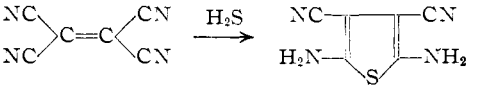
and their derivatives has led to the preparation of tetracyanoethylene (I), the first example of a percyanoölefin. This compound has been shown to be exceptionally reactive and readily undergoes a series of addition and substitution reactions.

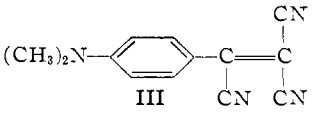
Treatment of dibromomalononitrile–potassium bromide complex[1] with copper powder in benzene under reflux yielded tetracyanoethylene in 65% yield. The product is a white crystalline solid melting at 198–200° in a sealed tube and subliming readily at temperatures above about 120°. (*Anal.* Calcd. for C_6N_4: C, 56.26; N, 43.74; mol. wt., 128. Found: C, 56.42, 56.39; N, 43.23, 43.50; mol. wt., 132.) Tetracyanoethylene is very stable thermally, being unchanged by brief treatment at 600°, and it is resistant to the action of oxygen at moderate temperatures, although it will burn in air.

Tetracyanoethylene is a mild oxidizing agent and converts mercaptans to disulfides, being itself reduced to tetracyanoethane in the process. By treatment with hydrogen sulfide in the presence of pyridine, tetracyanoethylene is converted readily to 2,5-diamino-3,4-dicyanothiophene (II) (92% yield). (*Anal.* Calcd. for $C_6H_4N_4S$: N, 34.13; S, 19.53. Found: N, 34.06, 34.22; S, 19.37.)



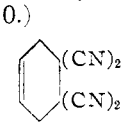
I II

It also reacts with alcohols to give 2,2-dicyanoketene acetals and with N,N-dialkylanilines to give *p*-tricyanovinylaryl amines, a new class of dyes of high tinctorial strength. For example, *p*-tricyanovinyl-N,N-dimethylaniline (III), m.p. 173–175°, has λ_{max} 514 mμ and ϵ_{max} 41,500. (*Anal.* Calcd. for $C_{13}H_{10}N_4$: C, 70.25; H, 4.54; N, 25.21. Found: C, 70.31; H, 4.51; N, 25.11.)

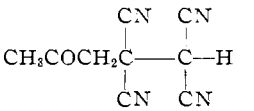


III

Tetracyanoethylene is a very active dienophile, condensing quantitatively with butadiene at 0° to give 4,4,5,5-tetracyanocyclohexene (IV), m.p. 201–202°. (*Anal.* Calcd. for $C_{10}H_6N_4$: C, 65.92; H, 3.32; N, 30.76. Found: C, 65.84, 65.67; H, 3.44, 3.42; N, 30.59, 30.65.)[2] Monoalkylation of ketones having hydrogen alpha to a carbonyl group occurs in the presence of acid catalysts to give α-tetracyanoethyl ketones.[3] For example with acetone in the presence of boron trifluoride at room temperature, 4,4,5,5-tetracyano-2-pentanone (V) is formed in 90% yield; m.p. 118–120° dec. (*Anal.* Calcd. for $C_9H_6N_4O$: C, 58.06; H, 3.25; N, 30.10. Found: C, 58.26, 58.47; H, 3.21, 3.22; N, 30.04, 30.10.)



IV



V

(1) L. Ramberg and S. Wideqvist, *Arkiv. Kemi, Mineral Geol.*, **12A**, No. 22, 12 pp. (1937); *C. A.*, **32**, 2511 (1938).

(2) R. E. Heckert and N. E. Searle, U. S. Patent 2,781,393 (1957).

(3) W. J. Middleton, U. S. Patent 2,762,837 (1956).

Tetracyanoethylene slowly evolves hydrogen cyanide when exposed to moist air at room temperature.

A large number of other reactions of tetracyanoethylene and of related compounds are under investigation, and detailed reports on this research are being prepared for publication.

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EFFECTS OF RING SIZE ON THE REACTIONS OF CYCLIC OLEFINS: HALOHYDRINS FROM METHYLENECYCLOALKANES[1]

Sir:

As part of a study of the effects of ring size on the orientations of addition reactions with cyclic olefins, we have included additions of hypohalous acids to a series of methylenecycloalkanes (ring sizes C_4 through C_7). Although we observed no orientation effects when hydrogen bromide was the addend,[2] significant differences were obtained with hypohalous acids. Additions of hypohalous acids to acyclic 1-alkenes always occur predominantly or exclusively with "normal" orientation (primary halogen).[3] We have found however that addition of HOCl to methylenecycloalkanes gives mixtures of chlorohydrins, with "abnormal" orientation predominating with the 4- and 6-membered ring compounds,[4] and that addition of HOBr to these olefins gives only "abnormally" oriented bromohydrins.

Freshly distilled aqueous HOCl or HOBr solution[5] was added in portions to a stirred aqueous suspension of an equivalent amount of methylenecycloalkane at 15°. The mixture was stirred for an hour longer and the layers were separated. The infrared spectrum of the dried organic layer was recorded before distillation. The fractions obtained on distillation were identified by comparison with authentic samples previously synthesized. Both the spectrum taken before distillation and the proportions of distillate in the fractions were used in estimating product distributions. These data are summarized in Table I. From isobutylene and HOBr we obtained a 77% yield of addition product which was about 97% 1-bromo-2-methyl-2-propanol.

(1) This work was supported in part by Research Corporation and in part by the Petroleum Research Fund of the American Chemical Society.

(2) J. G. Traynham and O. S. Pascual, *J. Org. Chem.*, **21**, 1362 (1956).

(3) For example, see P. B. D. la Mare and A. Salama, *J. Chem. Soc.*, 3337 (1956).

(4) Formation of 1-chlorocyclohexylmethanol only from methylenecyclohexane and HOCl has been reported by M. Tiffeneau, P. Weill and B. Tchoubar, *Compt. rend.*, **205**, 144 (1937).

(5) N-Bromosuccinimide could be substituted for HOBr solution without affecting product distributions. See C. O. Guss and R. Rosenthal, THIS JOURNAL, **77**, 2549 (1955).

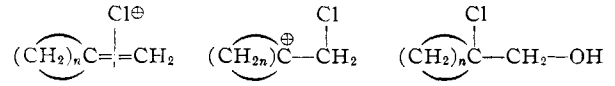
TABLE I

PRODUCT DISTRIBUTIONS IN HYPOHALOUS ACID ADDITIONS TO METHYLENECYCLOALKANES

Ring size	Hypochlorous acid: Total yield, %	Proportion of total, %: >C(Cl)CH₂OH	>C(OH)CH₂OH	Other product	Hypobromous acid: Total yield, %	Proportion of total, %: >C(Br)CH₂OH	Other products
C_4	72	60	40	none[a]	78	99	1[b]
C_5	64	41	58	1[b]	67	91	9[c]
C_6	92	67	32	1[b]	89	98	2[d]
C_7	86	35	64	1[b]	87	87	13[d]

[a] No rearrangement products were found. [b] Slight absorption attributable to a carbonyl group (probably in cycloalkanecarboxaldehyde) appeared in the infrared spectrum of the product. [c] Methylenecyclopentane oxide. [d] Cycloalkanecarboxaldehyde.

The preponderance of "abnormally" oriented products from the 4- and 6-membered rings is consistent with the view that trigonal carbons in those rings are unfavored.[6] The initially formed pi-complex (I) may rearrange (as usual) to the conventional carbonium ion (II),[3,7] or it may suffer direct attack by water to give III. Rearrangement of I to II is the less favored path for 4- and 6-membered rings, but is satisfactory for 5- and 7-membered



I II III

rings.[8] The formation of large amounts of III even from 5- and 7-membered rings, when acyclic olefins give corresponding products only in very small amounts, indicates that this explanation is incomplete and suggests an importance of the ring structure itself in directing orientation. That suggestion is further supported by the complete contrast between HOBr additions to methylenecycloalkanes and to isobutylene.

Since "abnormal" products were not obtained with HBr as addend,[2] it appears that the size of the attacking cation (or the "activity" of the attacking particle[9]) may have an important role in determining the actual orientation with these olefins. We hope that our continuing studies will reveal more explicit information about these effects.

Authentic 1-chloromethylcycloalkanols (except for 1-chloromethylcyclobutanol) were synthesized by hydrolysis of the appropriate methylenecycloalkane dichloride with an aqueous suspension of $CaCO_3$.[10] These chlorohydrins all reduced permanganate, gave precipitates with NaI in acetone and with alcoholic $AgNO_3$, produced immediate cloudiness in Lucas reagent and showed infrared absorption near 7.25 μ (tertiary alcohol). Authentic 1-halocycloalkylmethanols were synthesized by the action of hydrochloric or hydrobromic acid on the appropriate olefin oxide. These halohydrins all reduced permanganate, gave precipitates with alcoholic $AgNO_3$ but none with NaI in acetone, gave negative Lucas tests and showed no infrared absorption near 7.25 μ.

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RECEIVED MARCH 1, 1957

(6) H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954).

(7) Rearrangement of the protonated olefin (pi-complex) to a more conventional carbonium ion has been shown to be an important part of acid-catalyzed olefin hydration; R. W. Taft, Jr., *ibid.*, **74**, 5372 (1952); R. W. Taft, Jr., E. L. Purlee, P. Riesz and C. A. DeFazio, *ibid.*, **77**, 1584 (1955).

(8) A more complete discussion of this point is found in ref. 2.

(9) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

(10) C. E. Sparks and R. E. Nelson, *ibid.*, **58**, 1010 (1936).

URIDINE DIPHOSPHATE N-ACETYLGLUCOSAMINE AND URIDINE DIPHOSPHATE GLUCURONIC ACID IN MUNG BEAN SEEDLINGS

Sir:

Whereas the presence of uridine diphosphate N-acetylglucosamine (UDPaG) has been reported in penicillium, yeast and animal tissues[1-3] and uridine diphosphate glucuronic acid (UDPGuc) in liver tissue, these nucleotides have hitherto been unknown in higher plants.

In the present communication evidence is presented for the existence of UDPaG and UDPGuc in mung bean seedlings. Furthermore, these seedlings contain a hitherto unknown enzyme which catalyzes the reaction between UDPGuc and pyrophosphate to form uridine triphosphate (UTP) and presumably D-glucuronic acid 1-phosphate. While UDPGuc may be considered a possible precursor of the synthesis of polyuronides in plants, the function of the UDPaG is at present obscure.

The two nucleotides were isolated from 10 kg. of mung bean seedlings using methods described by Ginsburg, *et al.*[4] The nucleotide fraction eluted from the Dowex-1-Cl^- column by 0.01 *N* HCl–0.15 *N* NaCl was further purified by paper chromatography.[3] In this way 14 μmoles of a nucleotide (I) corresponding in R_f to authentic UDPaG (R_f 0.45) was separated. A second nucleotide fraction, eluted by 0.01 *N* HCl–0.06 *N* NaCl, was further purified by paper electrophoresis in formate buffer at *p*H 3.5[4,5] to yield 4 μmoles of a nucleotide (II) corresponding to UDPGuc in electrophoretic mobility.

Hydrolysis of both nucleotides with 0.1 *N* HCl at 100° for 10 minutes liberated chiefly uridine diphosphate, while hydrolysis with 1.0 *N* HCl yielded

(1) L. F. Leloir, Proc. 3rd Intern. Congr. Biochem., Brussels, 1955, p. 154.

(2) E. Cabib, L. F. Leloir and C. E. Cardini, *J. Biol. Chem.*, **203**, 1055 (1953).

(3) E. E. B. Smith and G. T. Mills, *Biochim. et biophys. Acta*, **13**, 386 (1954).

(4) V. Ginsburg, P. K. Stumpf and W. Z. Hassid, *J. Biol. Chem.*, **223**, 977 (1956).

(5) A. M. Crestfield and F. W. Allen, *Anal. Chem.*, **27**, 422, 424 (1955).