PENTACYCLIC TRITERPENOID BACKBONE REARRANGEMENT: CONSTITUTION OF BREIN
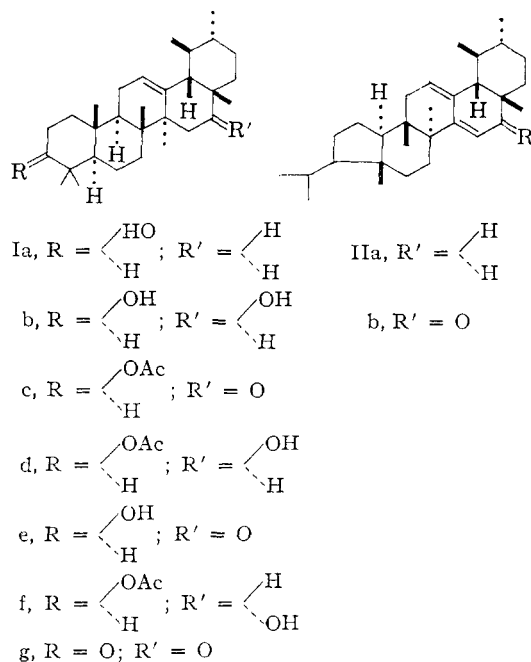
Sir:

Dehydration of α-amyrin (Ia) under various conditions gives a product, "*l*-α-amyradiene" in which the double bonds are conjugated and heteroannular, and whose structure has been shown[1] to be (IIa). We believe that this remarkable molecular rearrangement, referred to as a backbone rearrangement,[2] in addition to its intrinsic mechanistic interest, affords a useful and widely-applicable method[3] for structure elucidation in the ursane and oleanane groups of triterpenoids. As an example, we now wish to report its utilization in establishing the structure of brein, a pentacyclic triterpenoid first isolated[4] in 1851 as a constituent of *Manila elemi* resin.

Significant structural work due to Morice and Simpson[5] and Büchi, Jeger and Ruzicka[6] culminated in brein being represented as urs-12-ene-3α,21 (or 22)-diol.[7] Our re-investigation shows that brein is urs-12-ene-3β, 16β-diol (Ib).

The earlier assignment of the unusual 3α-hydroxyl configuration has been questioned[8] on the basis of molecular rotation differences. Direct chemical evidence on the 3-configuration was adduced. Partial acetylation of brein gives the diol monoacetate (Id), which on chromic acid oxidation yields breinonol-B acetate (Ic, m.p. 210–212°, $[\alpha]_D$ + 47°), alternatively obtained by catalytic hydrogenation of breindione (Ig) and acetylation. In our hands, Wolff–Kishner reduction of (Ic) gave α-amyrin (Ia) in high yield, thus establishing that brein has a 3β-hydroxyl group.

Subjection of the key intermediate, breinonol-B (Ie, m.p. 226–227°, $[\alpha]_D$ + 87°) to the backbone rearrangement by treatment with phosphorus pentoxide in benzene gave a product (IIb), which we were unable to obtain crystalline, but which was characterized by its ultraviolet absorption spectrum (λ^{EtOH} 240 mμ, ε 4900 and 293 mμ, ε 9100), characteristic of a *heteroannular conjugated dienone*,[9] and not a conjugated diene. This indicated the location of the ketone group in breinonol-B and consequently the second hydroxyl group in brein, at C-16.

Additional support for this conclusion was provided by this series of experiments which also established the configuration of the C-16 hydroxyl group. Reduction of breindione (Ig) with sodium

Ia, R = $\diagup$ HO $\diagdown$ H ; R' = $\diagup$ H $\diagdown$ H   IIa, R' = $\diagup$ H $\diagdown$ H

b, R = $\diagup$ OH $\diagdown$ H ; R' = $\diagup$ OH $\diagdown$ H   b, R' = O

c, R = $\diagup$ OAc $\diagdown$ H ; R' = O

d, R = $\diagup$ OAc $\diagdown$ H ; R' = $\diagup$ OH $\diagdown$ H

e, R = $\diagup$ OH $\diagdown$ H ; R' = O

f, R = $\diagup$ OAc $\diagdown$ H ; R' = $\diagup$ H $\diagdown$ OH

g, R = O; R' = O

borohydride and then acetylation gives a diol monoacetate ($C_{32}H_{52}O_3$, $[\alpha]_D$ + 47°, m.p. 202–205°) which differs from (Id) but which gives (Ic) on oxidation and must therefore be the 16-epimer (If) of brein. Since the 16-hydroxyl group of brein is acetylated under conditions in which (If) is resistant, it has the equatorial conformation. Brein consequently is represented as urs-12-ene-3β,16β-diol. Dehydration of (If) and 3β-acetoxyurs-12-en-15-ol[10] with phosphorus oxychloride in pyridine gives, in low yield in each case, the same product, ursa-12,15-dien-3β-yl acetate ($C_{32}H_{50}O_2$, m.p. 228–229°, $[\alpha]_D$ + 40°).

Satisfactory analyses have been obtained for all new crystalline compounds.

(1) M. B. E. Fayez, J. Grigor, F. S. Spring and R. Stevenson, *J. Chem. Soc.*, 3378 (1955).

(2) G. Brownlie, F. S. Spring, R. Stevenson and W. S. Strachan, *Chem. and Ind.*, 1156 (1955).

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(4) S. Baup, *Jahresbericht für Chemie*, 528 (1851).

(5) I. M. Morice and J. C. E. Simpson, (a) *J. Chem. Soc.*, 795 (1940); (b) 198 (1942).

(6) G. Büchi, O. Jeger and L. Ruzicka, (a) *Helv. Chim. Acta*, **29**, 442 (1946); (b) **31**, 139 (1948).

(7) For a review of the evidence, see J. Simonsen and W. C. J. Ross, "The Terpenes," Vol. IV, Cambridge University Press, New York, N. Y., pp. 148–155.

(8) W. Klyne and W. M. Stokes, *J. Chem. Soc.*, 1079 (1954).

(9) For the spectrum of 3α-hydroxy-12-ketochola-7,9(11)-dienic acid, which has an identical chromophore, see H. Heusser, K. Eichenberger, P. Kurath, H. R. Dallenbach and O. Jeger, *Helv. Chim. Acta*, **34**, 2106 (1951).

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ON THE THERMAL AND RADIATION-INDUCED CHAIN REACTION BETWEEN METHANE AND ETHYLENE

Sir:

Previous publications from this laboratory have emphasized the use of nuclear radiation as a convenient initiator, and, therefore, a powerful tool for elucidating the mechanism of ordinary hydrocarbon free radical chain reactions.[1–4] Provided it can be shown that the radiation-induced reaction is free radical in nature, one has available a new probe with which reactions can be initiated

(1) P. J. Lucchesi, D. L. Baeder and J. P. Longwell, *Proc. Fifth World Petroleum Congress*, New York, N. Y., June, 1959.

(2) P. J. Lucchesi and C. E. Heath, THIS JOURNAL, **81**, 4770 (1959).

(3) W. Bartok and P. J. Lucchesi, *ibid.*, **81**, 5918 (1959).

(4) P. J. Lucchesi, B. L. Tarmy, R. B. Long, D. L. Baeder and J. P Longwell, *Ind. Eng. Chem.*, **50**, 879 (1958).

at virtually any experimental conditions. In turn, since dosimetry gives the rate of initiation and conversion data yield the rate of propagation, the radiation technique can give valuable insight into the nature of long chain reactions.

Our recent work has emphasized radiation-induced reactions between low molecular weight paraffins and olefins at rather high temperatures and pressures. Some observations made on the methane–ethylene reaction seem to warrant publication at this time although the work aimed at deciding whether this reaction is free radical or ionic in nature is still incomplete. The results are of definite interest regardless of which one of these alternative mechanisms is ultimately accepted.

Experimental.—Static experiments were made in electrically heated stainless steel systems having a surface/volume ratio of 1 cm.$^{-1}$. The radiation source consisted of a 3200 curie Co^{60} source,[4] and the dosimetry was done by Fe^{++}–Fe^{+++} conversion[5] with an uncertainty of $\pm$ 15%. Radiation and thermal experiments were made in identical reactors and at the same conditions using Phillips pure grade ($>$ 99.5%) methane and ethylene. Products were analyzed by gas-liquid partition chromatography to $\pm$4% of the amount present. The experimental conditions were: 55 atm. total pressure, 10 mole per cent. initial C_2H_4 concentration, 343–426° temperature, and 0.12 $\times$ 10^6 rad./hr. (absorbed). The radiation yields are integral G values obtained directly from the radiation-induced reaction since at identical conditions no thermal reaction was observed.

Results and Discussion.—The homogeneous gas phase reaction between CH_4 and C_2H_4 is a notoriously slow process, presumably as a result of the slow unimolecular formation of $CH_3\cdot$ and $H\cdot$ from CH_4. The results of thermal experiments showed no conversion in six hours at 343°. In the presence of radiation, the reaction between CH_4 and C_2H_4 gave 3.1% conversion of CH_4 and 27.0% conversion of C_2H_4. The total reaction product contained, in mole per cent., 3.0 C_2H_6, 30.4 C_3H_8, 1.4 C_3H_6, 15.7 iso-C_4H_{10}, 21.2 C_4H_8, 12.0 iso-C_5H_{10}, and 5.8 C_6H_{12}. The radiation yield at these conditions is 1200 molecules of C_3 and higher molecular weight products per 100 ev. absorbed. At 426° both the thermal and radiation-induced reactions are appreciably rapid. For example, the thermal reaction gives in six hours CH_4 and C_2H_4 conversions of 5.0% and 80%, respectively. At this temperature a CH_4 conversion of 4.1% and a C_2H_4 conversion of 71.0% were obtained after two hours of irradiation. There is, therefore, a thermal reaction at 426° that is accelerated by radiation. Above 426° the thermal reaction is so rapid that acceleration by radiation is difficult to notice.

Work now in progress is designed to obtain detailed product composition *versus* conversion data for both the thermal and the radiation-induced reaction. A strict comparison at the same conditions and conversions is, of course, the best direct evidence one can use in deciding whether the radiation-induced reaction is an ionic

(5) N. J. Miller, *J. Chem. Phys.*, **18**, 70 (1950).

or free radical chain process. However, it is very instructive to speculate on the meaning of the work reported here. If the reaction is indeed an ionic process, then it is to our knowledge the first reported ionic chain reaction of hydrocarbons at these conditions. If the process is free radical in nature, which is in our opinion more likely, then the above initiation step cannot be correct. This initiation rate should proceed at a rate given approximately by $10^{13}e^{-101,000/RT}$ (CH_4) molec. cc.$^{-1}$ sec.$^{-1}$, where 10^{13} is the normal unimolecular pre-exponential factor, (CH_4) is the methane concentration, and 101,000 kcal./mole is the CH_3–H bond strength. At about 50 atm. of methane this rate is negligibly small at 800°K., being in the order of 10^5–10^6 molec. cc.$^{-1}$. sec.$^{-1}$. Now the high G value obtained at 343° establishes the chain nature of the reaction and, furthermore, provides an approximate value for the chain length at the conditions of this work. However, the product of the above initiation rate and of the known chain length, which should give the value of the reaction rate, is smaller by many orders of magnitude than the observed thermal rate at 426°. Therefore, equation (1) cannot represent the initiation step.

However, a plausible initiation step can be written which removes the difficulty. This involves a bimolecular initiation between CH_4 and C_2H_4

$$CH_4 + C_2H_4 \longrightarrow CH_3\cdot + C_2H_5\cdot \qquad (1)$$

Such an initiation step is rarely discussed,[6] but is in fact highly likely since the reverse radical disproportionation reaction is well established and proceeds with zero or very low activation energy. Therefore, step (1) should have an activation energy not appreciably greater than its endothermicity. From available data on heats of formation,[6,7] the endothermicity of (1) is estimated to be 60 kcal./mole. Therefore, initiation by step (1) should proceed at an approximate rate of $10^{-10}\cdot$ $e^{-60,000/RT}(CH_4)(C_2H_4)$, where 10^{-10} is the normal bimolecular collision number. At 50 atm. methane, 5 atm. ethylene, the initiation rate calculated from this expression is approximately that required to explain the measured thermal rate corresponding to the chain lengths estimated from this work.

(6) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Princeton University Press, Princeton, New Jersey, 1958.

(7) M. Szwarc, *Chem. Rev.*, **47**, 75 (1950).

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AN INVESTIGATION OF THE REACTION PRODUCTS OF BIS-CYCLOPENTADIENYLTITANIUM DICHLORIDE AND VARIOUS ALUMINUM ALKYLS BY ELECTRON SPIN RESONANCE

Sir:

Bis-cyclopentadienyl titanium dichloride was allowed to react with about a thousandfold excess of several aluminum alkyls in benzene solution and the electron spin resonance (e.s.r.) spectra of these solutions were observed at 3.2 cm. wave length and at 20°. The concentration of the titanium compound was between 10^{-4} and 10^{-3} molar in each case. The reactions with several aluminum