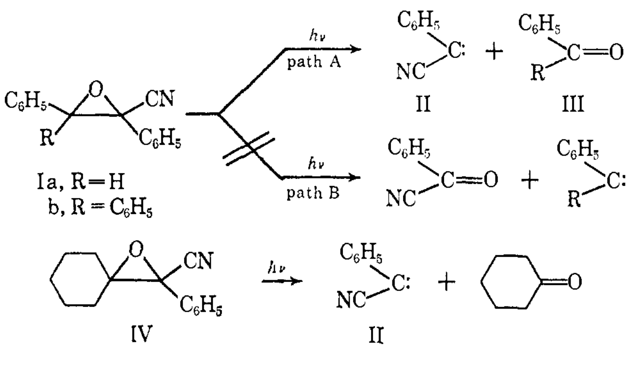
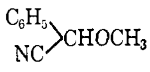
(1) (a) Presented in part at the Fourth Caribbean Symposium held in Kingston, Jamaica, Jan 2, 1967; (b) H. Kristinsson and G. W. Griffin, *Angew. Chem.*, 77, 859 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 868 (1965); (c) H. Kristinsson and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 3259 (1966); (d) H. Kristinsson, *Tetrahedron Letters*, 2343 (1966); (e) P. Petrellis and G. W. Griffin, unpublished results; (f) A. M. Trozzolo, W. A. Yager, G. W. Griffin, H. Kristinsson, and I. Sarkar, *J. Am. Chem. Soc.*, in press.

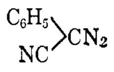
oxiranes, including *trans*-2,3-diphenyloxirane, tri- and tetraphenyloxiranes,[1b,c] and 2,3-dimethyl-2,3-diphenyloxirane,[1d] to arylcarbenes. We have now extended the method to other substituted phenyloxiranes and have found that these provide convenient precursors for substituted arylcarbenes, including cyanophenylcarbene (II), methoxyphenylcarbene,[1e] and carbomethoxyphenylcarbene.[1e] The versatility of the method is apparent from the variety of oxiranes studied to date which fragment to cyanophenylcarbene (II), namely the epoxynitriles Ia, Ib, and IV.



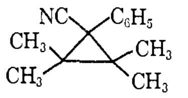
In a typical experiment a methanol solution (0.1 *M*) of *trans*-2,3-diphenyl-2-cyanooxirane (Ia), prepared by peroxidation of *trans*-1-cyanostilbene (mp 70°) according to the method of Payne and Williams,[2] was irradiated[3] for 16 hr. The *major* volatile product obtained was α-methoxyphenylacetonitrile (V) (62%). Phenylcarbene and diphenylcarbene are known to react with protic solvents such as methanol to give the corresponding methyl ethers.[4] Convincing evidence has been presented that ether formation in these cases involves initial protonation of the carbene and subsequent reaction with the solvent.[4] It is unlikely, however, that this mechanism is operative in the conversion of II to V since the cyano group should greatly destabilize the protonated carbene. Despite these mechanistic considerations our contention that II is implicated in the formation of V is supported by the fact that diazophenylacetonitrile[5] (VI) also affords V upon heating at reflux in methanol in the presence of freshly prepared copper catalyst.[6]


$(C_6H_5)(NC)CHOCH_3$

V


$(C_6H_5)(NC)CN_2$

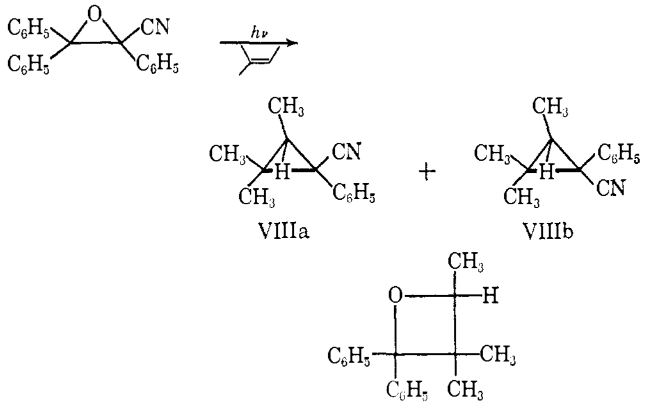
VI



VII

Photolysis of Ia in 2,3-dimethyl-2-butene (0.5 *M*; 10-hr irradiation) affords 2,2,3,3-tetramethyl-1-cyano-1-phenylcyclopropane (VII), mp 89°, bp 100–104° (0.25 mm) (28%), and 2-phenyl-3,3,4,4-tetramethyloxetane. The nmr spectrum of VII exhibits two signals of equal intensity at τ 8.96 and 8.53 in addition to the aromatic signal centered at τ 2.7. The infrared spectrum of VII determined in carbon tetrachloride shows significant bands at 3.25 (w), 3.27 (w), 3.31 (w), 3.33 (s), 3.39 (s), 3.42 (s), 3.48 (m), 4.46 (vs), 6.75 (m), 6.90 (s), 7.30 (s), 7.93 (w), 8.44 (w), 8.99 (s), 9.30 (w), 9.90 (m), 10.20 (w), 10.39 (w), 10.78 (m), 12.44 (s), 14.28 (s), 14.93 (w), 15.15 (w), 17.64 (m) μ. An authentic sample of VII was obtained for purposes of comparison by heating 2,3-dimethyl-2-butene and diazophenylacetonitrile (VI) at the reflux temperature in the presence of copper catalyst.[6]

Similar photochemical results were obtained with 2,3,3-triphenyl-2-cyanooxirane (Ib) (mp 138–139°) and the spirooxirane IV (bp 112° (0.4 mm)) which were obtained in high yield (90 and 75%, respectively) by treating 2,2-diphenyl-2-chloroacetophenone[7,8] and 1-benzoyl-1-bromocyclohexane[9a,b] with sodium cyanide in methanol for 30 (25°) and 10 min (at reflux), respectively. The yields of V are 71% in the case of Ib (0.3 *M*; 36-hr irradiation) and 15% from IV (0.3 *M*; 48-hr irradiation). The oxiranes Ib and IV afford VII in yields of 70 (0.3 *M*; 36-hr irradiation) and 20% (0.3 *M*; 48-hr irradiation), respectively.



The addition of cyanophenylcarbene (II), generated from Ib by photolysis, to 2-methyl-2-butene was also achieved. According to expectations two isomeric 2,2,3-trimethyl-1-phenyl-1-cyanocyclopropanes (VIIIa,b) were obtained in the ratio 1.86:1. The isomer stereochemistry was assigned on the basis of nmr data. The signals attributed to the *cis,vic*-dimethyl groups of VIIIa, the major product, appear at a lower field position (τ 8.61 and 8.58, six protons) than those of the related protons of VIIIb doublet (τ 8.92 and 9.05 (sh), six protons) which are significantly shielded by the *cis* aromatic nucleus. In addition, the cyclopropyl proton of VIIIb is deshielded by the *cis*-cyano substituent. This appears as a multiplet which is partially

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(2) G. B. Payne and P. H. Williams, *J. Org. Chem.*, **26**, 658 (1961).

(3) All irradiations were conducted in quartz vessels with degassed samples at 35° using a Rayonet Chamber Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16 8-w low-pressure mercury lamps. Yields were determined by glpc on a 30% DC Hyvac column (2 m × 8 mm), and also by distillation of the volatile products. No attempt was made to find optimum conditions. All new compounds gave satisfactory combustion analyses for carbon, hydrogen, and nitrogen.

(4) W. Kirmse, "Carbene Chemistry," Academic Press, Inc., New York, N. Y., 1964, p 86.

(5) R. Breslow and C. Juan, *J. Am. Chem. Soc.*, **80**, 5991 (1958). The method for the preparation of VI was modified slightly and the acidity of the system was adjusted to a pH of 2 by addition of concentrated hydrochloric acid prior to the diazotization step.

(6) F. Ebel, R. Brynner, and P. Mangelli, *Helv. Chim. Acta*, **12**, 23 (1929).

(7) C. L. Stevens and J. DeYoung, *J. Am. Chem. Soc.*, **76**, 718 (1954). The corresponding bromide also may be used.

(8) An alternate route to the previously unprepared nitrile Ib involving addition of diphenyldiazomethane to benzoyl cyanide has been described recently. See G. F. Bettinetti and A. Donetti, *Gazz. Chim. Ital.*, **96**, 965 (1966).

(9) (a) C. L. Stevens and E. Farkas, *J. Am. Chem. Soc.*, **74**, 618 (1952). (b) The 1-benzoyl-1-bromocyclohexane is available from Columbia Organic Chemicals Co., Inc., Columbia, S. C.

masked by the sharp singlet at τ 8.48 (three protons) assigned to the remaining methyl. The remaining methyl signal in the spectrum of VIIIa appears at τ 9.18, and the cyclopropyl hydrogen at τ 8.98.

The infrared spectrum of VIIIa (neat) has significant absorption bands at 3.28 (m), 3.30 (m), 3.36 (s), 3.39 (s), 3.42 (s), 3.50 (m), 4.47 (vs) 6.71 (s), 6.90 (s), 8.69 (m), 8.88 (m), 8.98 (m), 9.07 (s), 9.30 (m), 9.77 (s), 9.98 (w), 10.60 (w), 12.70 (s), 13.40 (s), 14.30 (vs), 14.80 (w), 16.53 (w), 17.54 (m), 19.40 (m) μ; $\lambda_{\max}^{\mathrm{CCl_4}}$ for VIIIb: 3.25 (w), 3.27 (m), 3.30 (m), 3.33 (s), 3.38 (s), 3.42 (s), 3.49 (m), 4.48 (vs), 6.71 (m), 6.87 (s), 6.94 (s), 7.30 (m), 8.95 (m), 9.05 (m), 9.30 (m), 9.71 (m), 9.90 (m), 9.98 (w), 10.18 (m), 10.35 (w), 10.47 (m), 10.89 (w), 12.75 (s), 13.10 (s), 14.28 (vs), 14.81 (w), 17.54 (m) μ.

A priori it would appear that the nonbonded interactions in the transition state leading to VIIIa should be less significant than those involved in the formation of the alternate isomer VIIIb. Indeed VIIIa is formed in higher yield, but it must be emphasized that cyclopropanes are known to fragment and/or isomerize photochemically,[1c] and the stability of VIIIa and VIIIb under the reaction conditions must be confirmed before any mechanistic significance can be attached to the stereochemical results.[9a]

Concomitant fragmentation of Ia in the alternate manner (path B) to give phenylcarbene and benzoyl cyanide and of Ib to diphenylcarbene and benzoyl cyanide was expected on the basis of our previous work.[1b,c] However, only traces of benzyl methyl ether and benzhydryl methyl ether (<5%) were produced upon irradiation of these oxiranes in methanol, and no benzoyl cyanide was detected. Furthermore, when Ib was irradiated in 2,3-dimethyl-2-butene and 2-methyl-2-butene, only the corresponding benzophenone oxetanes, mp 105–109° (lit.[10] 106–109°) and 120–122° (lit.[10] 123–125°), were detected among the by-products. It must be concluded that in the case of Ia and Ib the preferred mode of fragmentation is almost entirely by path A to give cyanophenylcarbene.

Esr and luminescence studies conducted in collaboration with Trozzolo and Yager[1f] confirm that carbene intermediates are generated upon photolysis of tri- and tetraphenyloxiranes. These results, in addition to those described herein, provide convincing evidence that phenylcyanocarbene is implicated in the photoreactions of Ia, Ib, and IV. The spin states of the carbene(s) generated from these precursors are under study.

Acknowledgments. We wish to thank the Army Research Office (Durham) for financial support of this research and Professor R. C. Petterson of Loyola University (New Orleans) for helpful discussions during the course of the study.

[9a] NOTE ADDED IN PROOF. We have recently confirmed that VIIIa and VIIIb are stable under the reaction conditions. Thus it appears that the thermodynamically more stable isomer VIIIa is favored in the addition of II to 2-methyl-2-butene.

[10] D. R. Arnold, R. L. Hinman, and A. Glick, *Tetrahedron Letters*, 1425 (1964).

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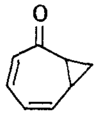
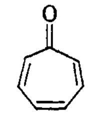
Received February 6, 1967

Photochemical Transformations of 2,3-Homotropone

Sir:

We wish to report the results of our examination of the photochemical behavior of 2,3-homotropone (I), a cyclic ketone which, because of its unique structural features, would be expected to undergo several competitive reactions from its photoexcited state. In common with other homoconjugated systems, the effects of the cyclopropyl group in I are not insignificant,[1] but such conjugation is not favorably disposed to permit the existence of a ring current such as is present in tropone (II).[2]

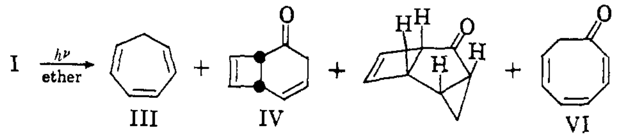

I


II

Exposure of a dilute solution of I[3] in anhydrous ether to a Hanovia 200-w mercury arc lamp for 2 hr, using internally cooled quartz or Pyrex vessels, resulted in the complete disappearance of I and clean conversion to a mixture of four substances as determined by vapor phase chromatography (vpc) (see Chart I). Preparative vpc of the reaction mixture permitted the isolation and purification of the four components. The products were identified (in their order of elution) as cycloheptatriene (III, 6%), bicyclo[4.2.0]octa-4,7-dien-2-one (IV, 15%), 1α,2α,4α,6α-tricyclo[4.2.0.0^{2,4}]oct-7-en-5-one (V, 68%), and 1,3,5-cyclooctatrien-7-one (VI, 11%). Spectral comparisons with authentic samples served to confirm the structures of III, IV,[4] and VI.[5]

The elemental analysis of the major component (V) (*Anal.* Calcd for C_8H_8O: C, 79.97; H, 6.71. Found: C, 79.95; H, 6.78) indicated it to be a photoisomer.

Chart I



III IV V VI

The colorless liquid exhibited pertinent infrared absorption (in CCl_4) at 3030 and 1720 cm^{-1}, a near-infrared band at 1.6339 μ (molar absorptivity = 0.385),[6] and the following ultraviolet spectrum: $\lambda_{\max}^{\mathrm{isooctane}}$ 271 mμ (ϵ 76), 278 (86), 296 (114), 306 (118), 318 (107), and 334 (56). These data were strongly indicative of a nonplanar β,γ-unsaturated ketone, as indicated by the high intensity n → π^* transition,[7] in which the cyclopropyl group had been retained and a strained double bond had been introduced. These conclusions were reinforced by the nmr spectrum which suggested, *inter alia*, the presence of only two vinyl protons. Furthermore, catalytic hydrogenation of this ketone led to the uptake of 1 molar equiv of hydrogen; the resulting dihydro derivative af-

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[1] J. D. Holmes and R. Pettit, *J. Am. Chem. Soc.*, **85**, 2531 (1963).

[2] C. E. Keller and R. Pettit, *ibid.*, **88**, 606 (1966).

[3] 2,3-Homotropone was prepared by a modification of the procedure of Holmes and Pettit.[1] We wish to thank Professor Pettit for his synthetic procedure in advance of publication.

[4] The authors are indebted to Professor G. Büchi for making available to them the infrared spectrum of IV: G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **84**, 3104 (1962).

[5] A. C. Cope and B. D. Tiffany, *ibid.*, **73**, 4158 (1951); C. Ganter, S. M. Pokras, and J. D. Roberts, *ibid.*, **88**, 4235 (1966).

[6] P. G. Gassman and F. V. Zalar, *J. Org. Chem.*, **31**, 166 (1966).

[7] A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962).