nine *in vivo* and the participation of the ethyl group directly or indirectly in the formation of choline, creatine, etc. The formation of such ethyl analogs *in vivo* at the expense of the normal methyl derivatives may at least in part account for the inhibition of growth of rats by ethionine. The data reported in this communication show that the ethyl group carbon of ethionine tagged with C-14 in the methylene carbon of the ethyl group appears in the creatine and choline of rat tissues. The radioactivity of the isolated choline was confined to the "trimethyl" amine moiety of the molecule.

Ten milligrams of C^{14}-ethionine (total activity 3.72×10^6 counts per minute) was injected intraperitoneally into each of two adult female rats of Wistar strain which were maintained on a complete casein diet. Six days later the food was withdrawn from the cages, the rats were fasted for 2 days, then sacrificed. From the entire carcass, minus the hide, choline was isolated as the reineckate and creatine as the creatinine potassium picrate. Choline reineckate was then converted to choline chloroplatinate. After the specific activities of the products were determined, choline chloroplatinate was degraded to "trimethyl" amine which was isolated as the hydrochloride. The activities of the compounds were determined directly on the weighed samples spread over an area of 5 sq. cm. in a G–M counter with a mica window of 1.8 mg. per sq. cm. The data are summarized in Table I.

TABLE I

	Specific activity, counts/min./millimole
C^{14}-Ethionine	6.06×10^7
Choline reineckate	7.83×10^3
Choline chloroplatinate	1.55×10^4
"Trimethyl" amine hydrochloride	8.9×10^3
Creatinine potassium picrate	2.36×10^3

The above data suggested the de-ethylation of ethionine in the rat. The removal of the ethyl group of ethionine may have proceeded *via* the formation of ethanol which, on oxidation, would eventually lead to the formation of acetic acid. To test this possibility, 10 mg. of C^{14}-ethionine was injected intraperitoneally into two adult rats which were maintained on a complete casein diet which was supplemented with 1% of S-benzyl-L-cysteine. We have shown previously that S-benzyl-L-cysteine is acetylated in the rat.[2] From pooled 3-day samples of urine of these rats analytically pure N-acetyl-S-benzyl-L-cysteine was isolated with the specific activity of 1.84×10^4 counts/minute/millimole. Complete data will be reported at a later date.

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RECEIVED MARCH 20, 1950

(2) J. A. Stekol, *ibid.*, **124**, 129 (1938).

THE REACTIONS OF METHYL RADICALS WITH HYDROCARBONS

Sir:

It has been shown[1] that the methane and ethane formed when acetone is photolyzed at 26 and 122° may be quantitatively accounted for by the reactions

$$CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3 \quad (1)$$
$$CH_3 + CH_3 = C_2H_6 \quad (2)$$

We have investigated the photolysis between temperatures of 100 and 300°, at total pressures of from 3.7 to 100 mm. and with a thirty-fold variation of light intensity. Reactions (1) and (2) account quantitatively for all the methane and ethane produced. We found no indication that reaction (2) was subject to a third-body restriction or took place at the wall of the reaction vessel.

When a paraffin hydrocarbon is mixed with the acetone, methane is also produced by reaction (3)

$$CH_3 + RH = CH_4 + R \quad (3)$$

Then

$$R_{CH_4}/R^{1/2}_{C_2H_6} = k_1/k_2^{1/2}\,[Ac] + k_3/k_2^{1/2}\,[RH]$$

where k_1, k_2 and k_3 are the velocity constants of reactions (1), (2) and (3), R_{CH_4} and $R_{C_2H_6}$ are the rates of production of methane and ethane and [Ac] and [RH] are the concentrations of acetone and paraffin. The velocity constant of reaction (2) may be expressed as $k_2 = P_2Z \exp(-E_2/RT)$. Because no absolute measure of the methyl radical concentration is available, the results are expressed in terms of $P_2^{1/2}$ and $^1/_2E_2$. We have investigated the photolysis of acetone and deuterated acetone alone, acetone in the presence of six hydrocarbons and deuterated acetone in the presence of ethane. In each case excellent Arrhenius plots were obtained; we estimate the error in the relative activation energies to be less than ± 0.2 kcal. When the proportions of hydrocarbon and acetone were altered, the rates of formation of methane and ethane altered as predicted by the above mechanism. Our results are contained in Table I. The results show first that

TABLE I

Reactant	$E - {}^1/_2E_2$ kcal.	$P/P_2^{1/2} \times 10^2$
Acetone	9.7	9.5
Deuterated acetone	10.3	...
Ethane	10.4	5.2
Neopentane	10.0	4.9
n-Butane	8.3	2.7
n-Pentane	8.1	2.5
n-Hexane	8.1	2.9
Isobutane	7.6	2.3
2,3-Dimethylbutane	6.9	1.7

in the series of the paraffin hydrocarbons the energy of activation for the abstraction of a primary hydrogen atom by a methyl radical is greater than that for the abstraction of a second-

(1) L. M. Dorfman and W. A. Noyes, Jr., *J. Chem. Phys.*, **16**, 557 (1948).

(2) W. A. Noyes, Jr., and L. M. Dorfman, *ibid.*, **16**, 788 (1948).

ary atom which is greater than that for a tertiary atom. Second, the steric factors for these reactions are at most 10^{-3}. Dorfman and Gomer[3] reached a similar conclusion about the magnitude of the steric factors from the results of their studies of a number of similar methyl radical reactions.

(3) L. M. Dorfman and R. Gomer, *Science*, **110**, 439 (1949).

DIVISION OF CHEMISTRY A. F. TROTMAN-DICKENSON
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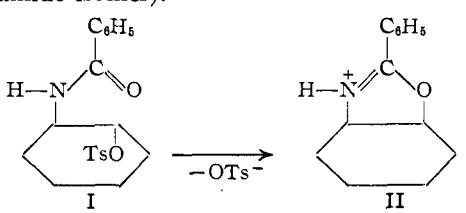
RECEIVED MARCH 29, 1950

THE NEIGHBORING BENZAMIDO GROUP IN ADDITION AND SUBSTITUTION

Sir:

Neighboring groups which participate in nucleophilic replacement processes with relatively large driving forces[1] can be expected to participate in addition[2] to the olefinic linkage which is initiated by electrophilic attack of some reagent on the multiple linkage.

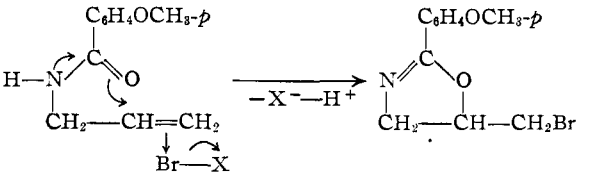
The benzamido and other acylamino groups are examples of so-called complex[2,3] neighboring groups with rather large driving forces. Benzamido can be compared with acetoxy from the first order rate of ionization of *trans*-2-benzamidocyclohexyl *p*-toluenesulfonate (I) in absolute ethanol at 74.51°, 1.78×10^{-3} sec.$^{-1}$, which is *ca.* 200 times the value for the *trans*-2-acetoxycyclohexyl ester[4] (and some 1000 times that of the *cis*-benzamido isomer).



I II

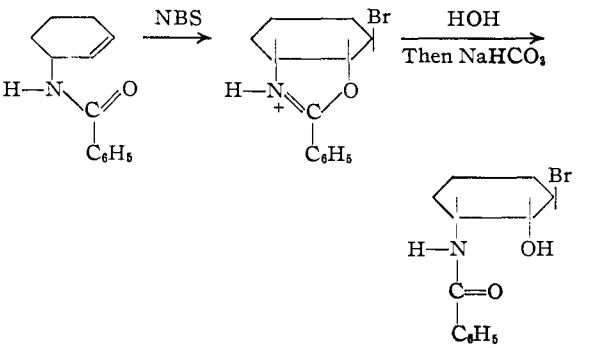
Solvolysis of I in ethanol or acetic acid produces the oxazolinium ion II as the first product[3] and this may be isolated either as the water-soluble *p*-toluenesulfonate, m. p. 160–161°, as the picrate, m. p. 155.5°, or as the free oxazoline, m. p. 47°. For example, oxazolinium toluenesulfonate is obtained in 95% yield from heating I several minutes in anhydrous acetic acid.

The acylamino group turns out to participate in addition in a very useful manner. For example, N-*p*-methoxybenzoylallylamine (III) gives, on treatment in acetic acid with N-bromosuccinimide, (which, incidentally, we have used for several years as a positive bromine source in hydroxylic solvents) a 95% crude yield of the bromoöxazoline IV, m. p. 91–91.5°.



IIII IV

This reaction is interesting theoretically and on the practical side constitutes a way for setting up three functional groups with a definite stereochemical relation. We illustrate with the cyclohexenyl case



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RECEIVED FEBRUARY 25, 1950

THE STRUCTURE OF QUINAMINE[1]

Sir:

In 1945 quinamine, an indole alkaloid of the cinchona family,[2] was considered to have structure I.[3] In 1949 Robinson[4] suggested an alternate formulation II to account for the dihydroindole nature of quinamine (spectrum, coupling reaction with diazobenzenesulfonic acid). Very recently[5] structure III was proposed for quinamine based upon the elegant conversion of quinamine into cinchonamine (V) with lithium aluminum hydride.

We have now effected the reverse transformation of cinchonamine into quinamine with the aid of dilute peracetic acid. Since all attempts of converting indole derivatives into 2,3-epoxides by oxidation with peracids have so far failed, we should like to propose the expression IV for quinamine.

The action of peracetic acid results probably first in the formation of a β-hydroxyindolenine derivative (VI) in accordance with the general course of oxidation in the indole series.[6] Inter-

(1) I am indebted to Research Corporation, New York, for financial assistance of this work.

(1) Winstein and Grunwald, THIS JOURNAL, **70**, 828 (1948).

(2) Winstein, paper before Organic Division at the St. Louis meeting of the American Chemical Society, September, 1948.

(3) Winstein, paper at Eleventh National Organic Symposium, Madison, Wisconsin, June, 1949.

(4) Winstein, Hanson and Grunwald, THIS JOURNAL, **70**, 812 (1948).

(2) Henry, Kirby and Shaw, *J. Chem. Soc.*, 524 (1945).

(3) Kirby and Shaw, *ibid.*, 528 (1945); Kirby, *ibid.*, 725 (1949).

(4) Robinson, Festschrift Paul Karrer, Zürich, 1949, p. 40; *J. Chem. Soc.*, in press (quoted from ref. 5).

(5) Goutarel, Janot, Prelog and Taylor, *Helv. Chim. Acta*, **33**, 150 (1950).

(6) Witkop, THIS JOURNAL, **72**, 1428 (1950).