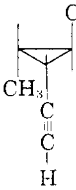
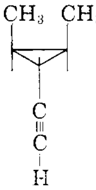
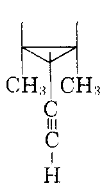
and triplet state natures, from which derives their respective chemical properties, the singlet state species, carbenes, having non-radical properties (for the main part electrophilic) and undergoing stereospecific *cis* addition to olefins, the triplet state species, methylenes, undergoing non-stereospecific additions to olefins. The bivalent carbon species examined thus far have been characterized as: *carbenes*, CH_2,[3] $CHCH_2CH_3$,[7] CBr_2,[2,4] CCl_2,[8] CHCOOEt,[3,5] $CHCOCH_3$[10]; and *methylenes*, $(C_6H_5)_2C$,[5] oxygen atoms (ground state).[11]

Symmetry considerations employed to rationalize the stability of triplet $(C_6H_5)_2C$ suggested that $H{-}C{-}C{\equiv}C{-}H \longleftrightarrow H{-}C{\equiv}C{-}C{-}H$, with three sp hydridized carbon atoms, would also be in a triplet state, and thus a methylene.

Propargylene, C_3H_2, has been generated by photolysis of diazopropine (from reactions of N-nitroso-N-proparglyurea with aqueous base). If propargylene is generated in the presence of *cis*-2-butene, three isomeric 2,3-dimethyl-1-acetylenylcyclopropanes (A,B,C) are produced in ratios 1:2.5:4.0. In the presence of *trans*-2-butene the identical products (retention times and infrared spectra of the pure compounds) are obtained in ratios 63:2.3:1. Absorption bands at 3.05–3.10 and 4.70–4.77 μ, uptake of 2.0 moles of H_2 (platinum catalyst), identity of tetrahydro (A) with the product from *trans*-2-butene and ethylcarbene, and (B) and (C) with the products from *cis*-2-butene and ethyl carbene, oxidation of (A), to the known *trans*-2,3-dimethylcyclopropane carboxylic acid,[2] makes possible structure assignments


(A)


(B) and (C)



The pattern of relative rates of addition of diphenylmethylene,[6] propargylene and ground state oxygen atom[11] are not identical, emphasizing that the occurrence or absence of stereospecificity in olefin additions is the best criterion for distinguishing methylenes and carbenes.

Molecular orbital considerations indicate that linear or nearly linear[12] C_3H_2, having three sp hydridized carbon atoms and six electrons for distribution among the p-orbitals, is a cylindrically symmetrical compound with two low lying π-orbitals which accounts for four electrons. The next higher molecular orbitals are nearly equivalent[12] and non-bonding, so that they are occupied singly by the two remaining electrons, localizing one electron on each of the terminal carbons. Hund's stabilization of the order of 30–50 kcal. is realized when the two non-bonding electrons have parallel spins, thus rationalizing the triplet nature of propargylene.

DEPARTMENT OF CHEMISTRY PHILIP S. SKELL
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA JOHANN KLEBE

RECEIVED NOVEMBER 25, 1959

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(10) P. S. Skell and R. M. Etter, unpublished results.

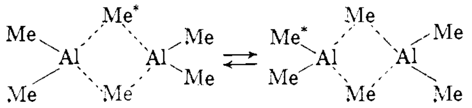
(11) S. Sato and R. J. Cvetanović, *Can. J. Chem.*, **37**, 953 (1959). See also for references to earlier work with oxygen atoms by Cvetanović and co-workers.

(12) H. A. Jahn and E. Teller, *Proc. Roy. Soc., London*, **A161**, 220 (1957).

PROTON MAGNETIC RESONANCE SPECTRUM OF ALUMINUM TRIMETHYL DIMER

Sir:

It has been shown using X-ray diffraction data[1] that aluminum trimethyl exists in the solid state as a dimer with two methyl groups forming bridges between the aluminum atoms. The compound also appears to be predominantly dimeric in benzene solution[2] and in the gaseous state.[3] It is therefore surprising that the room temperature proton magnetic resonance spectrum[4] of the liquid consists of a single peak rather than a pair of signals with relative intensities 1:2 corresponding to protons in bridging and in terminal methyl groups, respectively. This indicates either that all the protons are magnetically equivalent or that the two species are involved in a rapid exchange process which may be represented as


(1)

To decide between these possibilities we have examined the proton resonance spectrum at 56.445 mc. of a liquid solution containing approximately 12 mole per cent. of Al_2Me_6 in cyclopentane, between 25 and −75°. At the low temperature we observed the two signals expected for the bridge structure. We detected no further splitting of the smaller peak, showing that the protons in the bridging methyl groups remain magnetically equivalent at −75°. Using the solvent resonance as an internal standard we found chemical shifts of +1.04 p.p.m. and +2.17 p.p.m., respectively, for the protons of the bridging and the terminal methyl groups. As the temperature increases the peaks first broaden and eventually coalesce to a single, sharp peak at +1.79 p.p.m., precisely the weighted average of the low-temperature shifts. This behavior is characteristic of an exchange process.[5]

We are studying the detailed temperature-dependence of this spectrum in order to obtain the activation energy of reaction (1) as accurately as possible. The data already obtained indicate that this energy is between 6 and 14 kcal./mole. The heat of dissociation of the dimer is 20.2 kcal./mole at 100 to 150° in the gaseous phase.[3] We conclude that $AlMe_3$ monomer probably is not formed as an intermediate in (1) but that the ex-

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(1) P. H. Lewis and R. E. Rundle, *J. Chem. Phys.*, **21**, 986 (1953).

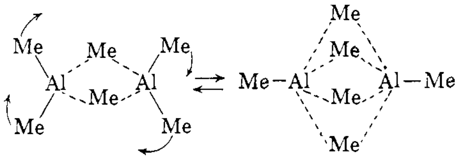
(2) K. S. Pitzer and H. S. Gutowsky, THIS JOURNAL, **68**, 2204 (1946).

(3) A. W. Laubengayer and W. F. Gilliam, *ibid.*, **63**, 477 (1941).

(4) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 296.

(5) Ref. 4, pp. 218 ff.

change is an intramolecular process. Formation of the transition state may involve the breaking of one C–Al bond, or perhaps a deformation of the molecule in which no bonds are broken, leading to a structure having four bridging methyl groups at the corners of a square, *i.e.*



The 3d orbitals of the aluminum atom then would be expected to contribute to the bonding, involving four electron pairs in six-center molecular orbitals.

This work was made possible by grants from the Purdue Research Foundation, E. I. du Pont de Nemours and Company, and the National Science Foundation. We thank Professor Grant Urry and Mr. James Nuss for the sample of Al_2Me_6.

[6] Lubrizol Corporation Predoctoral Fellow.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY NORBERT MULLER
LAFAYETTE, INDIANA DONALD E. PRITCHARD[6]

RECEIVED NOVEMBER 23, 1959

THE SYNTHESIS OF ALDOSTERONE FROM PROGESTERONE BY THE AMPHIBIAN ADRENAL[1]

Sir:

The mammalian adrenal cortex forms both glucocorticoids[2,3] and mineralocorticoids[4,5] from progesterone. In the lower vertebrates, where the major function of the adrenal cortex may be electrolyte regulation, the pathways of corticosteroid biosynthesis are not known. Recent evidence[6] indicates that aldosterone is the most abundant corticosteroid produced by the adrenals of the American bullfrog. This communication reports that the adrenals of the same species synthesize aldosterone from C^{14}-labeled progesterone.

Minced adrenal tissue (0.5 g.) from 6 bullfrogs (*Rana catesbeiana*) was incubated as described,[6] in an atmosphere of 95% O_2–5% CO_2 at 26° for 3 hr. in 5 ml. of isotonic Krebs–Ringer bicarbonate solution (*p*H 7.4) containing 0.2% glucose, in the presence of 5 units of bovine adrenocorticotrophic hormone and 0.15 mg. of progesterone-4-C^{14} (7.40×10^6 c.p.m.). After incubation, 1.70×10^6 c.p.m. of tritium-labeled aldosterone[7] was added as an internal standard and 0.5 mg. of nonradioactive *dl*-aldosterone as carrier. The incubation mixture was extracted with ethyl acetate and the extract washed with water and evaporated. The sequence of paper chromatographic separations shown in Table I next was carried out. After the completion of each chromatogram, the aldosterone zone was located by scanning the paper with ultraviolet light (254 mμ), then eluted, and an aliquot was counted in a Tricarb liquid scintillation spectrometer to determine the H^3/C^{14}. Tritium and C^{14} were measured simultaneously by the discriminator-ratio method[8] at a photomultiplier voltage of 1230 and discriminator settings of 10–100 for channel 1 and 100 to infinity for channel 2. After the completion of the second chromatogram (Table I), the eluate containing aldosterone was acetylated with acetic anhydride in pyridine and the third and fourth chromatographic separations were carried out on the 18,21-diacetoxy derivative of aldosterone.

TABLE I

PURIFICATION OF ISOLATED C^{14}-ALDOSTERONE

	Chromatographic System	Steroid	H^3/C^{14}
1	Toluene/propylene glycol	Aldosterone	4.4
2	Toluene:ethyl acetate 9:1/ methanol:water 1:1	Aldosterone	5.1
3	Methylcyclohexane:toluene 4:1/methanol:water 4:1	18,21-diacetoxy-aldosterone	5.3
4	Methylcyclohexane:toluene 4:1/formamide	18,21-diacetoxy-aldosterone	5.2

The agreement in the ratio of tritium to C^{14} after the second, third and fourth chromatograms was taken as evidence that the C^{14} containing moiety was chemically indistinguishable from the aldosterone-H^3 which had been added to the incubation mixture. The ratio of cpm. aldosterone-H^3 to c.p.m. purified aldosterone-C^{14} was 5.2. The c.p.m. of aldosterone-C^{14} which was present after incubation was therefore 3.3×10^5 (1.70×10^6/5.2).

The conversion of progesterone-C^{14} to aldosterone to the extent of 4.4% ($3.3 \times 10^5/7.40 \times 10^6$) indicated that a biosynthetic pathway characteristic of the mammalian adrenal cortex was present to a significant degree in a lower vertebrate. The yield of aldosterone was comparable to that reported[5,9] for capsule strippings of bovine adrenal glands. The results suggest a simple biosynthetic method for the preparation of labeled aldosterone.

VETERANS ADMINISTRATION HOSPITAL
BRONX 68, NEW YORK STANLEY ULICK
DEPARTMENTS OF BIOCHEMISTRY AND OF
OBSTETRICS AND GYNECOLOGY SAMUEL SOLOMON
COLLEGE OF PHYSICIANS AND SURGEONS
COLUMBIA UNIVERSITY, NEW YORK 32, N. Y.

RECEIVED NOVEMBER 13, 1959

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[1] This work was supported in part by a grant from the American Cancer Society.

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[6] H. Carstensen, A. C. J. Burgers and C. H. Li, THIS JOURNAL, **81**, 4109 (1959).

[7] Randomly-labeled aldosterone-H^3 was prepared by irradiating *dl*-aldosterone with tritium (K. E. Wilzbach, *ibid.*, **79**, 1013 (1957)), then exchanging with methanol and a chromatographic purification to a constant specific activity of 1.3 microcuries per microgram.

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