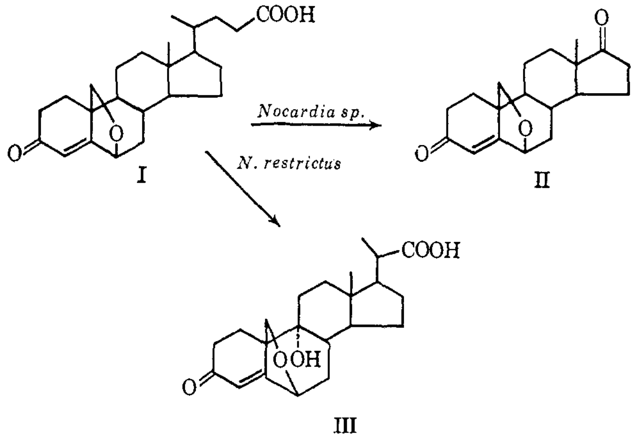
Table II. Acetate-^{14}C from Lithocholic Acid-24-^{14}C

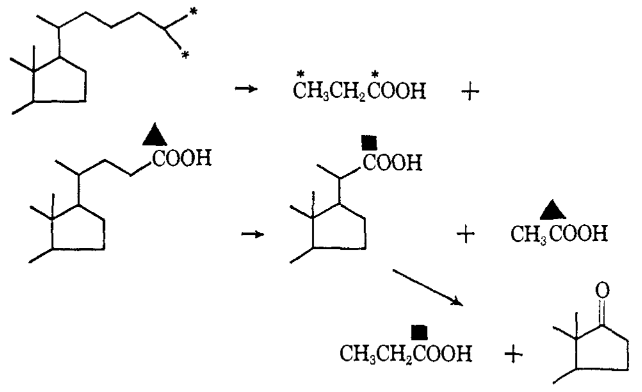
S-Benzylisothiuronium acetate, mp 138–141.5°	
No. of recrystallization	Specific activity, counts/min mmole
First	14,460
Second	14,760
Third	15,360
Fourth	15,960
Distribution of ^{14}C in acetate	
	Radioactivity, counts/min
Sodium acetate	3410
Carbon 1	3280
Carbon 2	3

recrystallizations. Schmidt degradation[3] of the molecule revealed that the radioactivity resided exclusively in the carboxyl carbon (Table II).

When 3-oxo-6,19-oxidochol-4-en-24-oic acid[7] (I; 200 mg) was incubated with *Nocardia sp.*[8] (ATCC 19170), 6,19-oxidoandrost-4-ene-3,17-dione (II; 30 mg), mp 182–185°, was obtained. On the other hand, when I (1.5 g) was exposed to *N. restrictus*, 353 mg of a product (III) was isolated: mp 231–234°; $[\alpha]^{26}\text{D}$ −66° (dioxane); $\lambda_{\max}^{\text{alc}}$ 241 mμ (ϵ 11,000); $\lambda_{\max}^{\text{nujol}}$ 3.00, 5.82, 5.90, and 6.06 μ. Its nmr[9] spectrum showed bands at τ 4.11 (1 H, singlet, vinylic H at C-4), 5.39 (1 H, doublet, J = 5 cps, H at C-6), 5.93 (doublet) and 6.60 (doublet) (2 H, J = 10 cps, CH_2O at C-19), 8.90 (3 H, doublet, J = 8 cps, 21-CH_3), and 9.26 (3 H, singlet, 18-CH_3). Molecular weight analysis (mass spectrum) gave 374 and carbon and hydrogen analysis was in good agreement with $C_{22}H_{30}O_5$. Since III remained unchanged after treatment with pyridine and acetic anhydride or chromic trioxide in acetic acid, the newly introduced hydroxyl group must occupy a tertiary position. On the basis of the deshielding effect, caused by this newly introduced hydroxyl group on the vinylic proton band at C-4 (−0.16 ppm),[10] and the fact that *N. restrictus* is a known 9α-hydroxylator,[11] III was tentatively assigned the structure 9α-hydroxy-6,19-oxidobisnorchol-4-en-3-on-22-oic acid.



These data support the view that the degradation of the cholesterol side chain by microorganisms[12] involves carbon–carbon bond fission at C-24–C-25, C-22–C-23, and C-17–C-20, resulting in the formation of 2 moles of propionic acid and 1 mole of acetic acid.



This mode of formation of 17-keto steroids from cholesterol differs from that of the mammalian system[13] which involves the cleavage of the C-20–C-22 bond, yielding isocaproic acid and pregnenolone; subsequent breakage of the C-17–C-20 bond gives 17-keto steroids.[13,14]

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[7] This compound was synthesized by the hypoiodite reaction according to the sequence reported by J. Kalvoda, *et al.*, *Helv. Chim. Acta*, **46**, 1361 (1963).

[8] This organism was formerly named CSD-10.

[9] Nuclear magnetic resonance spectra were determined on a Varian Associates recording spectrometer (A-60A) at 60 Mc in deuterated dimethyl sulfoxide. Chemical shifts are reported in τ values (parts per million) [G.V.D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958)].

[10] K. Tori and E. Kondo, *Steroids*, **4**, 713 (1964).

[11] C. J. Sih, *Biochim. Biophys. Acta*, **62**, 541 (1962).

[12] Similar results were obtained with other microorganisms of the genera *Mycobacterium*, *Corynebacterium*, and *Arthrobacter*, indicating this to be a general degradative pathway.

[13] K. Shimizu, M. Gut, and R. I. Dorfman, *J. Biol. Chem.*, **237**, 699 (1962).

[14] This investigation was supported in part by research grants from the National Institutes of Health (AM-4874 and AM-6110) and the National Science Foundation (GB-1903).

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Automerization of Naphthalene in the Presence of Aluminum Chloride

Sir:

We wish to report preliminary results concerning a new reaction of naphthalene (I): isotopic scrambling of the ^{14}C label from position α into positions β and γ (*i.e.*, the bridge carbon atoms 9 and 10) under the influence of aluminum chloride.

Naphtalene-1-^{14}C (1 mole) was heated in benzene (7 moles) for 2 hr at 60° with commercial anhydrous aluminum chloride (0.95 mole), exposed to the atmosphere during grinding in the mortar. After hydrolysis and removal of the solvent, the recovered and purified naphthalene (about half the initial amount was obtained by distillation) was nitrated by nitric acid in acetic acid, then reduced with zinc powder in ethanol–acetic acid to 1-naphthylamine (II). The attempt to perform a systematic degradation by conversion of II into benzo[*h*]quinoline *via* a Skraup reaction and by subsequent oxidation and decarboxylation failed, because benzo[*h*]quinoline does not afford quinolinic acid on oxidation with potassium permanganate. Therefore 1-naphthylamine was oxidized by potassium permanganate to phthalic acid (III) which was converted into carbon dioxide (IV) and anthranilic acid (V) by a Schmidt degradation.

Table I. Radioactivities (in microcuries/mole) of Degradation Products of Naphthalene

	Compd I	Compd II	Compd III	Compd IV	Compd V
(a) Nonisomerized	852 ± 8		858 ± 8	210 ± 3	
(b) Isomerized		860 ± 9	671 ± 7	76 ± 2	590 ± 30

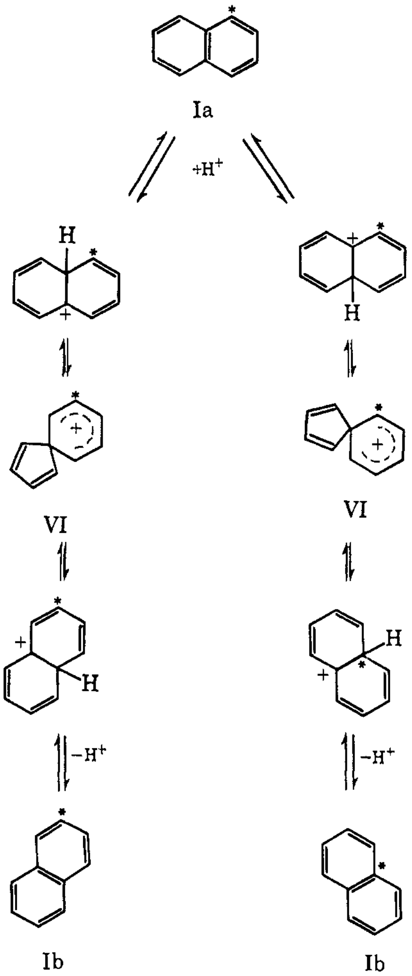
Radioactivity measurements of compounds I–V (II as the picrate) before (a) and after (b) treatment with aluminum chloride were performed by combustion followed by counting $^{14}CO_2$ in length-compensated Geiger–Müller counters.[1] Results are presented in Table I.

The exclusive localization of the label in the α position of the starting naphthalene-1-^{14}C (Ia) is proved by the complete conservation of the radioactivity in phthalic acid (IIIa) and by the 1/4.1 times as large activity of one α-carbon atom (as IVa). After treatment with aluminum chloride, the total activity is conserved (in IIb), but approximately statistical distribution of the label between the four α-, four β-, and two γ-carbon atoms in naphthalene is reached. The somewhat lower activity of one α position (evidenced by IVb) than the theoretical value for statistical scrambling (85–87 μcuries/mole) can be due to isotopic effects in the Schmidt degradation. The difference in activity between IIb and IIIb leads to the activity of one β-carbon equal to 94 ± 6 μcuries/mole. The total activity of IIb combined with the previous experimental figures leads to the activity of γ (9 or 10) position equal to 90 ± 14 μcuries/mole. These experimental values yield a calculated activity of 596 ± 31 μcuries/mole for Vb, which compares excellently with the experimental value. The larger experimental error in this case reflects the larger scatter of experimental activities for different runs.

A plausible mechanism of this reaction can be depicted as involving protonation of naphthalene by the protonic acid formed from atmospheric moisture and aluminum chloride.[2,3] Whereas protonation of the α positions, which are reactive toward electrophilic attack, does not lead to rearrangement, protonation of carbons 9 or 10 followed by a 1,2 shift leads to a symmetrical cation, VI, which can subsequently undergo reverse 1,2 shifts leading to the observed scrambling.

The 9-protonated intermediate could react by two other possible mechanisms: valence tautomerization to a cyclodecapentaene cation followed by hydride shifts and ring closure, or abstraction of a hydride ion from a Scholl reaction intermediate leading to binaphthyl and dihydronaphthalene which when rearranges and dehydrogenates.

An intermediate similar to VI (but with a saturated five-membered ring) occurs in the anthrasteroid rearrangement.[4] We believe that the isomerizations of polycyclic aromatic compounds caused by aluminum chloride involve the same process as that depicted above for naphthalene: tetraphene–chrysene,[5] 7-methyltetraphene – 2-methylchrysene,[6] picen–dibenz[*a,h*]anthracene,[6] benzo[*l*]tetraphene–benzo[*a*]naphthacene,[7] etc.[8]



Reactions which violate the principle of minimal structural change, and in which the initial and final states are structurally identical, can be evidenced either by isotopic labeling as was done for naphthalene in the present work (they are then named *isotopic rearrangements* or *isotopic isomerizations*) or by nmr spectroscopy when the process is rapid enough (they are then named *degenerate rearrangements* or *degenerate valence isomerizations*). We propose to distinguish, in reactions which violate the principle of minimal structural change, between the terms *isomerization* and *rearrangement* by applying them to two of the three possibilities of reactions affecting the molecular and structural formulas and to name the third possible process, which conserves both these formulas, *automerization*. These terms are presented in Table II; isomerizations are

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(1) C. Măntescu and A. Genunche, *Studii Cercetari Chim. Acad. R. S. România*, 13, 1101 (1965).

(2) C. D. Nenitzescu, M. Avram, and E. Sliam, *Bull. Soc. Chim. France*, 1266 (1955).

(3) C. Măntescu, A. Genunche, D. Duta-Cristu, and A. T. Balaban, *J. Labelled Compds.*, 2, 267 (1966).

(4) N. L. Wender in "Molecular Rearrangements," Vol. 2, P. de Mayo, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1963, p 1063.

(5) A. Dansi and E. Salvioni, *Gazz. Chim. Ital.*, 71, 549 (1949).

(6) N. P. Buu-Hoi and D. Lavit, *Proc. Chem. Soc.*, 120 (1960); N. P. Buu-Hoi and D. Lavit-Lamy, *Bull. Soc. Chim. France*, 1657 (1957); 1398 (1962); 341 (1963).

(7) M. Zander, *Naturwissenschaften*, 49, 300 (1962).

(8) A. Dansi, *Bull. Soc. Chim. France*, 101 (1962); N. P. Buu-Hoi and D. Lavit-Lamy, *ibid.*, 102 (1962); D. Lavit-Lamy and N. P. Buu-Hoi, *ibid.*, 2613, 2619 (1966); *Chem. Commun.*, 92 (1966).

Table II. Definition of Rearrangement, Isomerization, and Automerization

Molecular formula	Structural formula	Name
Not conserved	Not conserved	Rearrangement
Conserved	Not conserved	Isomerization
Conserved	Conserved	Automerization

thus a particular case of rearrangements, and automerizations a particular case of isomerizations.

Automerizations of carbon atoms evidenced by isotopic labeling were recently reviewed.[9] The thermal automerizations of bullvalene,[10] homotropylidene,[11] etc., were evidenced by nmr spectra. A photochemical automerization of carbon atoms in benzene is plausible in view of recent data.[12]

According to the proposed definitions the benzidine, phenylhydroxylamine, Beckmann, Claisen, and Stevens rearrangements and a few others should be termed isomerizations. Only processes such as the neopentylic, pinacolic, benzilic, Demjanov, Wolff, and Curtius rearrangements, etc., are named in agreement with this definition.

Further work is being done in our laboratory in order to degrade systematically the isomerized anthranilic acid (Vb).[13] The possibility of the isotopic automerization of naphthalene and phenanthrene was mentioned in 1965.[14]

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[9] A. T. Balaban and D. Fărcaşiu, plenary lecture delivered at the 2nd International Conference on Methods of Preparing and Storing Labelled Compounds, Brussels, Nov 28–Dec 3, 1966 (to appear in the proceedings published by Euratom).

[10] G. Schröder, J. F. M. Oth, and R. Merényi, *Angew. Chem.*, **77** 774 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 752 (1965).

[11] W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963); *Tetrahedron*, **19**, 715 (1963).

[12] K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **86**, 2307 (1964); **88**, 2066 (1966); L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *ibid.*, **87**, 675 (1965); D. Bryce-Smith, *et al.*, *Chem. Commun.*, 512, 593, 643 (1966).

[13] H. Steinberg and F. L. J. Sixma, *Rec. Trav. Chim.*, **81**, 185 (1962).

[14] A. T. Balaban and Z. Simon, *Rev. Roumaine Chim.*, **10**, 1059 (1965).

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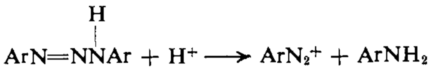
The Generation of Vinyl Cations from Vinyltriazenes

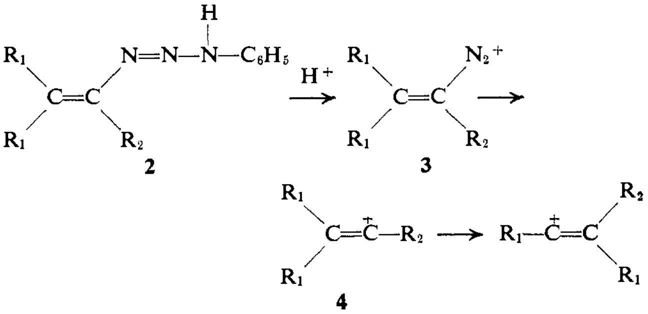
Sir:

The classical reaction of diaryltriazenes (diazoaminobenzenes) with acid to give aryldiazonium ions[1] suggested to us a potentially convenient way to generate vinyldiazonium ions[2] from the analogous vinyltriazenes (**2**).[3] This type of intermediate might then lose nitrogen to give the corresponding vinyl cation, a type of species that has been the subject of considerable study by a number of investigators in recent years.[4] The purpose of this note is to report the synthesis of selected vinyltriazenes (**2a–d**)[5] and their reactions with acids to give products that are believed to arise from intermediate vinyl cations.



$$\mathrm{ArN{=}N\overset{H}{N}Ar + H^+ \longrightarrow ArN_2^+ + ArNH_2}$$

1



a, $R_1 = R_2 = C_6H_5$
b, R_1 = *p*-tolyl; $R_2 = C_6H_5$
c, $R_1 = C_6H_5$; $R_2 = CH_3$
d, $R_1 = C_6H_5$; $R_2 = H$

All triazenes were synthesized by reaction of the appropriate Grignard reagent with phenyl azide.[1] The triazene structure assignments were based on standard criteria[6] plus ozonolysis to ketones to exclude the triazoline structural possibility that could not be excluded by routine methods. All of the triazenes were found to be sensitive to acid, reacting, for example, with acetic acid at room temperature in a matter of seconds with essentially quantitative nitrogen evolution. The products of reaction of **4a–d** with various acids are given in Table I. Points of particular interest are the following.

(1) In all cases, the products are those that would be expected to arise from simple cation formation followed by reaction with nucleophile either before or after rearrangement. Furthermore, the potential generality of this reaction as a synthetic method for producing triarylvinyl derivatives is emphasized by the fact that, even when the conjugate base of the acid is as weakly nucleophilic as the toluenesulfonate ion, 20% of the corresponding vinyl sulfonate is formed.

(2) The reactions are accompanied by more or less rearrangement, the amount of rearrangement being consistent with the reaction involving a vinyl cation intermediate. For example, triazene **2b**, in pure acetic acid, gives about 20% rearranged product (to 80% unrearranged). However, when potassium acetate is added, as the vinyl cation intermediate would predict, rearrangement is suppressed. In fact, in the presence

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[1] *Cf.* H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, Chapter 8.

[2] For an elegant study of the diazotization of selected primary vinylamines with isoamyl nitrite and nitrosyl chloride to give products that probably arise from intermediate vinyldiazonium ions, see D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *J. Am. Chem. Soc.*, **87**, 863 (1965).

[3] The reaction of acid with aliphatic triazenes has also been studied and found to give products expected from aliphatic diazonium ions. See, for example, E. M. White and H. Scherrer, *Tetrahedron Letters*, **21**, 758 (1961), and ref 1.

[4] For a very thorough review of vinyl cations, see P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, **88**, 4990 (1966).

[5] The position of the proton is not known. For conceptual convenience, it is placed next to the phenyl.

[6] With the exception of 2c, which was too unstable to yield to normal analytical techniques, all new compounds gave acceptable analyses.