

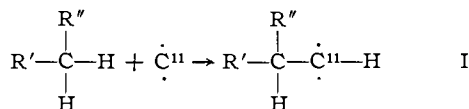
TABLE I

PRODUCTS OF REACTION OF ATOMIC CARBON WITH ALKANES

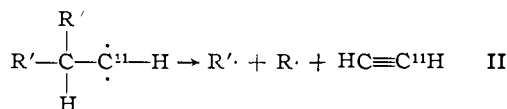
All yields are % total volatile activity as determined by passing an aliquot of the sample directly through the counter. ~2% O₂ was present in all samples to minimize radiation induced reduction of unsaturated hydrocarbon products, and to act as a scavenger for C atoms⁴ and for radicals. Blanks denote that the product was undetected, having a yield of $\lesssim 1\%$. Cyclopropane and the butene-2's were also sought and have a yield of $\lesssim 1\%$.

	Reacting molecule			
	CH ₄	C ₂ H ₆	C ₃ H ₈	cyclo-C ₃ H ₆
Carbon monoxide	26.8	25.2	19.0	15.0
Methane	1.5	<2	<2	<2
Ethane	3.1	<2	2.0	
Ethylene	28.0	19.5	12.1	
Acetylene	30.0	32.7	29.5	65.5
Propane		5.1	.7	
Propene		5.0	.6	
Allene			1.4	
Propyne			2.7	2.3
Isobutane			2.0	
n-Butane			3.9	
Isobutene			2.4	
Butene-1			3.0	
Butadiene-1,3			1.2	7.4

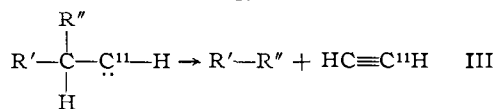
Table I gives some of the significant products observed in several saturated hydrocarbons. The most striking result is the high yield of acetylene. This has been observed in each of the ten hydrocarbons of varying structure and bond type that we have investigated. This high yield is explained readily if C-H bond insertion is assumed. Suf-



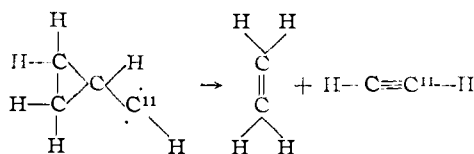
ficient energy may be made available by this insertion to rupture two C-C bonds directly where the spin conservation rule is obeyed.



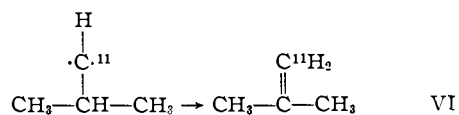
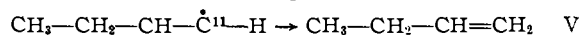
Alternatively the carbene produced in reaction I may be collisionally de-excited to the singlet state. When this happens the molecule would immediately decompose by reaction II or by reaction III (which has a lower energy requirement)



There are several specific points supporting this mechanism: (1) It is difficult to conceive of any mechanism other than insertion of C or CH into a C-H bond which would yield acetylene from methane. (2) The carbene intermediate formed by C atom insertion may decompose in other ways which do not yield acetylene (discussed below). However, with cyclopropane decomposition to acetylene should be particularly favored because stable products can be formed by simple electronic rearrangement with little nuclear motion



This is true only of the carbene formed by insertion into cyclopropane. Experimentally cyclopropane yields about twice as much acetylene as any of nine other hydrocarbons we have studied. Acetylene formation from cyclopropane is also significantly greater than that from cyclobutane. (3) Products present in smaller yield than acetylene can result from more complex modes of rearrangement of the intermediate carbene. For example in the reaction with propane sufficient energy is available to yield ethylene, propylene, allene, methylacetylene, and butadiene, all of which are observed. (4) The small yields of butenes-1 and isobutene from propane are interesting. These may result from deactivation of the intermediate carbenes without decomposition



By these considerations most of the products may be rationalized. The yields of built-up saturates are in exception.⁵ Such products are significant but are never the major yields. They may be formed by the reactions of the CH₂ radical⁶ which in turn arises from H atom pick-up by the carbon atom.

(4) M. Pandow, *et al.*, *J. Inorg. and Nuclear Chem.*, **14**, 153 (1960).

(5) Previously observed by A. Wolf and C. MacKay and W. F. Libby: see A. Wolf, *Angew. Chemie*, **71**, 237 (1959).

(6) W. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959).

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THE PHOTOLYSIS OF ORGANIC
NITRITES. III. OXIDATIVE FISSION
OF CARBON-CARBON SINGLE BONDS
IN α -OXYGENATED ALCOHOLS¹

Sir:

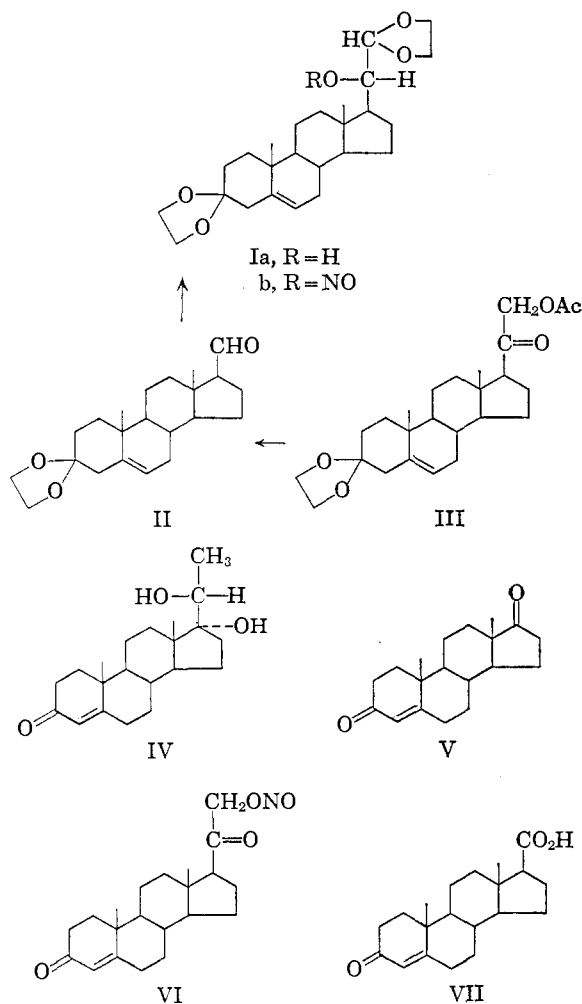
A recent paper by a group of Japanese workers² describes the preparation of 3,3,21,21-bis-(ethylene-dioxy)-5-pregnen-20 β -ol (Ia) by means of a Mattox-Kendall rearrangement of Compound S, and then reduction. Since this compound appeared to be a promising starting material for the synthesis of 18-oxygenated substances related to aldosterone *via* the irradiation of 20-nitrites^{3a,b,c} it was converted to its nitrite (Ib) by treatment with

(1) Paper II of this series: C. H. Robinson, O. Gnoj, A. Mitchell, R. Wayne, E. Townley, P. Kabasakalian, E. P. Oliveto and D. H. R. Barton, *J. Am. Chem. Soc.*, **83**, 1771 (1961).

(2) K. Tsuda, N. Ikekawa and S. Nozoe, *Chem. Pharm. Bull. (Japan)*, **7**, 519 (1959).

(3) (a) D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet, *J. Am. Chem. Soc.*, **82**, 2640 (1960); (b) D. H. R. Barton and J. M. Beaton, *ibid.*, **82**, 2641 (1960); (c) A. L. Nussbaum, F. E. Carlon, E. P. Oliveto, E. Townley, P. Kabasakalian and D. H. R. Barton, *ibid.*, **82**, 2973 (1960).

nitrosyl chloride in pyridine and photolyzed in benzene for a one-hour period, by means of a 200-watt mercury lamp, at 20°. The resulting material had unexpected bands in the infrared spectrum at 3.69 and 5.83 μ , and its elementary analysis was in agreement with the formula $C_{22}H_{32}O_3$.



It was therefore assigned structure II, the 20-aldehyde.⁴

This assignment was buttressed by correlation with a compound of unequivocal structure. 3,3-Ethylenedioxy-21-acetoxy-5-pregnen-20-one⁵ (III) was converted to the mixture of 20,21-diols with lithium aluminum hydride and subsequent oxidative cleavage with potassium periodate in dioxane⁶ gave an ethylenedioxy-aldehyde identical with II.

Similarly, an attempt to extend the nitrite irradiation method that had led to the preparation of 18-nitriloprogesterone^{3c} to the corresponding 17 α -hydroxy analog led to an unexpected result:

(4) A similar observation in the corresponding 11-oxygenated series by Dr. J. M. Beaton of the Research Institute for Medicine and Chemistry stimulated this present systematic study. We thank Dr. Beaton for informing us of his results.

(5) R. Antonucci, S. Bernstein, R. Lenhard, N. J. Sax and J. H. Williams, *J. Org. Chem.*, **17**, 1369 (1952).

(6) Periodic acid in methanol gave mixtures, presumably by *trans*-ketalization at C-3 and partial conversion to the acetal at C-20.

Treatment of 17 α ,20 β -dihydroxy-4-pregnen-3-one⁷ (IV) with nitrosyl chloride led to an ill-defined dinitrite⁸ which, upon irradiation, gave rise to 4-androstene-3,17-dione (V).

Finally, during the study of the behavior of 21-nitrites, a representative member (21-desoxy-corticosterone nitrite, VI, (m.p. 126–127° dec., [α]_D 157, ϵ_{241} 17,200, λ_{Nujol} at 5.81, 6.02, 6.10 and 6.19 μ) was irradiated in benzene. One of the conversion products isolated proved to be the known 3-keto-4-etiocholenic acid (VII).

It would appear, then, that in the special case where a nitrite is vicinally substituted by an oxygen-bearing moiety, photolytic oxidative fission occurs in competition with, and perhaps to the exclusion of, intramolecular hydrogen abstraction. The neighboring group may be a ketone, an alcohol or an acetate, and the full scope of the reaction is under investigation.⁹

(7) J. Romo, M. Romero, C. Djerassi and G. Rosenkranz, *J. Am. Chem. Soc.*, **73**, 1528 (1951).

(8) An attempt to prepare a mononitrite gave mixtures.

(9) A number of simple aliphatic 1,2-glycol dinitrites have been observed to undergo similar oxidative fission on pyrolysis; cf. L. P. Kuhn and L. DeAngelis, *J. Am. Chem. Soc.*, **76**, 328 (1954).

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THE FORMATION OF OXINDOLE ACETIC ACID FROM INDOLES BY A BASIDIOMYCETE

Sir:

During a study of the metabolism of indoles by Basidiomycetes in submerged culture, a compound was found in the spent beers of *Hygrophorus conicus* which gave a blue-green spot on a papergram sprayed with Ehrlich reagent. This compound, which was produced from both tryptamine and indole-3-acetic acid in good yields, was isolated and proven to be oxindole-3-acetic acid. No isolation of oxindole-3-acetic acid from a natural source has been reported, although Klämbt¹ published chromatographic evidence for its presence in an extract of maize.

The high yield of oxindoleacetic acid from tryptamine reported here indicates that the indoleacetic acid oxidase produced by *Hygrophorus conicus* differs from that of *Omphalia flavida*,² which converts indoleacetic acid to 3-methyl-oxindole.

Two 7-l. fermentors, each containing 5 l. of 4% malt extract and 2.5 g. of tryptamine, were inoculated with growing mycelium of *Hygrophorus conicus*. The fermentation was carried out at 27° and an aeration rate of 3 l./min. for one week. The beer was filtered, concentrated to 1.5, acidified (pH 2), and extracted with ethyl acetate. The desired compound was removed from the concentrated ethyl acetate solution with 5% NaHCO₃ and then taken back into ether. When the ether was removed *in vacuo* crystals formed (3.16 g.).

(1) H. Klämbt, *Naturwissenschaften*, **23**, 649 (1959).

(2) P. M. Ray and K. V. Thimann, *Arch. Biochem. Biophys.*, **64**, 175 (1956).