PHOTOCHEMISTRY OF AZOLES, PART VII. PHOTOSOLVOLYSIS OF ALKYLMERCAPTOAZOLES. AN APPLICATION TO SOME ACYCLIC MONOTERPENE DERIVATIVES.[a,b]

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Dedicated to Prof. Kyosuke Tsuda on the occasion of his 75th birthday

Abstract - Salts derived from 2-alkylmercapto-1-methylimidazoles 1b-e and 3-alkylmercapto-4-methyl-1,2,4-triazoles 2b-d have been found to undergo photochemical heterolytic fission of the S-alkyl bond in aqueous or methanolic solution to give solvolysis-type products.

1. Introduction. Photoinduced solvolysis of the system R-X (X = halides[3], acetate[4], ammonium[5] and sulfonium salts[6]) has previously been observed and carbocationic intermediates frequently postulated. However, these X groups have proved to be of limited applicability as photochemical leaving groups for producing cationic species of the type R^+; and, except in certain cases where R has been either benzyl or some specific bridged cyclic system, the intervention of ionic intermediates has not been established beyond doubt. This has now led to a search for new and more widely applicable leaving groups which could facilitate photosolvolysis reactions.

A priori such leaving groups would have to satisfy the following requirements:

a) The leaving group X should be transformable into a reactive photoexcited state.

b) The R-X bond should undergo efficient heterolysis by withdrawing the bond electrons into the X group, i.e. the latter should be electron deficient (serve as an electron sink).

c) Attachment to a variety of R groups should be facile.

In this paper a number of photoreactions of S-alkylated derivatives of 2-mercapto-1-methylimidazole and 3-mercapto-4-methyl-1,2,4-triazole, and of their salts, will be described.

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[a] Photochemical Reactions, 123rd communication[1]. [b] Part VI of this series[2]. [c] Part of this work was done at the Organic Chemistry Laboratory of The Eidgenössische Technische Hochschule, CH-8092 Zurich, Switzerland.

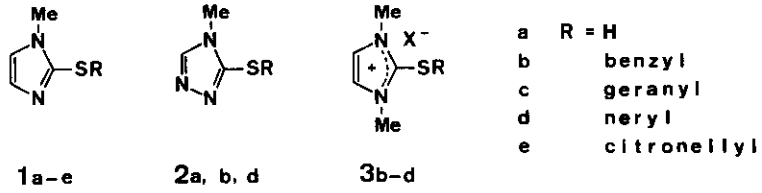
2. Results of photolysis. 2-Alkylmercapto-1-methylimidazoles 1b-e and 3-Alkylmercapto-4-methyl-1,2,4-triazoles 2b-d were prepared by treatment of 2-mercapto-1-methylimidazole (1a) and 3-mercapto-4-methyl-1,2,4-triazole (2a), respectively, with the corresponding alkyl halide in ethanol.

Quaternary salts 3b-d were prepared by reaction of methyl iodide with the corresponding alkylmercaptoazoles 1b-d in acetone.

Irradiation of 2-benzylmercapto-1-methylimidazole (1b) in methanol led to the S → N benzyl migration product 4[d] in 35 % and to the debenzylation product 1a in 32 % yield at about 80 % conversion of 1b.

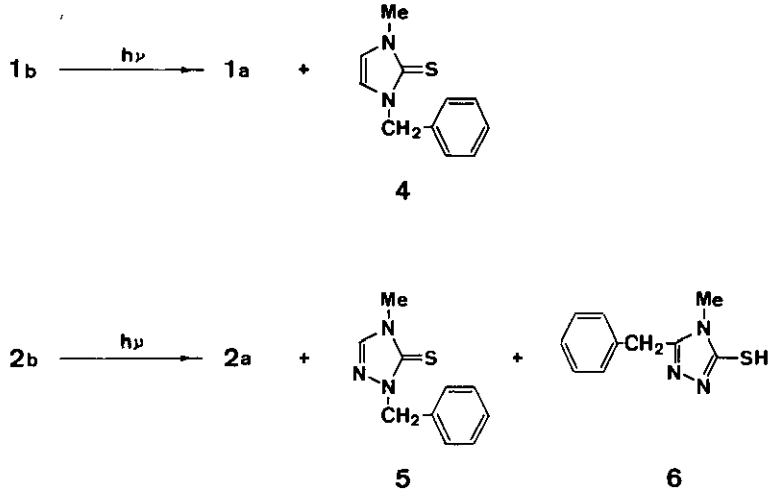
Similar irradiation of 3-benzylmercapto-4-methyl-1,2,4-triazole (2b) led to almost complete conversion, giving (a) the S → N benzyl migration product 5 (35 %), (b) S → C benzyl migration product 6 (13 %), and (c) debenzylation product 2a (47 %).

Scheme 1

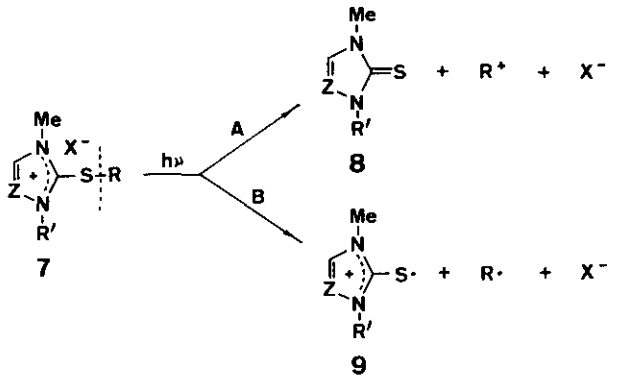


1a-e 2a, b, d 3b-d

Scheme 2



Scheme 3



These results now led to the belief that N-protonated or N-alkylated alkylmercaptoazoles as depicted in Scheme 3 (7, Z = CH, R' = H or alkyl) would be likely to undergo, at least partially, photochemical heterolytic S-R bond fission (path A), to give imidazoline-2-thiones (8, Z = CH, R' = H or alkyl) or 1,2,4-triazoline-3-thiones (8, Z = N, R' = H or alkyl) as the one fragment and reactive alkylcations (R^+) as the other.

In accord with this assumption, irradiation of 1b and 2b in acidic medium did, indeed, proceed with almost complete suppression of benzyl migration: Compound 1, on irradiation in acidic methanol[d], gave compound 4 in only 12 % yield at 75 % conversion; irradiation of 2b under the same condition gave compound 5 in only 5 % yield at ca 80 % conversion; and none of 6 was isolated. At the same time, in both cases, a mixture of more volatile products was formed; composed (through solvent participation) of benzyl methyl ether (10), o- (11) and p-cresyl methyl ether (12); in 55 %, 0.2 % and 0.6 % yield respectively, from 1b, and in 53 %, 0.3 % and 0.3 % yield, respectively, from 2b (calculated on conversion of starting materials). There was no such conversion when solutions of 1b and 2b in acidic methanol were kept in the dark for several days at room temperature.

A similar heterolytic process was observed also with 2-benzylmercapto-1,3-dimethylimidazolium iodide (3b), but here the reaction proceeded more sluggishly and was inhibited further by iodine formation; hence product yields could not be determined accurately.

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[d] Photolysis was carried out using a medium pressure mercury lamp (either lamp A or B, see Experimental part) with a quartz immersion well ($\lambda > 235$ nm light).

This type of photolysis was now examined in the case of analogous acyclic monoterpene derivatives, a field where solvolytic reactions have received much attention in connection with biosynthetic pathways in the formation of cyclic terpenes.

Scheme 4

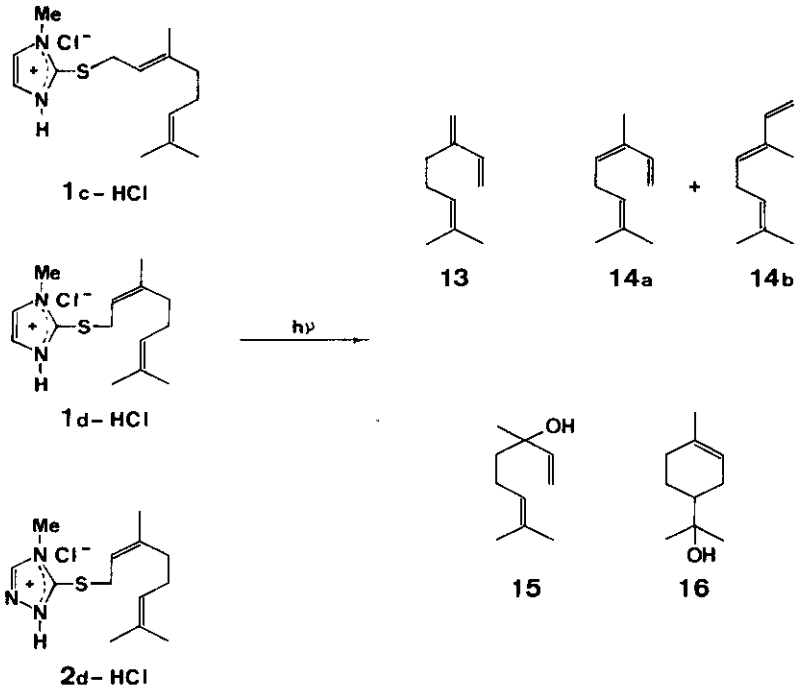


Table 1. Irradiation of 1c, 1d and 2d in acidic water

Run	Start. compd.	Irrad. temp.	Product ratio				Total yield (%)
			13	14	15	16	
1	1c	20°	40	10	45	5	55[a]
2	1d	20°	21	5	37	37	60[a]
3	1d	20°*	33	8	20	38	31[b]
4	1d	-20°*	57	14	7	21	16[b]
5	1d	-78°*	80	20	-	-	10[b]
6	2d	20°	8	2	23	67	61

a Photolysis by method a (see Experimental part)

b Photolysis by method b (see Experimental part)

• in glycerol - 0.1 N aq. HCl 1 : 1

Scheme 5

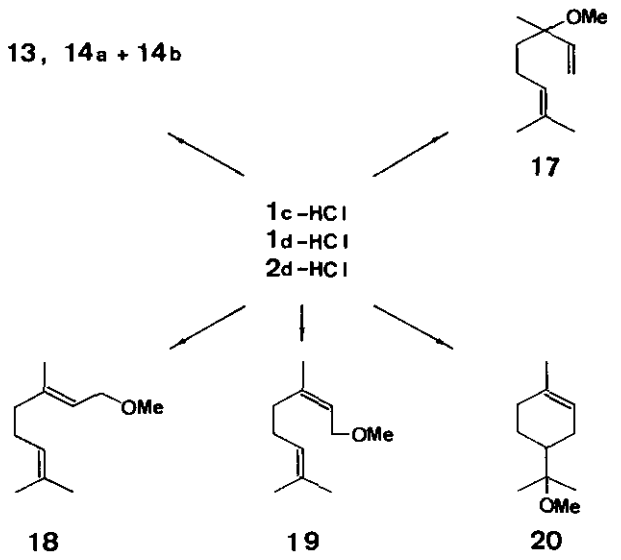
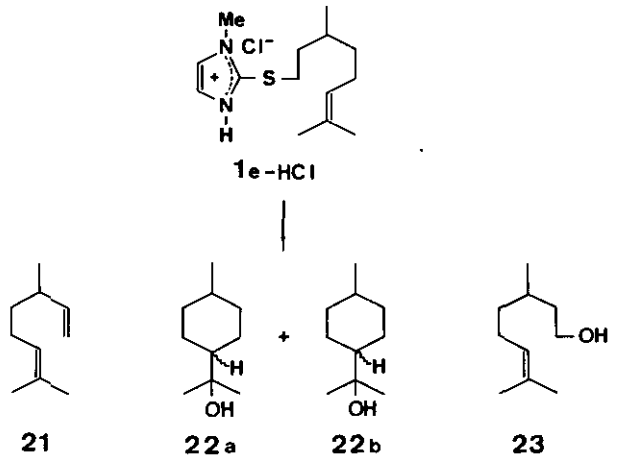


Table 2. Irradiation of 1c, 1d and 2d in acidic methanol

Run	Start. compd.	Product ratio						Total yield
		13	14	17	18	19	20	(%)
1	1c	40	10	27	21	-	-	52
2	1d	30	9	29	-	11	21	49
3	2d	17	5	31	-	19	29	45

Scheme 6



Irradiation of 2-geranylmercapto- (1c) and 2-nerylmercapto-1-methylimidazole (1d), and of 3-nerylmercapto-4-methyl-1,2,4-triazole (2d)[d] in acidic water gave mixtures of volatile products, separable by GC, and found to consist of myrcene (13), cis- (14a) and trans-ocimene (14b), linalool (15) and α-terpineol (16), in different ratios depending on the starting material as well as on the irradiation conditions (see Table 1).

On irradiation in acidic methanol, all three compounds 1c, 1d and 2d again gave products whose structures showed evidence of solvent participation, i.e. methoxy derivatives 17, 18, 19 and 20 ; as well as hydrocarbons 13, 14a and 14b ; in the relative amounts shown in Table 2.

Photolysis of 2-geranylmercapto- (3c) and 2-nerylmercapto-1,3-dimethylimidazolium iodide (3d)[d] in neutral aqueous solution gave the same volatile products as those obtained under acidic conditions from 1c and 1d, though at a lower reaction rate. Because of the difficulty in obtaining compounds 3c and 3d in pure form, the yields of their products could not be accurately determined.

The photolysis of 2-citronellylmercapto-1-methylimidazole (1e)[d] in acidic water was slow, giving a mixture of volatile products in ca 50 % yield. This consisted of a mixture of compound 21, and of alcohols 22a, 22b and 23 in the ratio, 9 : 3 : 2 : 1, together with about 10 % of unidentified products.

As a control measure, solutions of these azole derivatives were kept in the dark at room temperature and were found to be stable under these conditions for several days.

3. Structures of photoproducts. Products 13-16, 21 and 24 were identified by comparison with authentic specimens. Structure determination of other products was based on spectral and analytical data (see Experimental part).

Product 4, 5 and 6 are isomers of their precursors 1b and 2b, respectively, differing only in the position of the benzyl group; and their structures were easily determined from ^{1}H-NMR spectra in which 4, 5 and 6 showed two, one and no signals, respectively, due to the protons on the azole ring.

Compounds 17, 18, 19 and 20 were formulated as the methyl ethers of linalool, geraniol, nerol and α-terpineol, respectively, on the bases of spectral and analytical data. In each case the ^{1}H-NMR spectrum was very similar to that of the parent alcohol (except, of course, for the -OMe proton signal).

Two products obtained from the irradiation of 1a in acidic water were formulated as the diastereomeric alcohols 22a and 22b, and these were identical with the catalytic hydrogenation products of α-terpineol, although the relative stereochemistry of either has not been

determined as yet.

4. Discussion. In the photolysis of 1b and 2b in methanol, the formation of benzyl migration and debenzylation products (Scheme 2) indicates ca 50 % recombination between benzyl and thioazole radicals[e] - this presumably occurs via S-benzyl heterolytic bond fission. On the other hand, in the case of the corresponding N-protonated and N-alkylated salts (structure 7 in Scheme 3), one expects, instead, heterolytic S-benzyl bond cleavage (via path A), giving stable imidazoline-2-thione or triazoline-3-thiones (8) as one fragment and the reactive benzyl cation as the other. Indeed, the intervention of the latter and of its canonical form is indicated by the formation of the methyl ethers 10, 11 and 12 when 1b and 2b were photolyzed in acidic and 3b in neutral methanolic solution.

Photochemical benzyl cation formation has previously been demonstrated in the case of benzyl acetates[4], benzyl ammonium salts[5] and benzyl sulfonium salts[6]. In these cases the benzyl group was the only chromophore present, and hence bond fission must have been initiated by its excitation. In our present case of salts of benzylmercaptoazoles, however, it would be reasonable to expect excitation of both benzyl and thioazole chromophores[e] and this should facilitate heterolytic S-benzyl bond fission.

That a mechanism requiring the excitation of the thioazole chromophore might apply in the case where group R in 7 is alkyl and not benzyl was indicated by the photolysis of the acyclic monoterpene derivatives, 1c-e and 2c-d in acidic, and of 3c-d in neutral medium. The incorporation of hydroxyl and methoxyl groups to a considerable extent into the products (see runs 1,2,3 and 6 in Table 1, and runs 1,2 and 3 in Table 2) was clear evidence of intervention of carbocations in these reactions.

The fact that photolysis of 1c and 1d in acidic methanol gave geranyl methyl ether (18) and neryl methyl ether (19), respectively, in considerable ratios, whereas photolysis in acidic water gave only trace amounts of geraniol and nerol appears to be due to the relative nucleophilicity of these solvents.

The formation of hydrocarbons such as 13, 14 and 21 could be explained by radical intermediates, although an alternative path involving proton elimination from an intermediate cation is also conceivable. The latter alternative is supported by the results obtained from irradiation of 1c and 1d in acidic water, in which the former gave a higher hydrocarbon/alcohol ratio than the latter. Perhaps this can be explained by assuming that

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[e] Such Claisen-type rearrangement of a variety of 2-alkylmercapto-1-methylimidazoles are known to result from thermolysis of these compounds[7].

the geranyl cation generated from 1c, contrary to the neryl cation generated from 1d, is geometrically unable to cyclize to give product 16, and that instead proton elimination takes place leading to increased hydrocarbon formation.

In conclusion it has been shown that photosolvolytic cleavage of compound 7 type R-X, whose R can be a group such as benzyl, allyl and alkyl, is a feasible process when the leaving group X is the salt form of a group such as 1-methylimidazole-2-thio and 4-methyl-1,2,4-triazole-3-thio.

Although admittedly the data so far obtained are for a limited number of examples only, this type of reaction may constitute a useful method of generating carbocation which can be carried out under a variety of conditions.

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Experimental Part

General. - Melting points (M.p.) were taken using a Büchi apparatus (type Dr. Tottori) and are not corrected. - UV spectra were measured on a Perkin-Elmer apparatus (model 402) or on a Shimadzu apparatus (model UV-300), the maxima are given in nm (extinction ε). - IR spectra were measured on a Perkin-Elmer-spectrophotometer (model 297) or on a Japan Spectroscopic Co. apparatus (model IR-S) and recorded in cm^{-1}. Mass spectra were measured on a Hitachi-Perkin-Elmer RMU-6M instrument or on a Shimadzu LKB-9000 instrument and recorded in m/e (relative intensity). - ^{1}H-NMR spectra were measured on a Varian H-100 or XL-100, or on a JEOL FX-100 instrument (100MHz); chemical shifts are given in ppm (in δ) relative to TMS (= 0 ppm) as internal standard; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, coupling constant J = in Hz.

Thin layer chromatography was carried out on Merck DC- Fertigplatten , Kieselgel 60 F-254, and column chromatography on silicagel Merck (0.063 - 0.200 mm) or WAKO C-200. Gas chromatography (GC) was performed on a Shimadzu apparatus (model 4-APF) or on a Varian apparatus (model 90-P).

For irradiation, medium pressure mercury lamps QM 125, Meda-Licht AG, Basel (lamp A) or UM-452, Ushio Electric Inc., Tokyo (lamp B) using quartz immersion well. For irradiation on a preparative scale a "circulating thin film apparatus" was used in order to

avoid the adhesion of insoluble material to the surface of immersion well.

1. Preparation of 2-alkylmercapto-1-methylimidazoles (1b-e) and 3-alkylmercapto-4-methyl-1,2,4-triazoles (2b, d). - 2-Benzylmercapto-1-methylimidazole (1b). - 3.42 g (0.03 mol) of 2-mercapto-1-methylimidazole (1a) and 3.78 g (0.03 mol) of benzyl chloride were disolved in 10 ml of ethanol and the solution was stirred at room temperature overnight. After evapolation of solvent the hydrochloride of 1b obtained was treated with aq. sodium carbonate to liberate free 1b which was extracted with ethyl acetate. Usual work up gave an oil. - UV (EtOH) : 219 (13000), 256 (5900); IR (CCl_4) : 3120, 3097, 3070, 3040, 2950, 1490, 700; ^{1}H-NMR ($CDCl_3$) : 7.32-7.26 (m, 3 H on pheny), 7.18-7.12 (m, 2 H on phenyl and H-C(4 or 5)), 6.89 (br s, H-C(4 or 5), 4.17 (s, 2 H of benzyl), 3,25 (s, H_3C-N(1)); MS : 204 (49, M^+), 149 (62), 91 (100).

$C_{11}H_{12}N_2S$ Calc. C 64.49 H 5.92 N 13.72 % Found C 64.51 H 5.88 N 13.38 %

All the other 2-alkylmercapto-1-methylimidazoles (1c-e, 2b and 2d) were prepared in the same way.

2-Geranylmercapto-1-methylimidazole (1c)[f]. - Liquid; UV (EtOH) : 250 (5300); IR (CCl_4) : 3120, 2975, 2930, 1665; ^{1}H-NMR ($CDCl_3$) : 7.06 (d, J = 2.0, H-C(4 or 5)), 6.90 (d, J = 2.0, H-C(4 or 5)), 5.32 (br t, J = 8.0, H-C(1')), 5.06 (m, H-C(6')), 3.66 (d, J = 8.0, H_2-C(1')), 3.63 (s, H_3C-N(1)), 2.1-1.85 (m, 4H on C(4' and 5')), 1.71, 1.62 and 1.57 (3s, three CH_3); MS : 250 (2, M^+), 212 (6), 181 (31), 115 (100).

$C_{14}H_{22}N_2S$ Calc. C 67.17 H 8.86 N 11.19 % Found C 67.45 H 8.71 N 10.95 %

2-Nerylmercapto-1-methylimidazole (1d)[f]. - Liquid; UV (EtOH) : 250 (5500); IR (CCl_4) : 3110, 2970, 2930, 2860, 1660; ^{1}H-NMR ($CDCl_3$) : 7.05 (d, J = 2.0, H-C(4 or 5)), 6.90 (d, J = 2.0, H-C(4 or 5)), 5.34 (t, J = 8.0, H-C(2')), 5.08 (m, H-C(6')), 3.68 (d, J = 8.0, H_2-C(1')), 2.1-1.9 (m, 4H on C(4' and 5')), 1.74, 1.72 and 1.63 (3s, three CH_3); MS : 250 (3, M^+), 217 (4), 181 (26), 149 (10), 136 (5), 114 (96).

$C_{14}H_{22}N_2S$ Calc. C 67.17 H 8.86 N 11.19 % Found C 67.40 H 8.61 N 11.33 %

2-Citronellylmercapto-1-methylimidazole (1e)[f]. - Liquid; UV (EtOH) : 250 (4500); IR (CCl_4) : 3110, 2960, 2920, 2850, 1675; ^{1}H-NMR ($CDCl_3$) : 7.06 (d, J = 2.0, H-C(4 or 5)), 6.92 (d, J = 2.0, H-C(4 or 5)), 5.08 (t, J = 8.0, H-C(6')), 3.62 (s, H_3C-N(1)), 3:08 (m,

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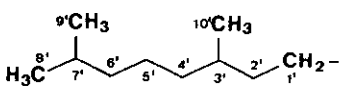
[f] Numbering of the carbons of the monoterpene moiety is given as shown below.



H_2-C(1')), 1.94 (m, H_2-C(5')), 1.68 and 1.58 (2s, H_3-C(8' and 9')), 1.6-1.1 (m, 5H on C(2', 3' and 4')), 0.91 (d, J = 8.0, H_3-C(10')); MS : 252 (16, M^+), 219 (3), 183 (7), 123 (25), 114 (100).

$C_{14}H_{24}N_2S$ Calc. C 66.63 H 9.59 N 11.10 % Found C 66.55 H 9.42 N 11.38 %

3-Benzylmercapto-4-methyl-1,2,4-triazole (2b). - M.p. 84-85° (from benzene/hexane); UV (EtOH) : 225 (8600), 250 (2000); IR ($CHCl_3$) : 3010, 1600, 1500; ^{1}H-NMR ($CDCl_3$) : 8.14 (s, H-C(5)), 7.32 (s, 5H on phenyl), 4.40 (s, 2H on benzylic carbon), 3.34 (s, H_3C-N(1)); MS : 205 (44, M^+), 190 (8), 170 (19), 91 (100).

$C_{10}H_{11}N_3S$ Calc. C 58.53 H 5.40 N 20.48 % Found C 58.50 H 5.35 N 20.33 %

3-Nerylmercapto-4-methyl-1,2,4-triazole (2d)[f]. - Liquid; UV (EtOH) : 250 (1900); IR (CCl_4) : 3110, 2980, 2925, 2840, 1660, 1510; ^{1}H-NMR ($CDCl_3$) : 8.16 (s, H-C(5)), 5.38 (t, J = 8.0, H-C(2')), 5.06 (m, H-C(6')), 3.87 (d, J = 8.0, H-C(5')), 3.60 (s, H_3C-N(1)), 2.1-1.9 (m, 4H on C(4' and 5')), 1.68, 1,65 and 1.60 (3s, H_3-C(8', 9' and 10')); MS : 251 (5, M^+), 218 (10), 136 (19), 116 (100).

$C_{13}H_{21}N_3S$ Calc. C 62.12 H 8.42 N 16.72 % Found C 62.44 H 8.50 N 16.48 %

2. Preparation of 2-benzylmercapto-1,3-dimethylimidazolium iodide (3b). - To 2.04 g (0.01 mol) of 1b in 5 ml of acetone was added 2.13 g (0.015 mol) of methyl iodide and the solution was left at 0 °C overnight. The product (pale yellow crystals) was collected by filtration and washed with acetone. - M.p. 207-210°; UV (EtOH) : 220 (20000), 264 (4400) shoulder; IR (CH_3CN) : 3150-2700, 1630; ^{1}H-NMR : 7.50 (s, H_2-C(4 and 5)), 7.4-7.2 (m, 3H on phenyl), 7.2-7.0 (m, 2H on phenyl), 4.18 (s, 2H on benzylic carbon), 3.62 (s, H_3C-N(1)); MS. : 218 (4, M^+-HI), 91 (100).

2-Geranylmercapto- (3c) and 2-nerylmercapto-1,3-dimethylimidazolium iodide (3d) were prepared in the same way as for 3b, but they could not be obtained in pure form and were used for irradiation in crude form.

3. Photolysis of 1b, 2b and 3b. - Photolysis of 1b. - 1) 600 mg of 1b in 100 ml of methanol was irradiated (lamp A, $\lambda > 235$ nm) for 5 h. After solvent removal the residue was chromatographed on silica to give 168 mg of 4 and 88 mg of 1a with the recovery of 125 mg of 1b. - 2) 600 mg of 1b in 0.1 N methanolic HCl was irradiated (lamp A, $\lambda > 235$ nm) for 5 h. The solvent and the volatile materials were distilled under reduced pressure. Column chromatography of the residue on silica afforded 55 mg of 4 and 153 mg of 1a with the recovery of 155 mg of 1b. Fractional distillation of the volatile materials gave a high boiling fraction (153 mg) which was composed of benzyl methyl ether (10) and o- (11) and

p-cresyl methyl ether (12) in a 55 : 0.2 : 0.6 ratio (determined by GC, 1.5 % PEG-6000).

1-Methyl-3-benzylimidazoline-2-thione (4). -M.p. 107-108° (from benzene/hexane); UV (EtOH) : 260 (15800); IR (CCl_4) : 3160, 3070, 2950, 1610, 1500; ^{1}H-NMR ($CDCl_3$) : 7.36 (m, 5H on phenyl), 5.90 (s, 2H on benzylic carbon), 3.67 (s, H_3C-N(1)); MS : 204 (64, M^+), 91 (100).

$C_{11}H_{12}N_2S$ Calc. C 64.69 H 5.92 N 13.72 % Found C64.61 H 5.95 N 13.56 %

- Photolysis of 2b. 1) 600 mg of 2b in 100 ml of methanol was irradiated (lamp B, $\lambda > 235$ nm) for 2.5 h. After solvent removel the residue was chromatographed on silica to give 210 mg of 5, 78 mg of 6 and 162 mg of 2a. 2) 600mg of 2b in 100 ml of 0.05 N methanolic HCl was irradiated (lamp B, $\lambda > 235$ nm) for 2 h. The solvent and volatile materials were distilled under reduced pressure. Column chromatography of the residue on silica afforded 25 mg of 5 and 178 mg of 2a with the recovery of 127 mg of 2b. Fractional distillation of the volatile materials gave a high boiling fraction (157 mg) which was composed of 10, 11 and 12 in a 53 : 0.3 : 0.3 ratio (determined by GC).

2-Benzyl-4-methyl-1,2,4-triazoline-2-thione (5). - M.p. 116-118° (from benzene); UV (EtOH) : 248 (7400); IR ($CHCl_3$) : 2900, 1545, 1480; ^{1}H-NMR ($CDCl_3$) : 7.71 (s, H-C(5)), 7.36 (m, 5H on phenyl), 5.39 (s, 2H on benzylic carbon), 3.59(s, H_3C-N(1)); MS : 205 (91, M^+), 91 (100).

$C_{10}H_{11}N_3S$ Calc. C 58.53 H 5.40 N 20.48 % Found C 58.50 H 5.31 N 20.53 %

4-Methyl-5-benzyl-3-mercapto-1,2,4-triazole (6). - M.p. 145-148° (from benzene/acetone); UV (EtOH) : 240 (12000); IR ($CHCl_3$) : 3480, 3400-2400 (broad), 3000, 1575; ^{1}H-NMR ($CDCl_3$) : 11.9 (br. s, H-S), 7.30 (m, 5H on phenyl), 4.20 (s, 2H on benzylic carbon), 3.35 (s, H_3C-N(1)); MS : 205 (85, M^+), 172 (11), 91 (100).

$C_{10}H_{11}N_3S$ Calc. C 58.53 H 5.40 N 20.48 % Found C 58.30 H 5.23 N 20.61 %

Photolysis of 3b. - 1 g of 3b in 100 ml of methanol was irradiated (lamp A, $\lambda > 235$ nm) for 5 h in the presence of solid sodium bisulfite. The solvent and volatile materials were distilled under reduced pressure. Column chromatography of the residue on silica afforded 156 mg of 8 (Z = CH, R' = CH_3). Conversion (%) of 3b could not be determined. After careful removal of the solvent from the distillate by evaporation the residual oil was analyzed by GC which showed the presence of 10.

1,3-Dimethylimidazoline-2-thione (8, Z = CH, R' = CH_3). - M.p. 128° (from benzene/acetone); UV (EtOH) : 261 (17000); IR ($CHCl_3$) : 3175, 3145, 2950, 1575; ^{1}H-NMR ($CDCl_3$) : 6.68 (s, H_2-C(4 and 5)), 3.63 (s, H_3C-N(1)); MS : 128 (100, M^+).

$C_5H_8N_2S$ Calc. C 46.87 H 6.29 N 21.87 % Found C 47.79 H 6.23 N 21.88 %

4. Photolysis of 1c, 1d and 2d in acidic water. - Method a : 2.5 g of 1c, 1d or 2d in 500 ml of 0.05 N aq. HCl was irradiated (lamp A, $\lambda > 235$ nm) for 5 h using a "circulating thin film apparatus". The suspension formed was extracted with pentane. The extract was washed with water and dried over sodium sulfate. The residue was distilled under reduced pressure to give a mixture of volatile products.

- Photolysis of 1c. - 1c gave 790 mg of a mixture containing myrcene (13), cis- (14a) and trans-ocimene (14b), linalool (15), and α-terpineol (16) in a ratio of 40 : 10 : 45 : 5 (determined by GC, 1.5 % PEG-6000). These products were isolated by preparative GC (15 % PEG-6000) and identified with authentic specimens. 14a and 14b could not be separated and they were determined in a mixture.

- Photolysis of 1d. - 1d gave 890 mg of a mixture containing 13, 14a and 14b, 15 and 16 in a ratio 21 : 5 : 37 : 37.

- Photolysis of 2d. - 2d gave 930 mg of a mixture containing 13, 14a and 14b, 15 and 16 in a ratio of 8 : 2 : 23 : 67.

- Method b : 50 mg of 1d either in 10 ml of 0.05 N aq. HCl or in 10 ml of a 1 : 1 mixture of glycerol and 0.1 N aq. HCl in a quartz tube (inner diameter 10 mm) was irradiated externally (lamp A, $\lambda > 235$ nm) for 2h. For low temperature photolysis the tube was immersed in a quartz Dewar vessel filled with cooling agent. The suspension formed was extracted with pentane, the extract was washed with water and dried over sodium sulfate. The residue after evaporation of pentane was again distilled with pentane to 0.5 ml of total volume and was analyzed by GC (1.5 % PEG-6000) to determine products yield. The results are shown in Table 1.

5. Photolysis of 1c, 1d and 2d in acidic methanol. - 2.5 g of 1c, 1d or 2d in 500 ml of 0.1 N methanolic HCl was irradiated (lamp B, $\lambda > 235$ nm) for 5 h using a "circulating thin film apparatus". After neutralization of the solution with aq. sodium bicarbonate, methanol was removed at atmospheric pressure and to the concentrate was added 200 ml of 5 % aq. HCl. The suspension formed was extracted with pentane. The extract was worked up as in method a in the photolysis in water.

- Photolysis of 1c. - 1c gave 750 mg of a mixture containing 13, 14, 17, 18 and 20 in a ratio of 40 : 10 : 27 : 21 : 0.7.

3-Methoxy-3,7-dimethylocta-1,6-diene (linalyl methyl ether) (17). - Liquid; IR (CCl_4) : 3090, 2980, 2940, 2830, 1640; ^{1}H-NMR (CCl_4) : 5.84-5.52 (m, H-C(2)), 5.13 (br. s, H-C(6)), 5.0 (d, J = 8.0, H-C(1)), 4.8 (d, J = 8.0, H-C(1)), 3.03 (s, H_3C-O), 2.1-1.7 (m, H_2-C(5)), 1.64 and 1.57 (2s, H_3C-C(7 and 8)), 1.52-1.32 (m, H_2-C(4)), 1.15 (s, H_3C-C(3)); MS : 168

(1, M^+), 153 (3), 136 (20), 85 (100).

$C_{11}H_{20}O$ Calc. C 78.51 H 11.98 % Found C 78.73 H 12.04 %

1-Methoxy-3,7-dimethylocta-2-trans-6-diene (geranyl methyl ether) (18). - Liquid; IR (CCl_4) : 2965, 2920, 1670; ^{1}H-NMR ($CDCl_3$) : 5.35 (br. t, J = 7.0, H-C(2)), 5.10 (m, H-C(6)), 3.94 (d, J = 7.0, H-C(1)), 3.33 (s, H_3C-O), 2.15-2.01 (m, 4H on C(4 or 5)), 1.68 and 1.60 (2s and 1s, three CH_3); MS : 168 (2, M^+), 153 (1), 136 (6), 69 (100).

$C_{11}H_{20}O$ Calc. C 78.51 H 11.98 % Found C 78.55 H 12.21 %

1-Methyl-4-(2'-methoxyprop-2'-yl)cyclohex-1-ene (α-terpinyl methyl ether) (20). - Liquid; IR (CCl_4) : 2975, 2930, 2900, 2830, 1450, 1380, 1365; 1190, 1160, 1140, 1085, 1075, 920; ^{1}H-NMR (CCl_4) : 5.3 (m, H-C(2)), 3.07 (s, H_3C-O), 2.1-1.5 (m, 7H), 1.60 (s, H_3C-C(1)), 1.02 (2s, H_3-C(2')); MS : 168 (2, M^+), 153 (2), 136 (29), 73 (100).

$C_{11}H_{20}O$ Calc. C 78.51 H 11.98 % Found C 78.66 H 11.75 %

Photolysis of 1d. - 1d gave 780 mg of a mixture containing 13, 14, 17, 19 and 20 in a ratio of 30 : 9 : 29 : 11 : 21. Formation of a trace amount of 18 was also observed.

1-Methyl-3,7-dimethylocta-2-cis-6-diene (neryl methyl ether) (19). - Liquid; IR (CCl_4) : 2965, 2920, 2860, 2820, 1670; ^{1}H-NMR (CCl_4) : 5.23 (br.t, J = 8.0, H-C(2)), 5.04 (m, H-C(6)), 3.77 (d, J = 8.0, H_2-C(1)), 3.16 (s, H_3C-O), 2.1-1.9 (m, 4H on C(4 and 5)), 1.71, 1.65 and 1.58 (3s, three CH_3); MS : 168 (13, M^+), 153 (4), 136 (14), 69 (100).

$C_{11}H_{20}O$ Calc. C 78.51 H 11.89 % Found C 78.69 H 11.69 %

Photolysis of 2d. - 2d gave 810 mg of a mixture containing 13, 14, 17, 19 and 20 in a ratio of 17 : 5 : 31 : 19 : 29. Formation of a trace amount of 18 was also observed.

6. Photolysis of 3c and 3d. - 3 g of 3c or 3d in 500 ml of water was irradiated (lamp A, $\lambda > 235$ nm). To the solution 5 g of sodium thiosulfate was added in order to reduce iodine formed during the photolysis. The reaction proceeded slower than the cases of 1c and 1d in acidic water. The suspension formed was extracted with pentane, and the extract was worked up as in method a in the photolysis of 1c, 1d or 2d in acidic water . The product ratio was analyzed by GC (15 % SE-52). Photolysis of 3c and 3d gave a mixture of 13, 14a and 14b, 15 and 16 in 36 : 15 : 41 : 8 and in 32 : 23 : 23 : 22 ratio. The total yield was low (less than 20 %).

7. Photolysis of 1e. - 2.5 g of 1e in 500 ml of aq. 0.05 N HCl was irradiated (lamp B, $\lambda > 235$ nm) for 7 h using a "circulating thin film apparatus". The suspension formed was extracted with pentane and the extract was worked up as in other cases, to give ca 700 mg if a mixture of the product containing citronellene (21), 22a, 22b and citronellol

(23) in aratio of 9 : 3 : 2 : 1, with about 2 % of unidentified products.

1-Methyl-4-(2'-hydroxyprop-2'-yl)cyclohexane (22a). - Liquid; IR (CCl_4) : 2920, 2850; ^{1}H-NMR ($CDCl_3$) : 1.85-1.20 (m, 10H), 1.16 (2s, two H_3C-C(2')), 0.87 (d, J = 8.0, H_3C-C(1)); MS : 156 (1, M^+), 141 (4), 123 (10), 59 (100).

$C_{10}H_{20}O$ Calc. C 76.86 H 12.90 % Found C 77.08 H 12.99 %

22b. - Liquid; IR (CCl_4) : 2920, 2840, 1475, 1445, 1380, 1365, 1160, 1140, 910; ^{1}H-NMR : 1.6-1.45 (m, 6H), 1.3-1.2 (m, 4H), 1.17 (2s, two H_3C-C(2')), 0.96 (d, J = 8.0, H_3C-C(1)); MS : 156 (1, M^+), 141 (2), 123 (4), 69 (100).

$C_{10}H_{20}O$ Calc. C 76.86 H 12.90 % Found C 76.92 H 12.79 %

22a and 22b were obtained also by catalytic hydrogenation of α-terpineol over 10 % palladium on charcoal.

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