application of this reaction. A mixture of 1,3-dimethyl-6-aminouracil and a slight excess of diethyl azodicarboxylate in a chlorobenzene suspension gave 1,3-dimethyl-5-(1,2-dicarbethoxyhydrazino)-6-aminouracil (**7**), mp 147.3° (77%). Portionwise addition of lead tetraacetate to **7** in glacial acetic acid solution at 50–55° over a period of 1 hr gave upon cooling 1,3-dimethyl-7-hydroxy-6-azalumazine (**8**), mp 281.7° dec (66%) (lit.[11] mp 284–285° dec). Chlorination with phosphorus oxychloride to the 7-chloro derivative **9**,[16] mp 250.5° (98%), conversion with hydrazine hydrate in ethanol at room temperature to **10**, mp 247.2° (95%), and finally stirring overnight at room temperature with mercuric oxide[10] in water gave 1,3-dimethyl-6-azalumazine (**6**), mp 212.4° (49%).

1,3-Dimethyl-5-(1,2-dicarbethoxyhydrazino)-6-aminouracil (**7**) also proved to be a convenient intermediate for purine synthesis. Thus, refluxing **7** for 1 hr in anhydrous formic acid or for 3 hr in ethanol with excess Raney nickel resulted in cleavage of the N–N bond to give 1,3-dimethyl-5-carbethoxyamino-6-aminouracil (**11**), mp 213.2° (74%),[17] which was converted to 1,3-dimethyluric acid (**12**), mp 412–415° dec (87%),[18] on heating. The latter compound could be prepared directly from **7** in 52% yield by heating with formamide and anhydrous formic acid. Phosphorus oxychloride in dimethylformamide converted **7** to 8-dimethylaminotheophylline (**13**), mp 337–338° (72%), while phosphorus oxychloride and N-methylformanilide in toluene gave 8-(N-methylanilino)theophylline (**14**), mp 273° (67%). This appears to be a general method for the synthesis of 8-aminopurines.

[16] This compound is reported to melt at 251–253°.[11] Previous attempts to convert this compound to 1,3-dimethyl-6-azalumazine were reported to be unsuccessful.

[17] W. Traube, *Ber.*, 33, 3035 (1900), reported mp 206–207°.

[18] H. Biltz and M. Heyn, *Ann.*, 423, 185 (1921), reported mp 408–410° dec.

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Ion Injection. Excited t-$C_4H_9^+$ Reactions in Liquid Isobutylene

Sir:

Vibrationally excited ions exhibit less selectivity in their reactions than thermal ions. Ions produced in the liquid phase are expected to be thermalized rapidly at the time of formation. However, vibrationally excited ions are commonly produced in the gas phase both by electron or photon impact and by ion–molecule reactions. In the ion-injection method,[1–3] ions are produced by photolysis in the gas phase and injected into the liquid with an electric field. Thus the possibility arises for injecting excited ions into the liquid and for examining whether these excited ions will show reactive selectivity in the liquid phase. The formation and reaction of t-$C_4H_9^+$ in isobutylene by the ion-injection method illustrate these possibilities.

Isobutylene was photolyzed by krypton resonance lines (10 eV) to produce only the $C_4H_8^+$ ion which then reacted by eq 1. The t-$C_4H_9^+$ ion was injected into

$$C_4H_8^+ + i\text{-}C_4H_8 \longrightarrow t\text{-}C_4H_9^+ + C_4H_7 \qquad (1)$$

liquid isobutylene at −128° by an electric field of 60 V/cm. Only C_8 and C_{12} products are observed under our experimental conditions.[3] The distribution of C_8 products was measured by gas chromatography.[3] The dependence of the C_8 products on added argon and neon and on temperature is shown in Tables I and II, respectively.

Table I. Effect of Added Argon and Neon on C_8 Products from t-$C_4H_9^+$ Reaction with Liquid Isobutylene[a]

Added gas		C_8 product distribution, %[b]			
Type	Pressure, torr	224-TMP[c]	224-TMP-2[d]	223-TMP[e]	344-TMP-2[f]
None		4	49	19	28
Ar	0.05	4	55	16	25
Ar	0.10	4	59	14	23
Ar	0.20	3	62	13	22
Ar	0.50	3	67	12	18
Ar	1.0	4	65	11	18
Ar	2.0	4	71	10	15
Ar	3.0	4	76	7	13
Ar	5.0	5	76	8	11
Ar	10.0	4	78	8	10
Ar	12.0	4	77	7	12
Ar	15.0	5	76	8	11
Ne	1.0	5	52	17	26
Ne	2.0	5	55	15	25
Ne	5.0	4	51	17	28
Ne	10.0	4	49	18	29

[a] Conditions: −400 V, 120-min photolysis, −128° (0.04 torr of isobutylene). [b] Relative C_8 yield and C_8/C_{12} ratio are constant for all experiments. [c] 2,2,4-Trimethylpentane, ±1%. [d] 2,4,4-Trimethylpentene-2, ±4%. [e] 2,2,3-Trimethylpentane, ±2%. [f] 3,4,4-Trimethylpentene-2, ±2%.

Table II. Phase and Temperature (Vapor Pressure) Effects on C_8 Products from t-$C_4H_9^+$ Reaction with Isobutylene

Vapor pressure, μ	Temp, °C	Per cent C_8 in products[a]	224-TMP[b] (% of C_8)	244-TMP-2[c] (% of C_8)	223-TMP[d] (% of C_8)	344-TMP-2[e] (% of C_8)
540	−110	75	4	49	20	27
280	−115	70	4	52	16	28
140	−120	74	5	49	17	29
80	−124	73	5	50	18	27
40	−128	76	4	49	19	28
6	−138	76	5	60	14	21
4	−140[f]	80	6	84	4	6
1	−145[g]	91	7	84	3	6

[a] 120-min photolysis time. [b] 2,2,4-Trimethylpentane, ±1%. [c] 2,4,4-Trimethylpentene-2, ±4%. [d] 2,2,3-Trimethylpentane, ±2%. [e] 3,4,4-Trimethylpentene-2, ±3%. [f] Freezing point. [g] Solid.

The reaction selectivity of t-$C_4H_9^+$ can be measured quantitatively from the C_8 products. The per cent of 2,2,4-trimethylpentane plus 2,4,4-trimethylpentene-2 represents the percentage of attack of t-$C_4H_9^+$ at the primary double-bond carbon in isobutylene, and the per cent of 2,3,3-trimethylpentane plus 3,4,4-trimethylpentene-2 represents the percentage of attack of t-$C_4H_9^+$ at the tertiary double-bond carbon in isobutylene. Thermal ions preferentially attack at the primary double-bond carbon.

The C_8 reaction product yields illustrate that t-$C_4H_9^+$ reacts nonselectively at both the primary and tertiary carbons in isobutylene. t-$C_4H_9^+$ is formed by reaction 1 which is estimated to be 10–20 kcal/mole exothermic in the gas phase. It is postulated that vibrationally

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[1] E. W. Schlag and J. J. Sparapany, *J. Am. Chem. Soc.*, 86, 1875 (1964).

[2] J. J. Sparapany, *ibid.*, 88, 1375 (1966).

[3] N. S. Viswanathan and L. Kevan, *ibid.*, 89, 2482 (1967).

excited t-$C_4H_9^+$ is formed in the gas phase and exhibits this by nonselective reactivity in the liquid phase. Two independent sets of experiments support this. When t-$C_4H_9^+$ is deexcited in the gas phase by collisions with added argon, its reaction selectivity toward liquid isobutylene increases. When reaction 1 takes place in the liquid phase, nonexcited t-$C_4H_9^+$ is formed which exhibits considerable reaction selectivity toward isobutylene.

Argon and neon were tested as deexciters for t-$C_4H_9^+$. Both can deexcite vibrational levels of molecules as well as act as moderators for translational energy.[4] Table I shows that reaction selectivity for the primary carbon increases from 53% with no added argon to 76% with 3 torr and above added argon. However, from 1 to 10 torr of neon shows no effect on the C_8 distribution. If neon and argon were acting entirely as translational energy moderators, 3 torr of Ar would be equivalent to 4.5 torr of neon.

The absence of ion translational energy effects on the C_8 distribution is also indicated by the lack of an applied field effect. We conclude that vibrational deexcitation is occurring and that argon is much more effective for vibrational deexcitation than is neon. Such a large difference in vibrational deactivation efficiency between neon and argon is somewhat surprising. However, deactivation of ions may be more sensitive to polarizability effects than is deactivation of neutral molecules. Further studies of this point are in progress.

The deexcitation experiments were done at a liquid isobutylene temperature of $-128°$ where the vapor pressure is 0.04 torr. $C_4H_9^+$ makes one to two collisions before reaching the liquid at this pressure under our experimental conditions. Maximum effective deexcitation by argon occurs at 3–4 torr which means that about 100 collisions of $C_4H_9^+$ with argon are necessary for maximum reaction selectivity. The selectivity of deexcited $C_4H_9^+$ never rises above 78%, whereas percentages approaching 90–100% are expected. The limiting observed value of 78% may be due to those $C_4H_9^+$ ions that are formed in a narrow layer above the liquid and are not deexcited before being injected.

Table II shows that the reaction selectivity of t-$C_4H_9^+$ can also be increased by lowering the liquid temperature. Lowering the temperature lowers the isobutylene vapor pressure. At 0.04 torr and above, $C_4H_8^+$ makes one or more gas-phase collisions with isobutylene to form vibrationally excited t-$C_4H_9^+$. However, below 0.04 torr more and more of the $C_4H_8^+$ ions are directly injected into the liquid. Reaction 1 then occurs in the liquid phase and the product t-$C_4H_9^+$ ion is vibrationally deexcited. At vapor pressures of only 0.004 torr the reaction selectivity reaches 90%. This suggests that thermal energy t-$C_4H_9^+$ ions are indeed quite selective in their reaction with isobutylene. In fact, 2,4,4-trimethylpentene-2 accounts for 84% of all the C_8 products.

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(4) V. N. Kondrat'ev, "Chemical Kinetics of Gas Reactions," Addison-Wesley Inc., Reading, Mass., 1964, Chapter 6.

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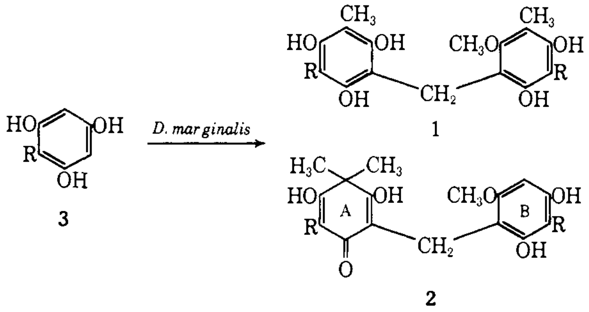
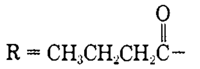
The Incorporation of Sodium Butyrate into Methylenebis(butyrylphloroglucinols) by a Novel Biosynthetic Pathway

Sir:

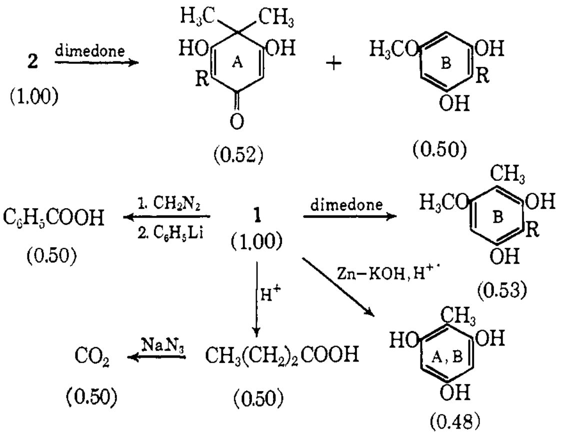
Recent work has shown that methylenebis(butyrylphloroglucinols) such as margaspidin (**1**) and desaspidin (**2**) are biosynthesized by oxidative dimerization of the methylated monomers of butyrylphloroglucinol (**3**)[1] and that all of the methyl groups are derived from methionine.[2]

Butyrylphloroglucinol (**3**) itself would seem to be derived from one butyrate and three malonate units or ultimately one acetate and four malonate units, all as their thiol ester or acyl carrier protein equivalents.[3] To prove the former, sodium butyrate-1-^{14}C (3.6×10^{12} dpm/mole, 0.5 mCi) was administered to *Dryopteris marginalis* tubers during a period of 4 days (0.17% average incorporation). Degradation[2] of recovered **1** (4.73×10^8 dpm/mole) and **2** (4.8×10^8 dpm/mole) with dimedone showed that the activity was equally distributed between the two butyrylphloroglucinol moieties as expected. However, further degradation of the methyl ether of **1** with phenyllithium as well as decarboxylation of the derived butyric acid (Schmidt degradation)[4] showed that only one-half of the total activity of **1** was located at the carbonyl carbons of the side chain and that the remainder of the side chain was essentially inactive. Assuming the butyrate-plus-three-malonate hypothesis, this requires that the activity of the three malonate units derived from catabolism of butyrate sum fortuitously to the same radioactivity as the side chain.





$$R = CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}-$$



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(3) P. R. Vagelos, *Ann. Rev. Biochem.*, **33**, 139 (1964).

(4) R. O. Brady, R. M. Bradley, and E. G. Trams, *J. Biol. Chem.*, **235**, 3093 (1960).