

Table I. R_f values of 8-Hydroxyadenine Pentofuranosides

Solvent	8-Hydroxy-adenosine	9- β -D-Arabinofuranosyl-8-hydroxy-adenine	9- β -D-Xylofuranosyl-8-hydroxyadenine
A	0.48	0.39	0.48
B	0.23	0.14	0.24
F	0.50	0.41	0.50
G	0.43	0.27	0.37

8-hydroxyadenosine (IX), which consumed rapidly 1 mole of periodate per mole. In spite of the careful examination of the reaction mixture of the cyclization, no 8,3'-anhydro isomer is isolated. Although the reason is not elucidated as yet, large steric distortion required for the formation of 8,3'-cyclonucleoside⁸ may inhibit the cyclization.

The synthesis and study of O-anhydro derivatives of other purine nucleosides are currently under investigation in this laboratory.

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The Irradiation of 1,1-Dichloro-2-phenylcyclopropane in Olefins. A Light-Induced Transfer of Dichlorocarbene¹

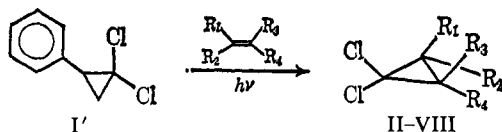
Sir:

Irradiation of solutions of 1,1-dichloro-2-phenylcyclopropane² (I) in olefins with light of $\lambda \geq 210$ m μ leads to rapid destruction of starting material and

Table I. Yields of 1,1-Dichlorocyclopropanes

Olefin	Product	Yield, %
<i>cis</i> -2-Butene	II	10
<i>trans</i> -2-Butene	III	9
<i>cis</i> -4-Methyl-2-pentene	IV	14
<i>trans</i> -4-Methyl-2-pentene	V	15
<i>trans</i> -2,5-Dimethyl-3-hexene	VI	12
2,3-Dimethyl-2-butene	VII	13
Cyclohexene	VIII	14

evolution of a mixture of products. Formally, at least, the major product of the reaction is derived from the addition of dichlorocarbene to the solvent olefin.



- II, $R_1 = R_3 = \text{CH}_3$; $R_2 = R_4 = \text{H}$
 III, $R_1 = R_4 = \text{CH}_3$; $R_2 = R_3 = \text{H}$
 IV, $R_1 = \text{CH}_3$; $R_3 = \text{HC}(\text{CH}_3)_2$; $R_2 = R_4 = \text{H}$
 V, $R_1 = \text{CH}_3$; $R_4 = \text{HC}(\text{CH}_3)_2$; $R_2 = R_3 = \text{H}$
 VI, $R_1 = R_4 = \text{HC}(\text{CH}_3)_2$; $R_2 = R_3 = \text{H}$
 VII, $R_1 = R_2 = R_3 = R_4 = \text{CH}_3$
 VIII, $R_1, R_3 = -\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$; $R_2 = R_4 = \text{H}$

The 1,1-dichlorocyclopropanes are formed in 9–15% yield (Table I). Irradiation of dilute solutions of I in olefins was carried out using as light source a Hanovia

(1) We thank the Lilly Research Laboratories for most generous support of this research. One of us (A. K.) is pleased to thank the National Science Foundation for two Undergraduate Participation Fellowships.

(2) W. J. Dale and P. E. Swartzentruber, *J. Org. Chem.*, **24**, 955 (1959).

type L 450-w high-pressure mercury arc filtered by a Vycor sleeve. Products were identified by comparison of their infrared spectra with those of authentic samples. New compounds (IV–VI) were identified by elemental analysis and comparison of their infrared spectra with those of samples prepared by the method of Doering³ or Robinson.⁴ Examination of the nuclear magnetic resonance spectra of the new compounds revealed no signals in the region expected of vinyl hydrogen⁵ or hydrogen bound to carbon bearing two chlorine atoms.⁶

The decomposition of I is akin to two other reactions recently discovered. Dvoretzky and co-workers⁷ have reported the photochemical cleavage of a number of arylcyclopropanes to arenes and methylene. Griffin and Kristinsson^{8,9} have uncovered the photochemical extrusion of phenylcarbenes from phenyloxiranes. Both these reactions are thought to go through carbenes. There is evidence that a carbene may be the reactive intermediate in the photochemical decomposition of I as well. Irradiation of I in *cis*-2-butene produces 10% of II but less than 0.5% (probably less than 0.1%) of III. The addition appears to proceed in a *cis* fashion. Halocarbenes, or at least the species produced in the base-catalyzed decomposition of haloforms, are known to add to olefins in this manner.^{10,11} Further, dichlorocarbene is known to be a powerful electrophile.^{12,13} When allowed to react with pairs of olefins, dichlorocarbene chooses the more substituted. The species formed in the photolysis of I bears a strong similarity to dichlorocarbene in this respect, adding to cyclohexene a little faster than to *cis*-4-methyl-2-pentene and preferring 2,3-dimethyl-2-butene to *cis*-4-methyl-2-pentene by a factor of *ca.* 100 (Table II).

Table II

Olefin pair	:CCl ₂ Source	Products ^a
2,3-Dimethyl-2-butene/ <i>cis</i> -4-methyl-2-pentene	CHCl ₃ ^b	VII/IV = 110
2,3-Dimethyl-2-butene/ <i>cis</i> -4-methyl-2-pentene	I	VII/IV = >100
Cyclohexene/ <i>cis</i> -4-methyl-2-pentene	CHCl ₃ ^c	VIII/IV = 1.81
Cyclohexene/ <i>cis</i> -4-methyl-2-pentene	I	VIII/IV = 2.24

^a Corrected for varying sensitivities on gas-liquid partition chromatography. ^b Measured at -80° ; $\text{K}^+\text{OC}(\text{CH}_3)_3$ as base.

These data suggest that the intermediate formed in the photolysis of I is very similar to dichlorocarbene both in its mode of addition and its electron-seeking demands. Moreover, the energy provided by the light used, *ca.* 135 kcal/mole, is adequate to break the

(3) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 1612 (1954).

(4) G. C. Robinson, *Tetrahedron Letters*, 1749 (1965).

(5) L. M. Jackman, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p 61.

(6) Reference 5, p 54.

(7) D. B. Richardson, L. R. Durrett, J. M. Martin, Jr., W. E. Putnam, S. C. Slaymaker, and I. Dvoretzky, *J. Am. Chem. Soc.*, **87**, 2763 (1965).

(8) H. Kristinsson and G. W. Griffin, *Angew. Chem.*, **77**, 859 (1965).

(9) H. Kristinsson and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 1579 (1966).

(10) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956).

(11) W. von E. Doering and P. M. LaFlamme, *ibid.*, **78**, 5447 (1956).

(12) W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

(13) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

two cyclopropane carbon-carbon bonds necessary to liberate dichlorocarbene. While the plethora of possible mechanisms, ranging from extrusion of dichlorocarbene to transfer of dichlorocarbon from excited I, makes us reluctant to insist upon dichlorocarbene at this time, both the available data and Occam's razor make it the most attractive candidate.

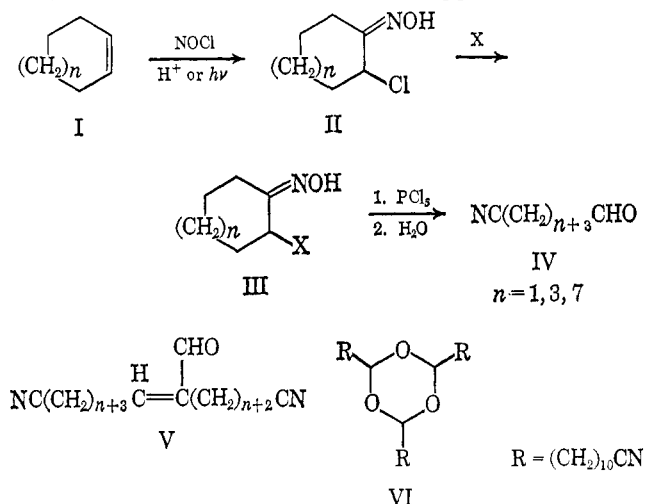
We have not yet been able to determine if the dichlorocarbene produced in this reaction undergoes the carbon-hydrogen insertion reaction. Further, we do not know if I may be fragmenting in more than one direction. Minor products, combining at least fragments of I and solvent molecules, are produced, however. The elucidation of their structures is being actively pursued.

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Synthesis of ω -Cyanoaldehydes through Carbon-Carbon Double Bond Cleavage of Cycloolefins

Sir:

We describe here a synthesis of ω -cyanoaldehydes by a novel sequence of apparent general applicability for carbon-carbon double bond cleavage of cycloolefins. ω -Cyanoaldehydes are not easily accessible, but are interesting synthetic intermediates, since the *termini* of the compounds are left in different oxidation states and may readily be separately modified. Only β -cyanoaldehyde has been prepared, by the oxo reaction of acrylonitrile¹ and the Michael reaction of acrolein,^{2,3} but such methods cannot be applied generally.



We have reported⁴ recently the displacement reactions of α -chlorocycloalkanone oximes, prepared by the addition of nitrosyl chloride to cycloolefins, with various nucleophilic reagents to give, *via* intermediates of α,β -unsaturated nitroso derivatives, α -substituted cycloalkanone oximes. Thus, oximes of 2-alkoxy-, 2-ethylthio-, and 2-alkylaminocycloalkanone have been

(1) J. Kato, H. Watanabe, T. Komatsu, R. Iwanaga, and T. Yoshida, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **64**, 2142 (1961).

(2) J. Tanaka, *J. Pharm. Soc. Japan*, **60**, 219 (1940).

(3) D. T. Warner and O. A. Moe, U. S. Patent 2,565,537; *Chem. Abst.*, **46**, 2565d (1952).

(4) M. Ohno, N. Naruse, M. Okamoto, S. Torimitsu, and I. Sakai, *Bull. Chem. Soc. Japan*, in press.

Table I. Yields of α -Substituted Oximes (III) and ω -Cyanoaldehydes (IV)

X	III, % ^a n = 1, 3, 7	IV, % ^b n = 1, 3, 7
-OCH ₃	72, 92, 80	64, 90, 82
-OEt	76, 91, 81	60, 82, 75
-SEt	45, 72, 85	32, 50, 52
	81, 85, 71	30, 69, 84
	72, 88, 77	31, 65, 51
	82, 84, 87	24, 11, 21

^a Over-all yields from cycloolefins. ^b Based on α -substituted oximes, using PCl₅ as Beckmann reagent.

prepared in excellent yields and were subjected to second-order⁵ Beckmann rearrangement under different conditions. The results are summarized in Table I.

2-Methoxycyclooctanone oxime (30 g) was treated with phosphorus pentachloride (50 g) in absolute ether (200 ml) at 0° for 5 hr and the product was carefully hydrolyzed with ice-water at 0-5°. The ethereal extract afforded a pale yellow liquid (21.1 g), infrared 2800 and 1725 (-CHO) and 2250 cm⁻¹ (-CN). It was converted to an acetal derivative by treatment with ethylene glycol in the presence of a catalytic amount of *p*-toluenesulfonic acid, infrared 2250 (-CN) and 1000-1100 cm⁻¹ (-C-O-C), bp 105-108° (0.25-0.3 mm). *Anal.* Calcd for C₁₀H₁₇NO₂: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.27; H, 9.47; N, 7.60. The 2,4-DNP showed mp 76-77°, yellow needles. *Anal.* Calcd for C₁₄H₁₇N₃O₄: C, 52.66; H, 5.37; N, 21.93. Found: C, 52.80; H, 5.32; N, 21.83. Oxidation of the cyanoaldehyde with potassium permanganate afforded suberic acid in quantitative yield. These results confirm the assignment of the structure to 7-cyanoheptanal (IV, n = 3). When 2-alkylaminocyclooctanone oximes were treated with either phosphorus pentachloride or acetic anhydride-acetic acid they afforded IV (n = 3) along with an aldol condensation product, 2-(5-cyanopentyl)-9-cyano-2-nonenal (V, n = 3), in 5-14% yields, infrared 2700 and 1680 (-C=CCHO) and 2250 cm⁻¹ (-CN); 2,4-DNP mp 112-113°, orange-red crystals. *Anal.* Calcd for C₂₂H₂₈N₆O₄: C, 59.98; H, 6.41; N, 19.08. Found: C, 60.04; H, 6.40; N, 18.94. 11-Cyanoundecanal (IV, n = 7) was obtained from α -alkoxy, α -ethylthio, and α -alkylamino oximes of 12-membered rings⁶ in fairly good yields. Its infrared spectrum displayed the usual bands for aldehyde and nitrile groups at 2700 and 1720 cm⁻¹, respectively. The ethylene acetal showed mp 48-49°. *Anal.* Calcd for C₁₄H₂₃NO₂: C, 70.25; H, 10.53; N, 5.85. Found: C, 70.10; H, 10.63; N, 5.79. The 2,4-DNP showed mp 90-92°, yellow

(5) Other types of electromerically assisted Beckmann reactions have been reviewed recently (H. P. Fischer and C. A. Grob, *Helv. Chim. Acta*, **45**, 2528 (1962); **46**, 936 (1963); H. P. Fischer, C. A. Grob, and E. Renk, *ibid.*, **45**, 2539 (1962)) and are also described in recent communications (R. L. Aurey and P. W. Scullard, *J. Am. Chem. Soc.*, **87**, 3284 (1965); Y. L. Chow, *ibid.*, **87**, 4642 (1965)).

(6) The most convenient method of the preparation of α -substituted cyclododecanone oximes is to use *cis,trans,trans*-1,5,9-cyclododecatriene as a starting material, *i.e.*, addition of nitrosyl chloride in the presence of hydrochloric acid, displacement with nucleophilic reagents, and catalytic hydrogenation with palladium-charcoal [M. Ohno, M. Okamoto, and K. Nukada, *Tetrahedron Letters*, 4047 (1965), and ref 4].