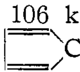
Examples are known where the molecule-ion derived from olefinic hydrocarbons reacts with the neutral olefin to form the even-electron carbonium ion,[5] *i.e.*, the protonated olefin. Elementary considerations suggest that any reaction characteristic of *protonated* intermediates should be subject to inhibition or modification in the presence of a strong Brönsted base. We wish to report an unambiguous example of this effect which proves, *ipso facto*, that the radiation-induced polymerization of cyclopentadiene is an *ionic* reaction.

Cyclopentadiene has been found to polymerize reproducibly when irradiated at $-78°$ with cobalt-60 gamma-rays. The preparative technique follows the description given for other monomers,[6] except for double distillation *in vacuo* below $-40°$, and subsequent storage[7] at $-78°$. By this procedure, the spontaneous formation of dimer was reduced to insignificant proportions. Irradiation beyond a dose of 6.0×10^{17} e.V.g.$^{-1}$, corresponding to 2.0% conversion, results in gel formation. The yield of polymer is linear with irradiation dose up to about 20% conversion ($G(—C_5H_6) = 25{,}000$). At doses exceeding 5.0×10^{19} e.V.g.$^{-1}$, the pure monomer is converted to a firm rubber, impervious to solvents. The extreme potency of ammonia in reducing the polymerization yield is shown by the representative data of Table I.

TABLE I

EFFECT OF AMMONIA ON THE RADIATION-INDUCED POLYMERIZATION OF CYCLOPENTADIENE AT $-78°$

Ammonia concentration, mole fraction $\times 10^3$	Dose $\times 10^{-18}$, e.V.g.$^{-1}$	Conversion to polymer, %
None	1.0	3.4
None	5.0	15.2
None	10.0	25.5
1.8	50.0	0.29
0.20	50.0	0.64
.012	50.0	1.30
.0054	50.0	2.7

The interpretation of the action of ammonia is clarified by several points: (a) ammonia has a high proton affinity, $P_{NH_3} = 202$ kcal./mole,[8] this being the reason why ammonia acts as a very efficient base for ion-molecule reactions involving proton transfer from hydrocarbon ions.[9] (b) Ammonia has a large dipole moment ($\mu = 1.46$ debye) which allows for strong ion-dipole interaction. (c) The ionization potential of ammonia ($I_{NH_3} = 234$ kcal./mole)[10] exceeds that of cyclopentadiene ($I_{C_5H_6} = 198$ kcal./mole)[11]; hence charge transfer from cyclopentadiene to ammonia is inapplicable. (d) An efficient reaction of a *neutral* hydrocarbon free radical with ammonia by hydrogen atom abstraction is precluded in this system by the fact that $D_{H-NH_2} = 106$ kcal./mole,[12] which must surely exceed the CH–H bond dissociation energy in cyclopentadiene. In any event, hydrogen atom transfer reactions with ammonia would lead to chain transfer rather than the termination which must apply here.

The preceding facts and arguments, taken together with the knowledge that cyclopentadiene polymerization is effected readily by a variety of Friedel–Crafts ionic catalysts,[13] compel the conclusion that ammonia interferes at such low concentrations by virtue of its possession of an unshared pair of electrons. In other words, the basicity of ammonia renders it an excellent ion scavenger. Apart from simple proton transfer to ammonia, we do not rule out the possible ammonolysis of a carbonium-ion intermediate, *viz.*, $R^+ + 2NH_3 \rightarrow R\text{–}NH_2 + NH_4^+$.

These results suggest the possible utility of ammonia as an ion scavenger in the radiation chemistry of hydrocarbon gases and liquids, especially where chain reactions of unknown mechanism are prevalent. Further work is in hand, and will be reported in due course.

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[5] D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **24**, 926 (1956).

[6] J. V. F. Best, T. H. Bates and Ff. Williams, *Trans. Faraday Soc.*, **58**, 192 (1962); *J. Chem. Soc.*, 1531 (1962).

[7] Irradiations were carried out at the Oak Ridge National Laboratory at a dose rate of 3.2×10^{17} e.V.g.$^{-1}$ min.$^{-1}$; we are indebted to Dr. C. J. Hochanadel for his very helpful coöperation.

[8] A. P. Altshuller, *J. Am. Chem. Soc.*, **77**, 3480 (1955).

[9] V. L. Tal'roze and E. L. Frankevich, *Doklady Akad. Nauk SSSR*, **111**, 376 (1956); see compilation by D. P. Stevenson and D. O. Schissler in "The Chemical and Biological Action of Radiations," Vol. V, Academic Press, London, 1961, pp. 257–259.

[10] K. Watanabe and J. R. Mottl, *J. Chem. Phys.*, **26**, 1773 (1957).

[11] W. C. Price and A. D. Walsh, *Proc. Roy. Soc. (London)*, **A179**, 201 (1941).

[12] Calculated from F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," N.B.S. Circular 500, 1952.

[13] P. J. Wilson, Jr., and J. H. Wells, *Chem. Revs.*, **34**, 1 (1944).

[14] Undergraduate research participant (summer 1962) supported by National Science Foundation under grant G-21638.

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RECEIVED SEPTEMBER 17, 1962

TRANSFORMATIONS OF EBURICOIC ACID. III.[1] A-NOR-3,11-DIKETO-14-METHYLPREGNANE DERIVATIVES

Sir:

In a previous communication from this laboratory[2] we reported the degradation of eburicoic acid to Δ^8-14-methylpregnene derivatives *via* the α-pyrone I. We now wish to describe the conversion of this key intermediate to 14-methyl-A-nor-3-ketopregnanes and Δ^5-pregnenes. Related compounds such as $\Delta^{3(5)}$-A-norpregnene-2,20-dione[3] have been shown to possess anti-androgenic activity of a high order.[4]

Oxidation of the pyrone I with $KMnO_4$ in acetone[5] furnished in 40% yield the Δ^8-diketo acid IIa, m.p. 252–255°; $[\alpha]_D + 85°$[6]; $\lambda_{\max}^{\text{alc}}$ 268 mμ ($\epsilon = 9{,}100$). Its methyl ester, m.p. 178–179°; $[\alpha]_D + 88°$; $\lambda_{\max}^{\text{alc}}$ 268 mμ ($\epsilon = 9{,}400$); on reduction with zinc and acetic acid gave the saturated diketo ester IIb, m.p. 262°; $[\alpha]_D + 70°$; which was converted with ethanedithiol in BF_3-etherate to the 7-thioethylene ketal IIc, m.p. 211–212°; $[\alpha]_D + 19°$; and thence with sponge nickel in ethanol to

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[1] Paper II of this series, G. W. Krakower, J. W. Brown and J. Fried, *J. Org. Chem.*, **27**, in press (1962).

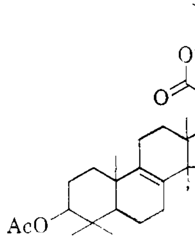
[2] D. Rosenthal, J. Fried, P. Grabowich and E. F. Sabo, *J. Am. Chem. Soc.*, **84**, 877 (1962).

[3] F. L. Weisenborn and H. E. Applegate, *ibid.*, **81**, 1960 (1959).

[4] L. J. Lerner, A. Bianchi and A. Borman, *Proc. Soc. Exptl. Biol. Med.*, **103**, 172 (1960).

[5] P. Hofer, H. Linde and K. Meyer, *Helv. Chim. Acta*, **43**, 1955 (1960), and earlier papers.

[6] Rotations in chloroform at 23°, unless indicated otherwise.



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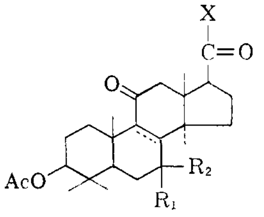
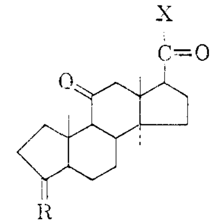
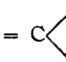


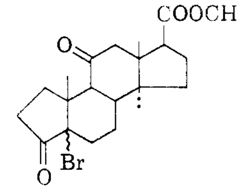
IIa, $R_1 + R_2 = O$; $X = OH$; Δ^8
IIb, $R_1 + R_2 = O$; $X = OCH_3$
IId, $R_1 = R_2 = H$; $X = OCH_3$



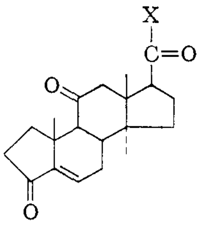


IIIa, $R = \mathrm{C}\!\left\langle\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_3}\end{matrix}\right.$; $X = OCH_3$; 5α

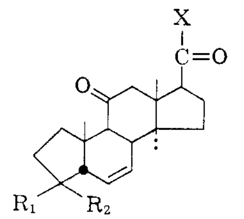
IIIb, $R = O$; $X = OCH_3$; 5α
IIIc, $R = O$; $X = OCH_3$; 5β
IIIe, $R = O$; $X = CH_3$; 5β
IIIg, $R = O$; $X = CH_2OAc$; 5β



Va, 5α-Br
Vb, 5β-Br



VIa, $X = OCH_3$
VIe, $X = CH_3$
VIg, $X = CH_2OAc$



VIIa, $R_1 + R_2 = \begin{matrix}\mathrm{OCH_2}\\|\\\mathrm{OCH_2}\end{matrix}$; $X = OCH_3$
VIIb, $R_1 + R_2 = O$; $X = OCH_3$

the 11-keto ester IId, m.p. 219–220°; $[\alpha]_D$ + 68°. Deacetylation of IId with N KOH in methanol at room temperature gave after remethylation with diazomethane the 3-hydroxy ester IIe,[7] m.p. 240–241°; $[\alpha]_D$ + 60°. Retropinacol rearrangement of IIe with PCl_5 in toluene at 0° gave the isopropylidene A-nor ester IIIa,[8] m.p. 150–151°; $[\alpha]_D$ + 63°; (acid, m.p. 266–267°; $[\alpha]_D$ + 43°), which on ozonolysis in ethyl acetate at −20°, and reduction of the ozonide with zinc and acetic acid at 20° gave the 3-keto-5α-(*trans*)-ester IIIb, m.p. 178–180°; $[\alpha]_D$ + 6°; opt. rot. disp. in CH_3OH: $[\alpha]_{308}$ −1,470°; τ_{19Me} 8.88; which with 0.01 N base or mineral acid or by heating at the m.p. gave the 5β-(*cis*)-ester IIIc,[9] m.p. 222–224°; $[\alpha]_D$ + 175°; opt. rot. disp. in CH_3OH: $[\alpha]_{312}$ + 2,560; τ_{19Me} 8.63.

The A-nor-5β-pregnane derivatives IIIe—IIIg were prepared: Saponification of IIIb or IIIc under helium gave the *cis*-acid, m.p. 270–272°; $[\alpha]_D$ + 184°; the acid chloride of which prepared with oxalyl chloride in benzene was converted to the diazoketone IIId, m.p. 173 and 204°; $[\alpha]_D$ + 250°. The latter with excess HI gave the methyl ketone IIIe, m.p. 220–221°; $[\alpha]_D$ 223°; and with HCl furnished the 21-chloro ketone IIIf, m.p. 176–177°; $[\alpha]_D$ + 194°; which latter with potassium acetate and potassium iodide in acetone gave the 21-acetoxy ketone IIIg, m.p. 227–229° and 235–236°; $[\alpha]_D$ + 199°; $\lambda_{\max}^{\mathrm{KBr}}$ 5.70, 5.78, 5.86 μ.

To introduce Δ^1- and Δ^5-unsaturation the bromination of IIIb was studied. Bromination in acetic acid in the presence of sodium acetate and a slight excess of HBr gave 65% of the 5α-bromide Va, m.p. 184 and 198°; $[\alpha]_D$ + 90°; opt. rot. disp. in CH_3OH: $[\alpha]_{330}$ + 360°; τ_{19Me} 8.74; and 10% of the 5β-bromide Vb, m.p. 160–161°; $[\alpha]_D$ + 45°; opt. rot. disp. in CH_3OH: $[\alpha]_{341}$ −506°; τ_{19Me} 8.51; separable by fractional crystallization. The 5β-bromide was the exclusive product when the $\Delta^{3(5)}$-enol acetate IV (m.p. 170–171°; $[\alpha]_D$ + 124°; $\lambda_{\max}^{\mathrm{KBr}}$ 5.70, 5.77, 5.88 μ; no n.m.r. signal in the region for vinyl protons; prepared from IIIb with isopropenyl acetate and *p*-toluenesulfonic acid) was brominated in the presence of excess sodium acetate. Both isomers must be 5-bromides since neither shows a single proton signal in the 6τ region (other than OCH_3) required for a 2-bromo-3-ketone.[10] The stereochemistry at C_5 is as shown: (1) so as to assign the *cis*-indanone structure Vb to the isomer possessing the less shielded 19-methyl group ($\Delta\tau_{5\alpha\mathrm{Br}-5\beta\mathrm{Br}} = 0.23$) in accordance with the fact that the *cis*-indanone IIIc possesses the less shielded 19-methyl group ($\Delta\tau_{5\alpha\mathrm{H}-5\beta\mathrm{H}} = 0.25$), (2) in conformity with Bose's rule,[11] and (3) on the basis of the behavior of the two bromides in elimination reactions. Treatment of the 5α-bromo ketone Va with lithium bromide in dimethylformamide gave in a *trans*-diaxial elimination exclusively the Δ^5-3-ketone VIa, m.p. 202–203°; $[\alpha]_D$ − 39°; $\lambda_{\max}^{\mathrm{alc}}$ 240 mμ (ϵ = 8,500); $\lambda_{\max}^{\mathrm{Nujol}}$ 5.75, 5.81, (3-keto) 5.87, 6.05 (Δ^5) μ[12]; τ_{6H} single proton, triplet centered at 3.45, J = 3.5 c.p.s.; whereas the 5β-bromoketone Vb furnished a 4:6 mixture of VIa and the Δ^1-3-ketone, m.p. 223–224°; $[\alpha]_D$ + 90°; $\lambda_{\max}^{\mathrm{alc}}$ 219 mμ (ϵ = 8,200); $\lambda_{\max}^{\mathrm{KBr}}$ 5.77, 5.88, 6.33 (weak)μ.

Completion of the pregnane side chain required the Δ^5-3-keto acid VIb, which could not be pre-

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[7] Hydrolysis with hot N KOH gave the corresponding acid, m.p. 335–345°; $[\alpha]_D$ +49° (MeOH).

[8] Following the procedure of Biellman and Ourisson (*Bull. Soc. Chim. France*, 331 (1962)) considerable amounts of chlorinated by-products were formed; 80–90% yields could, however, be obtained when a stream of helium was used instead of nitrogen (trace of O_2?) in the dark to avoid free radical chlorinations probably involving the 11-keto group. We are indebted to Dr. G. Ourisson for acquainting us with the inert gas-sweep technique during a visit to our laboratory.

[9] The position of equilibrium was determined by measuring the rotation at the opt. rot. disp. maximum after addition of KOH to methanol solutions of IIIb and IIIc. Equilibration occurred immediately; $[\alpha]_{312}$ + 2240 ± 100° indicating 92% ± 2% of the *cis* form IIIc; *cf.* J. F. Biellmann, D. Francetić and G. Ourisson, *Tetrahedron Letters*, **18**, 4 (1960), for equilibrium values for related indanone systems.

[10] W. G. Dauben, G. A. Boswell and W. H. Templeton, *J. Am. Chem. Soc.*, **83**, 5006 (1961).

[11] A. K. Bose, *Tetrahedron Letters*, 461 (1961). Although the axial haloketone rule (C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., New York, N. Y., 1960, p. 141) is not strictly applicable to cyclopentanone systems our assigned structures Va and Vb show the Cotton effects predicted by that rule.

[12] The intensities of the 3-keto and Δ^5-bands in this and other Δ^5-3-ketones are of the same order of magnitude characteristic of *cisoid* enones. *Cf.* R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960).

pared readily from VIa without protection of the 3-keto group by ketalization. Reaction of VIa with ethylene glycol and *p*-toluenesulfonic acid furnished mainly the Δ^6-3-ketal VIIa, m.p. 143–144°; $[\alpha]_D + 152°$; $\tau_{6,7H}$ 4.34 (two proton singlet) and the Δ^5-3-ketal, m.p. 150–151°; $[\alpha]_D + 25°$; τ_{6H} 4.18 (single proton, triplet $J = 3.5$ c.p.s.). The 5-hydrogen in VIIa is β since its hydrogenation product IIIh[13] (Pd/C in ethanol), m.p. 189–190° and 208–209°; $[\alpha]_D + 67°$; on hydrolysis with 80% acetic acid at room temperature, conditions which do not isomerize the *trans*-ketone IIIb, yielded the *cis*-ketone IIIc. Hydrolysis of VIIa with 80% acetic acid gave the Δ^6-3-ketone VIIb, m.p. 171–174°; $[\alpha]_D + 300°$; no absorption at 240 mμ; $\tau_{6H,7H}$ 4.13, 4.31; which with *N* HCl in methanol at room temperature isomerized to VIa.

Hydrolysis of VIIa with *N* KOH in methanol under helium gave the Δ^6-ketal acid VIIc,[14] m.p. 176–177°; $[\alpha]_D + 150°$; $\tau_{6,7H}$ 4.33 (2 proton singlet); The acid chloride, m.p. 140–150°; prepared from VIIc with oxalyl chloride in benzene was converted to the diazoketone and the latter with excess HI into the 21-methyl ketone VIe, m.p. 203–204°; $[\alpha]_D + 28°$; $\lambda^{\text{alc}}_{\text{max}}$ 240 mμ ($\epsilon = 8{,}100$); and with HCl in chloroform to the 21-chloro ketone VIf, m.p. 218–219°; $[\alpha]_D + 1°$; $\lambda^{\text{alc}}_{\text{max}}$ 241 mμ ($\epsilon = 8{,}700$). Treatment of VIf with potassium acetate and iodide in acetone gave the 21-acetoxy ketone VIg, m.p. 160–161°; $[\alpha]_D$ 0°; $\lambda^{\text{alc}}_{\text{max}}$ 240 mμ ($\epsilon = 9{,}300$).

(13) This product was identical with the product of direct ketalization of IIIb or IIIc.

(14) Similar hydrolysis of the Δ^5-ketal methyl ester VIb gave the Δ^5-ketal acid VIc, m.p. 237–238°; $[\alpha]_D$ +20°; τ_{6H} 4.18 (single proton). Deketalization of VIc and VIIc with boiling 0.05 *N* H_2SO_4 in methanol for 2 hours gave the Δ^5-3-keto acid VId, m.p. 296–299°; $\lambda^{\text{alc}}_{\text{max}}$ 240 mμ (ϵ = 9400).

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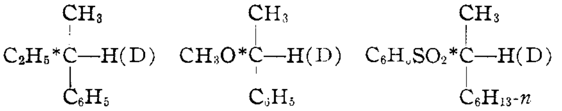
INTRAMOLECULAR PROTON TRANSFER IN A BASE-CATALYZED ALLYLIC REARRANGEMENT

Sir

In earlier work, hydrogen–deuterium isotope effects that ranged from 0.3 to 3.0 were observed for the base-catalyzed racemization and isotope exchange reactions of I,[1a] II[1a] and III.[1b]

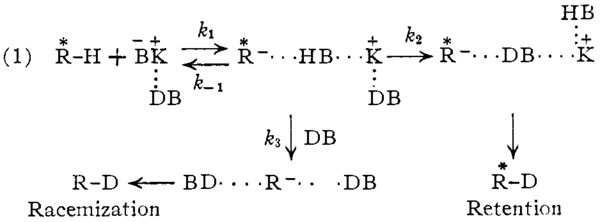


$C_2H_5{*}C(CH_3)(C_6H_5){-}H(D)$ I

$CH_3O{*}C(CH_3)(C_6H_5){-}H(D)$ II

$C_6H_5SO_2{*}C(CH_3)(C_6H_{13}\text{-}n){-}H(D)$ III

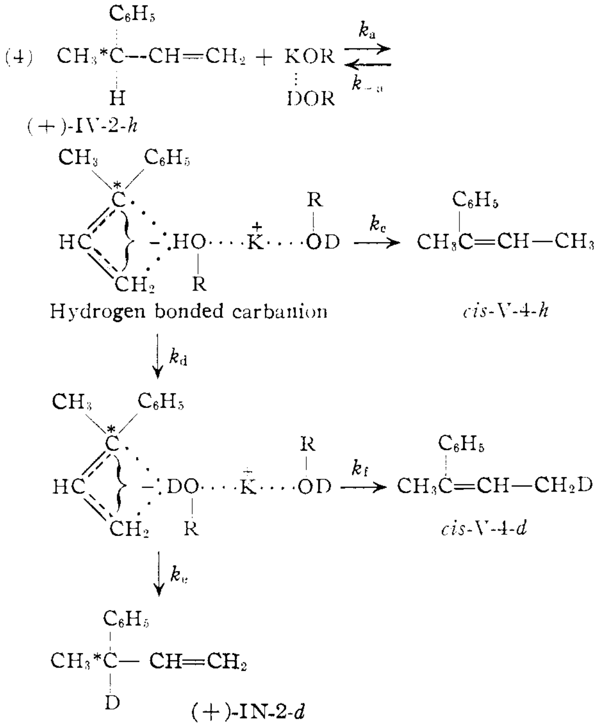
The low values and certain aspects of the stereochemical course of the reactions led to postulation of a mechanism embodied in equation (1). With solvents in which $k^H/k^D < 1$, then $k_{-1} > k_2$ or k_3. If $k_{\text{obs}}{}^{e}$ is the observed rate constant for isotopic exchange and $k_{\text{obs}}{}^{\alpha}$ for racemization, then equations (2) and (3) can be written, which provide isotope effects associated only with an equilibrium constant and the exchange of one hydrogen bonded carbanion for another.



$$(2)\quad k^{e}_{\text{obs}} = \frac{k_1}{k_{-1}}(k_2 + k_3) = K(k_2 + k_3)$$

$$(3)\quad k^{\alpha}_{\text{obs}} = \frac{k_1}{k_{-1}}k_3 = Kk_3$$

A clear implication of $k_{-1} > k_2$ or k_3 is that in a system such as IV with a driving force for rearrangement, an intramolecular base-catalyzed proton transfer is a distinct possibility. Such a process has been observed in *tert*-butyl alcohol-O-D (98% deuterated) with potassium *tert*-butoxide as catalyst.



Optically active (+)-IV-2-*h*[2] was dissolved in *tert*-butyl alcohol-O-D (0.386 *M*) which was 0.409 *M* in potassium *tert*-butoxide, and the solution was heated at 75° for 257 min. The olefin was recovered (75%) through pentane extraction, olefins IV and *cis*-V[2] were separated from one another by preparative vapor phase chromatography, and analyzed for deuterium and optical activity. Compound IV was completely free of deuterium,[3] and exhibited the same rotation as the starting material, $\alpha^{25}_D + 3.25°$ (l 1 dm., neat). Compound V contained only 0.46 of one atom of deuterium per molecule.[3] The nuclear magnetic resonance spectrum of *cis*-V indicated that most of this deuterium was at C-4. Clearly a *minimum* of 54% of the re-

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(1) (a) C. J. Cram, C. A. Kingsbury and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961); (b) D. J. Cram, D. A. Scott and W. D. Nielsen, *ibid.*, **83**, 3696 (1961).

(2) D. J. Cram, *ibid.*, **74**, 2141 (1952).

(3) Combustion and falling drop method.