should be formed. In view of this we have now carried out such experiments with ketene and found that triplet methylene is formed, as shown by its nonstereospecific reactions with butene-2[3,6,7,8] and lack of random CH insertion reactions.

We have studied reactions of triplet methylene generated in this manner with *cis*- and *trans*-butene-2 and isobutene. In all experiments the ratio of ketene to olefin was 1:10. At lower pressures the product composition varied as a result of secondary reactions of the non-stabilized "hot" adduct, as is also observed in the reactions of singlet methylene.[4] Steady values were obtained in the case of *cis*- and *trans*-butene-2 at approximately 50 cm. and, in the case of isobutene, at about 20 cm. The composition of the products in the high pressure region, expressed as percentage of the total C_5 compounds, is shown in the table.

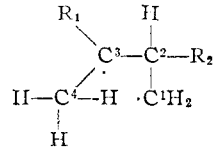
TABLE I

	Dimethylcyclopropane			Pentene-2		2-Me[a]	3-Me[b]	2-Me[c]
Reactant	*cis*-1,2	*trans*-1,2	1,1	*cis*	*trans*	B-1	B-1	B-2
trans-Butene-2	13.5	51.9	..	5.6	18.7	0.7	6.8	2.8
cis-Butene-2	21.6	31.3	..	19.3	12.3	0.7	8.1	3.7
cis-Butene-2[d]	28.1	27.1	..	17.0	16.5	..	10.5	4.0
Isobutene	..	..	91.0	..	..	6.5	0.5	2.3

[a] 2-Methylbutene-1. [b] 3-Methylbutene-1. [c] 2-Methylbutene-2. [d] The values obtained from diazomethane photolysis in the presence of excess inert gas (ref. 7).

Unlike singlet methylene, the triplet is seen to react nonstereospecifically with butene-2 and to give far more dimethyl-cyclopropane and 3-methylbutene-2. In the case of *cis*-butene-2 the results can be compared with those obtained from diazomethane photolysis in the presence of excess inert gas,[7] with which they agree reasonably well. In the isobutene reaction, comparison with singlet methylene[9,10] shows a large increase in the amount of 1,1-dimethylcyclopropane with corresponding reduction in the yields of other products.

The suggested mechanism for reaction of triplet methylene with olefins involves initial formation of a triplet addition complex (biradical I), in which partial rotation around the original carbon–carbon double bond is permitted and is responsible for the nonstereospecific formation of addition products.



(I)

In the biradical I, R_1 = H and R_2 = CH_3 for *cis*- and *trans*-butene-2, and R_1 = CH_3 and R_2 = H for isobutene. Closure of the $C^1C^2C^3$ ring gives the corresponding dimethylcyclopropane. Since there is no evidence for random insertion of triplet methylene into CH bonds, the olefinic C_5 products must be formed by rearrangement. This could occur by migration of H, and perhaps of CH_3 as well, in the biradical, *i.e.* (1) hydrogen migration from C^4 to C^1 (probably *via* a cyclic intermediate); (2) hydrogen migration from C^2 to C^1 (1,2-shift of hydrogen); (3) hydrogen migration from C^2 to C^3 (1,2-shift of hydrogen); (4) methyl migration from C^2 to C^1 or to C^3 (1,2-shift of methyl, occurring perhaps partly or entirely externally).

The products from these migrations in the case of *cis*- or *trans*-butene-2 would be (1) 3-methylbutene-1, (2) 2-methyl-butene-2, (3) 2-methylbutene-1 and (4) *cis*- and *trans*-pentene-2 and 3-methylbutene-1, and in the case of isobutene, (1) 2-methylbutene-1, (2) 2-methylbutene-2 and (3) 3-methylbutene-1. Examination of the product composition shows that the probability of these reactions appears to be in the order (4) > (1) > (2) > (3) for *cis*- and *trans*-butene-2 and (1) > (2) > (3) for isobutene. In the case of isobutene (4) is structurally not possible. This rearrangement scheme is consistent for the three olefins so far examined, but should of course be verified on a much larger number of examples. Further studies of the reactions of triplet methylene are in progress.

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A NEW CARBOCYCLIC STEROID STRUCTURE: 12,18-CYCLOSTEROIDS

Sir:

The steroid molecule has been subjected to the most varied chemical and photochemical transformations. Among the most interesting recent changes have been those involving the angular methyl groups,[1] resulting in the inclusion of the C-19 methyl group in cyclopropano[1j] and cyclobutano[1j] structures and the C-18 methyl group in cyclobutano[1d] and cyclopentano[1c] structures. Phyllanthol,[2] cycloartenol, cyclolaudenol, and cycloeucalenol[3] possess the angular methyl groups in the cyclopropano arrangement.

We wish to present herein the synthesis of the interesting pentacyclic 12,18-dehydrosteroidal ring system and the interconvertibility of the latter with the conanine structure.

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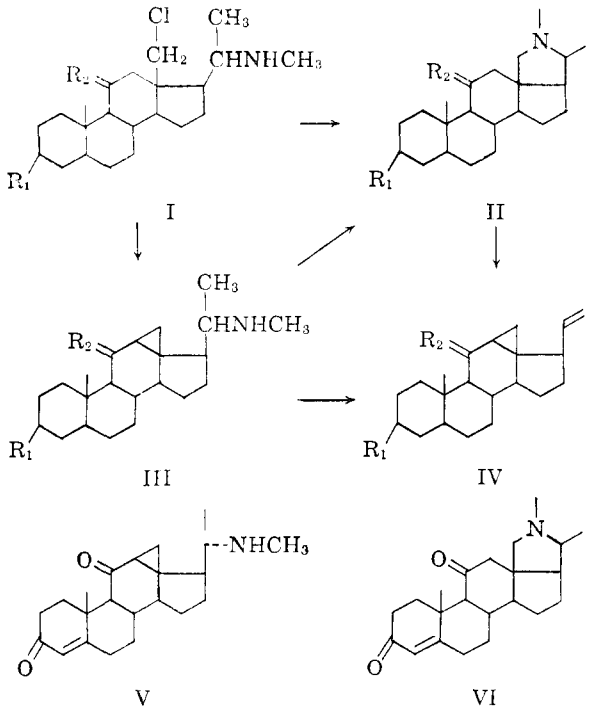
(2) D. H. R. Barton and P. deMayo, *J. Chem. Soc.*, 2178 (1953).

(3) For a summary of evidence, see L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, pp. 386–389.



	R_1	R_2	5H
a,	αOH	O=	β
b,	βOH	O=	α
c,	βOH	H_2	α

In the transformations of 18-chloro-amines Ia and Ib[4] with alkali, the conanines IIa and IIb obtained were accompanied by considerable yields of secondary amine by-products, which were isolable as the neutral amides. The initially distinguishing feature of these substances was their 11-keto carbonyl absorption at 5.98 μ (in addition to amide at 6.10 μ), indicating a modicum of conjugation for this carbonyl when contrasted with normal absorption at 5.88 μ in the cases of the conanines II and the parent amine precursors to I. Intense absorption at 202 mμ (ϵ = 5,600),[5] lack of same in the 240 mμ region, and sharp weak bands at 3.27 μ and 3.31 μ[6] (cyclopropyl methylene C–H stretching)[7] pointed to an 11-keto-12,18-cyclo structure III. The n.m.r. spectrum of IIIb was uninformative,[8] but definite evidence for the 12,18-cyclo structure was obtained from the 11-desoxo derivative IIIc (Wolff–Kishner reduction of IIIb), whose spectrum contained two complex signals, each equivalent to one proton, centered at τ 9.67 and 10.08[9] ($CHCl_3$ reference).

(4) J. F. Kerwin, M. E. Wolff, F. F. Owings, B. E. Lewis, B. Blank, A. Magnani, C. Karash, and V. Georgian, manuscript submitted for publication.

(5) For references to cyclopropyl–carbonyl conjugation in ultraviolet absorption, see E. M. Kosower, *Proc. Chem. Soc.*, 25 (1962), and *J. Am. Chem. Soc.*, **80**, 3261 (1958), and ref. 9.

(6) Spectrum determined with a Perkin-Elmer Model 137-G grating spectrophotometer.

(7) S. A. Liebman and B. J. Gudzinowicz, *Anal. Chem.*, **33**, 931 (1961).

(8) Cyclopropyl methylene is lowered to τ *ca.* 8.9 by conjugation with carbonyl as shown in the case [0.1,4]bicycloheptanone-2, G. Stork and J. Finici, *J. Am. Chem. Soc.*, **83**, 4678 (1961). With our compounds general methylene and methyl absorption obscure this region and prevent identification of cyclopropyl proton resonance peaks.

Corroboration for the 12,18-cyclo structure was obtained from further transformations: treatment of IIIb with HBr–HOAc (room temp.) cleaved the cyclopropyl ring with the production of the corresponding 18-bromo derivative[10] ($\lambda_{max}^{C=O}$ 5.88 μ, elemental analysis confirming), which was readily converted (aq. K_2CO_3) to the conanine IIb.

Cyclopropyl ring formation could also be effected by operating on the 11-ketoconanine IIb. The latter was transformed *via* the sequence: quaternization, Hofmann elimination to an 18-dimethylamino-20-pregnene, quaternization, and intramolecular alkylation ($NaOCH_3$/DMF) of the 18-trimethylammonium salt to the 12,18-cyclopregnene IVb (normal C=O absorption in all intermediates, but shifted to 6.0 μ[11] in IVb). Compound IVb also could be generated from IIIb by a Hofmann elimination sequence.

A representative substance in the Δ^4-3-keto series V (λ_{max}^{EtOH} 239 mμ (ϵ = 17,800); λ_{max}^{KBr} 3.00, 3.26, 3.30, 5.96–6.00, 6.20 μ) was readily available from the treatment of 18-chloro-20α-methylamino-4-pregnene-3,11-dione trifluoroacetate with alcoholic potassium hydroxide, whereas, treatment with potassium carbonate afforded 4-conanene-3,11-dione (VI) (λ_{max}^{EtOH} 239 mμ (ϵ = 18,000); λ_{max}^{KBr} 5.87, 5.98, 6.20 μ).

It is interesting to observe that *cyclopropyl ring formation competes, in media favoring enolization, with a very facile pyrrolidine ring closure,* even though the 11-keto steroid structure is conspicuous for its lack generally of reactivity transmittal toward C-12. Since under mild alkaline conditions conanine formation predominates, and since with acylated amine functions in I 12,18-ring formation results quantitatively, either ring system may be generated by choice.

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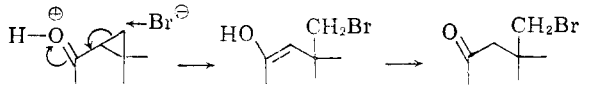
(9) K. Kocsis, P. G. Ferrini, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **43**, 2178 (1960), report a complex signal at τ *ca.* 10.0 for 4α,5-methylene cholestane, and R. McCrindle and C. Djerassi, *Chem. and Ind.*, 1311 (1961), report doublets at 20 and 35 c./s. for cyclopropyl hydrogens of the cycloartane nucleus. See also L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Ltd., London, 1959, p. 52.

(10) The direction of the cyclopropyl cleavage of IIIb with HBr is interesting. The usual mode of scission would have resulted in the generation of a methyl group by attachment of the proton on the methylene leading to a secondary or tertiary carbonium ion on a ring position. *cf.* D. H. R. Barton, J. E. Page and E. W. Warnhoff, *J. Chem. Soc.*, 2715 (1954), in the case of cycloartenol. That bromide ion has in fact become attached to methylene with the formation of 18-bromomethyl indicates that the 11-carbonyl has participated in a conjugative fashion as in this mechanistic scheme, *viz.*



(11) There are many instances recorded of carbonyl infrared absorption displaced toward longer wave lengths when conjugated with cyclopropyl. Among others, see R. N. Jones and F. Herling, *J. Org. Chem.*, **19**, 1252 (1954); A. Sandoval, G. Rosenkrantz and C. Djerassi, *J. Am. Chem. Soc.*, **73**, 2383 (1951); H. L. Slates and N. L. Wendler, *ibid.*, **81**, 5472 (1959), and ref. 9.

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