found the C.D. spectra to consist of multiple peaks over the range 320–360 mμ (see Fig. 1). The center of these peaks is in the wave length region at which the R.D. curves in methanol cross the zero degree line.

TABLE I

ROTATORY DISPERSION DATA

Compound	R.D. peak mμ	Zero degree crossing, mμ
Sugiol (I, $R_1 = R_2 =$ Me, $R_3 =$ H, $R_4 = i$-Pr, $R_5 =$ OH)	Plain up to 340	...
Sugiol benzoate	355	331
Nimbiol (I, $R_1 = R_2 = R_4 =$ Me, $R_3 =$ H, $R_5 =$OH)	Plain up to 350	...
Nimbiol benzoate	350	335
7-Oxototarol (I, $R_1 = R_2 =$ Me, $R_3 = i$-Pr, $R_4 =$ OH, $R_5 =$ H)	Plain up to 300	...
7-Oxototarol benzoate	353	331
7-Oxototarol methyl ether	367	350[a]
7-Oxopodocarpic acid (I, $R_1 =$ Me, $R_2 =$ COOH, $R_3 = R_4 =$ H, $R_5 =$ OH)	342	312[a]
Methyl 7-oxo-O-methyl-podocarpate	346	318[a]
Methyl 7-oxo-O-methyl-13-acetyl podocarpate	340	315[a]
7-Oxo-O-acetyl-podocarpic acid	354	325
Methyl 7-oxo-dehydroabietate (I, $R_1 = CO_2Me$, $R_2 =$ Me, $R_3 = i$-Pr, $R_4 =$ H)	350	325

[a] By extrapolation.

TABLE II

ULTRAVIOLET ABSORPTION DATA

Compound	$\lambda_{\max}^{\text{MeOH}}$ (ε)	$\lambda_{320}^{\text{MeOH}}$ (ε)	$\lambda_{350}^{\text{MeOH}}$ (ε)
7-Oxototarol benzoate	233 (23,340) 283 (2,662) 296 (2,300)	656	34
Methyl 7-oxopodocarpate	225 (12,200) 277 (15,700)	4,200	41
Methyl 7-oxo-O-methyl-13-isopropyl podocarpate	230 (14,300) 279 (13,350)	1,300	49
Sugiol benzoate		291	61

In view of the multiple peaks in the C.D. spectra of these conjugated ketones, one has to expect corresponding multiple peaks in their ultraviolet spectra. It is known[5] that ketones conjugated with a double bond, *e.g.*, testosterone, show corresponding multiple peaks in their R.D. and ultraviolet spectra.

Finding a diterpenoid (methyl O-methyl-7-oxopodocarpate) of adequate solubility in isoöctane, its R.D. and ultraviolet spectra were determined in this non-polar medium. The R.D. spectrum (see Fig. 1) now revealed a set of multiple peaks in the same area where the C.D. peaks occur for this type of compound.[7] The ultraviolet spectrum in isoöctane ($\lambda_{\max}^{\text{isooctane}}$ 358 (149), 345 (415), 331 (626), 310 (686), 291 (2683), sh 282, sh 276, 267.5 (17,727), 226 (17,141), 219.5 (17,568)) shows a close correspondence with the C.D. and the R.D. curves.

Djerassi and co-workers[5] have reported the absence of any noticeable ultraviolet absorption peaks (in methanol) in the region where 2α-iodocholestane-3-one shows a Cotton effect curve. We have now studied the C.D. of this ketone (in dioxane) and find a peak at 295 mμ. Cholestane-3-one has a peak at 299 mμ in its C.D. spectrum. The ultraviolet absorption spectrum of 2α-iodocholestane-3-one in isoöctane or in carbon tetrachloride failed, however, to show any absorption maxima in the 300 mμ region.

According to Eyring and co-workers[8] the rotational strength R_k of a chromophore is related to an induced dipole moment, $\mu_e{}^k$, and a magnetic dipole moment, $\mu_m{}^k$, as shown in the equation: $R_k = \mu_e{}^k \cdot \mu_m{}^k$. For ultraviolet absorption, the greater the induced electric dipole moment the greater is the intensity of transition. To account for the strong C.D. and R.D. spectra of the diterpenoid ketones and 2α-iodocholestane-3-one and the corresponding exceedingly weak ultraviolet absorption maxima, one has to assume that for these chromophores the induced electrical dipole moment is very small, but the magnetic dipole moment is sufficiently large.

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[7] Solvent effects on optical rotatory dispersion have been attributed to various factors including shifts in absorption spectra and conformational changes in the molecule; see N. C. Knelen, N. J. Krause, T. O. Carmichael and O. E. Weigang, *J. Am. Chem. Soc.*, **84**, 1738 (1962), and C. Tanford, *ibid.*, **84**, 1747 (1962).

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THE EFFECT OF RADIATION ON THE REACTIONS OF RECOIL CARBON-11 IN AMMONIA[1]

Sirs:

The ammonia system[2] in which carbon-14 recoil atoms[3] are produced by the $N^{14}(n,p)C^{14}$ reaction was the first in which essentially all of the radioactive carbon produced could be accounted for in isolable and identifiable species.

One of the factors affecting the chemistry of the system is the radiation[4] from all sources that the

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. Y. Yang and A. P. Wolf, *J. Am. Chem. Soc.*, **82**, 4488 (1960).

[3] The literature prior to 1960 has been reviewed in A. P. Wolf, *Ann. Rev. Nucl. Science*, **10**, 259 (1960).

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system gets while the nuclear transformation producing carbon-14 is going on. Studies have been made in which the unwanted reactor radiation has been reduced; the samples have been encased in lead[5] and in bismuth.[6] This procedure allowed the reduction of the radiation in each instance by about a factor of ten. Studies to date using carbon-11 have involved low but fixed levels of radiation.[7-10] It has been pointed out[3] that reactor studies involve such high doses that the systems (particularly gaseous and to a lesser extent liquid and solid) involved may have reached a "saturation" region with respect to radiolytic processes and that a small reduction in dose may not appreciably change the observed chemistry.

The production of carbon-11 by a $N^{14}(p,\alpha)C^{11}$ reaction is almost ideally suited to studying the chemistry of energetic carbon. A high level of activity is readily obtained, and the radiation dose can be varied by a factor of 10^5.

Irradiations of gaseous ammonia, purified as previously described,[2] were carried out with a 10 Mev proton beam from the Brookhaven 60″ cyclotron. Beam intensities varied from 0.1 to 5.0 μa. and exposure times were from 5 seconds to 10 minutes. The gas, at one atmosphere, was contained in a 50 ml., water-cooled, aluminum tank with a 3 mil aluminum window. Products were identified by carrier methods using gas chromatography for separations. Activities in each sample were determined by counting the effluent of the gas chromatograph.[2] Total gaseous activity was found to be in constant proportion to the number of protons traversing the target at all dose levels studied, thus the percentage yields at all dose levels can be compared to one another.

The variation of yield of methane-C^{11} and methylamine-C^{11} is plotted as a function of dose in Fig. 1.

Here as in the case of the carbon-14 work[2] it is again apparent that the major products are methane and methylamine. Significantly, we now have been able to demonstrate a product dose dependence. It is noteworthy that above 0.1 e.v./molecule ($\sim 5 \times 10^7$ rads), product composition characteristic of the "saturation"[3] region for this system is observed.[11]

The results clearly suggest that at least part of the methane-C^{11} is produced by radiolysis of the primary products in this system. Two experiments were done to check this hypothesis. Since we assume the conversion of methylamine molecules to be dependent on the concentration of radiolytically produced species then we should be able to increase the yield of methylamine-C^{11} by a large increase in the total methylamine concentration. First, small amounts of methylamine were added to the ammonia before irradiation to act as a protector for the methylamine-C^{11} which is formed. With 0.13 vol. % CH_3NH_2 (dose = 0.74 e.v./molecule) and 2.1 vol. % CH_3NH_2 (dose = 0.73 e.v./molecule) added, the methylamine-C^{11} yield went from an expected 3% to a found yield of 6 and 12%, respectively.

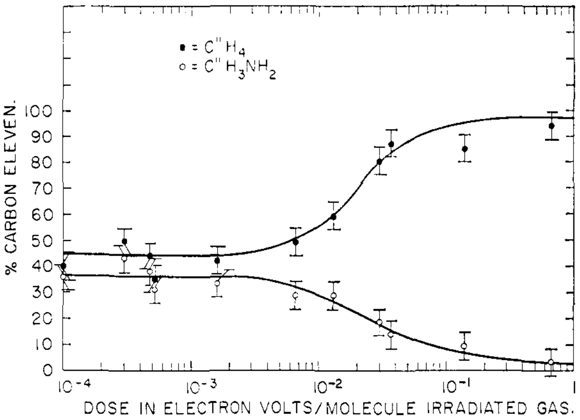

Fig. 1.—Methane-C^{11}-methylamine-C^{11} yields as a function of dose to the system.

Secondly, methane-C^{11} and methylamine-C^{11} were produced at intermediate doses (*e.g.*, 3×10^{-2} e.v./molecule; expect yields, $C^{11}H_4 \cong 80\%$, $C^{11}H_3NH_2 \cong 20\%$). The systems then were subjected immediately to further irradiation by the proton beam which had been attenuated by aluminum foils to below 3 Mev. (approximate threshold for carbon-11 production). A total dose of 3.9 e.v./molecule was then delivered to each sample. The yields characteristic of the "saturation" region were observed.

It is clear that reduction of methyl-C^{11}-amine to methane-C^{11} in the ammonia environment cannot be brought about by the direct radiolysis of the labeled methyl-C^{11}-amine but that reduction must involve as a first step either interaction with charged or with excited ammonia molecules resulting from the radiolysis of the total system. Reduction by hydrogen atoms can also be considered. Methyl-C^{11} radicals are probably involved to a minor extent only.[12] Reasonable mechanisms will be detailed in the full paper.

These experiments can leave no doubt that there is reaction between the "primary" products and one or more of the reactive species produced during the accompanying radiolysis.[13] It does not follow that the range 0.1 to 0.01 e.v./molecule, need be the critical range for all gaseous systems since the result will clearly depend on the radiation chemistry of each individual system.

At low dose levels, a third species (13% yield at 3×10^{-4} e.v./molecule, 19% yield at 1×10^{-4} e.v./molecule) as yet unidentified appears in varying yield. The material is trapped on the first few millimeters of a cetyl alcohol gas-liquid chromatography column and is readily reduced over

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(11) Most reactor studies reported to date are in this region and above, up to about 10-20 e.v./molecule. Product composition also can vary according to the phase at any given dose.[7]

(12) R. H. Schuler, private communication.

(13) The high yield of methyl-C^{14}-amine found in irradiated crystalline ammonium bromide (high dose), P. E. Yankwich and J. D. Vaughan, *J. Am. Chem. Soc.*, **76**, 5851 (1954), might be expected if we consider that the reaction between a recoil produced species and a radiolytically produced species probably is diffusion controlled under these conditions.

Raney nickel to give $C^{11}H_3NH_2$. Possible one carbon species with this behavior are methylenimine, cyclodiazomethane and diaminomethane. One carbon species may be the precursor of both methane and methylamine. The mechanism of the primary process is not dealt with here but will be considered in the full paper dealing with these experiments, unreported data and work in progress on this system.

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STEROIDS. CCII.[1] A NEW ROUTE TO 19-NOR STEROIDS

Sir:

The increasing importance of 19-nor steroids,[2a] particularly in the field of oral contraception,[2b] has made it attractive to investigate new routes to this class of compounds which do not proceed *via* Birch reduction[3] of ring A aromatic precursors, since the latter reaction in particular is inconvenient for large scale operations.

Recently we[4] and others[5–7] described chemical methods for the direct oxygenation of the C-19 methyl group, a primary prerequisite for the subsequent conversion to 19-nor steroids. However, none of these approaches offered a facile synthesis of 19-nor-Δ^4-3-ketones.

The conversion of several Δ^5-3β-alcohols into their corresponding 19-nor-Δ^5-3-ketones by an efficient process[8] is now described, which is exemplified by the conversion of pregnenolone acetate (I) into 19-norprogesterone (VIII) in an over-all yield of 37%.

Addition of hypobromous acid (N-bromoacetamide and aqueous perchloric acid) to pregnenolone acetate (I) in dioxane solution gave 5α-bromopregnane-3β,6β-diol-20-one 3-acetate (II) (m.p. 165–167°, $[\alpha]_D$ +6.5°.[9] Found for $C_{23}H_{35}BrO_4$: C, 60.36; H, 7.81; Br, 17.79; O, 14.17). Treatment of II with 1.2 moles of dry lead tetraacetate in anhydrous benzene[4,7] afforded 6β,19-oxido-5α-bromopregnane-3β-ol-20-one acetate (III) (m.p. 152–154°, $[\alpha]_D$ +58°, ν_{max}^{KBr} 907[10] cm.$^{-1}$. Found for $C_{23}H_{33}BrO_4$: C, 61.18; H, 7.31; Br, 17.91; O, 13.97). Mild alkaline hydrolysis of III gave the corresponding 3β-alcohol IV (m.p. 179–180°, $[\alpha]_D$ +61°. Found for $C_{21}H_{31}BrO_3$: C, 61.52; H, 7.70; Br, 20.19) which was oxidized with chromium trioxide in aqueous acetic acid and then directly converted with zinc dust in isopropyl alcohol[11] (reflux 24 hours) into 19-hydroxy-Δ^5 pregnene-3,20-dione (V). Treatment of V with oxalic acid in ethanol afforded 19-hydroxyprogesterone (VI) (m.p. 169–171°, $[\alpha]_D$ +182°, $\lambda_{max.}$ 243 mμ, log ε 4.22. Found for $C_{21}H_{30}O_3$: C, 76.07; H, 9.11; O, 14.69). Oxidation of VI with 8 *N* chromic acid in acetone solution furnished the corresponding 19-carboxylic acid VII (m.p. 147–149°, $[\alpha]_D$ +94°, λ_{max} 243 mμ, log ε 4.19. Found for $C_{21}H_{28}O_4$: C, 73.43; H, 8.22; O, 18.33) smoothly converted by acidic methanol[12] to 19-norprogesterone[13] (VIII) (m.p. 142–144°, $[\alpha]_D$ +141°).

In a similar manner dehydroisoandrosterone acetate (IX) gave 19-norandrostene-3,17-dione[14] (XV) (m.p. 166–168°, $[\alpha]_D$ +127°, λ_{max} 239 mμ, log ε 4.23) *via* 5α-bromoandrostane-3β,6β-diol-17-one 3-acetate (X),[4b,15] 6β,19-oxido-5α-bromoandrostane-3β-ol-17-one acetate (XI) (m.p. 187–188°, $[\alpha]_D$ +39°. Found for $C_{21}H_{29}BrO_4$: C, 59.24; H, 7.04; Br, 18.99), its corresponding 3β-ol XII (m.p. 209–211°, $[\alpha]_D$ +38°. Found for $C_{19}H_{27}BrO_3$: C, 59.74; H, 7.15; Br, 20.71), 19-hydroxy-Δ^4-androstene-3,17-dione[16] (XIII) (m.p. 168–170°, λ_{max} 243 mμ, log ε 4.21) and the 19-carboxylic acid XIV[12] (m.p. 148–150°, $[\alpha]_D$ +242°, λ_{max} 244 mμ, log ε 4.18. Found for $C_{19}H_{24}O_4$: C, 72.13; H, 7.69; O, 20.27).

19-Nor-17α-acetoxyprogesterone (XXIII) also was prepared from 17α-hydroxypregnenolone 3,17-diacetate[17] (XVI), by an alternate reaction sequence.

Reaction of 5α-bromopregnane-3β,6β,17α-triol-20-one 3,17-diacetate (XVII) (m.p. 184–186°, $[\alpha]_D$ −49°. Found for $C_{25}H_{37}BrO_6$: C, 58.41; H, 7.31; Br, 16.04; O, 18.23) with lead tetraacetate gave 6β,19-oxido-5α-bromopregnane-3β,17α-diol-20-one 3,17-diacetate (XVIII) (m.p. 202–208°,

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[9] All rotations in chloroform solution and ultraviolet spectra in 95% ethanol.

[10] All compounds with the 6β,19-oxide bridge were characterized by a sharp medium intensity band between 903–910 cm.$^{-1}$.

[11] In contrast to the 5α-bromo-6,19-oxides, the corresponding 5α-chloro-6,19-oxides [*e.g.*, 5α-chloro-6β,19-oxidoandrostane-3β-ol-20-one acetate (m.p. 186–189°, $[\alpha]_D$ +53°)] were recovered unchanged after treatment with zinc in isopropyl alcohol under reflux.

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