59. Photochemische Reaktionen

108. Mitteilung [1]

Photochemistry of *N*-Acylazoles. VI[1]). Photoreactivities of 1-Acyl-1,2,4-triazoles and of 2-Acyltetrazoles

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(23.I.80)

Summary

Contrary to the findings in the photolysis of *N*-acylimidazoles [2] irradiation of 1-acyl-1,2,4-triazoles afforded no photo-*Fries* product, but instead products formed *via* the corresponding acyl radicals and aldehydes. Photolysis of 2-acyltetrazoles gave in part the same products as those obtained from the irradiation of the corresponding acyl-triazoles as well as 2-alkyl-1,3,4-oxadiazoles. *N*-Acyltetrazoles didn't give any photo-*Fries* product neither.

Previously we have reported on the photochemical N→C acyl migration reaction shown by a variety of *N*(1)-acylimidazoles, as well as on their subsequent photoreactions affording *Norrish* Type II elimination products and/or cyclobutanol derivatives [2]. The former reaction constitutes a facile route to various 2- and 4(5)-substituted imidazoles; and the latter reactions provide some useful methods of degradation and of modification of certain carboxylic acid derivatives.

Having studied 1-, 2- and 4(5)-acylimidazoles in this regard, we turned our attention to the photochemistry of other *N*-acylazoles, and we now describe the photoreactions of some *N*(1)-acyl-1,2,4-triazoles and *N*(2)-acyltetrazoles (s. *Scheme 1*).

Results. – A. N-*Acyltriazoles.* Irradiation of 1-acetyl-1,2,4-triazole (**1**; *Scheme 1*) using either a low pressure mercury lamp or a medium pressure mercury lamp with a quartz immersion well (254 nm light and >235 nm light, respectively) gave no acyl rearrangement product even though the starting material was consumed (as followed by gas chromatography).

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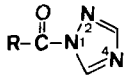
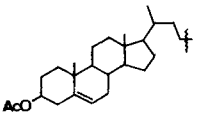
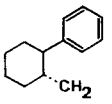
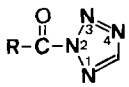
Scheme 1



1 R: CH_3 **10** R: 

2 R: $C_{17}H_{35}$ **17** R: 

7 R: $C_{14}H_{29}$-CH(CH$_3$)-CH_2CH_2 **29** R: 

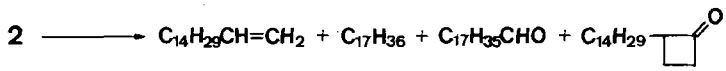


39 R: CH_3 **42** R: 

45 R: $C_{17}H_{35}$

Irradiation of 1-stearoyl-1,2,4-triazole (**2**; *Scheme 1*) with 254 nm light likewise gave no acyl migration product, but instead led to the formation of 1-hexadecene (**3**), heptadecane (**4**), octadecanal (**5**) and 2-tetradecylcyclobutanone (**6**; s. *Scheme 2*). Using >235 nm light only the hydrocarbons **3** and **4** were produced. The yields of the products of these irradiations are shown in *Table 1*.

Scheme 2



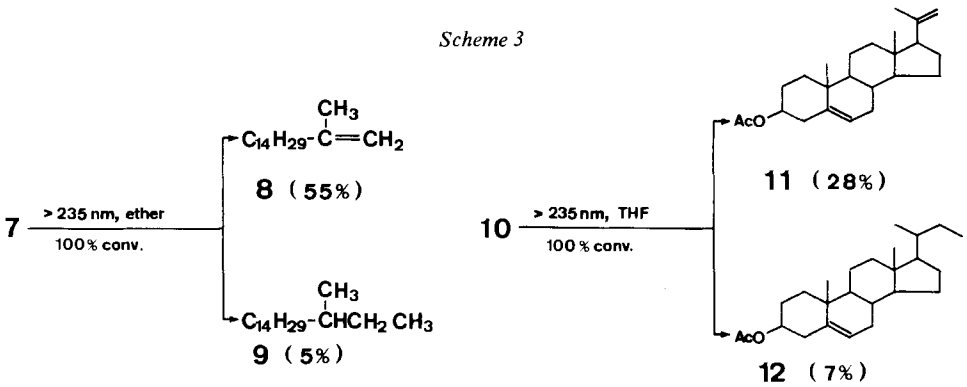
1-(4-Methylstearoyl)-1,2,4-triazole (**7**; *Scheme 1*), possessing a tertiary hydrogen atom in γ-position to the carbonyl group, was also irradiated, to compare its behaviour with the one of the corresponding *N*-acylimidazole [2b]; the yields of the hydrocarbons **8** and **9** were found to be 55 and 5%, respectively (s. *Scheme 3*). On the other hand, irradiation of 1-(3-acetoxy-5-cholen-24-oyl)-1,2,4-triazole (**10**; *Scheme 1*), with a tertiary γ-hydrogen atom too, gave side chain fragmentation product **11**, albeit in unexpected low yield (28%), together with product **12** (7%; s. *Scheme 3*).

Table 1. *Yields [%] of products from* **2**[a])

	254 nm ether (46% conv.)	254 nm ether (91% conv.)	>235 nm ether (100% conv.)
3	7.0 (15.0)	17.0 (19.0)	36.0 (36.0)
4	1.5 (3.5)	4.0 (4.5)	8.0 (8.0)
5	16.0 (35.0)	19.0 (21.0)	–
6	1.5 (3.5)	2.8 (3.0)	–

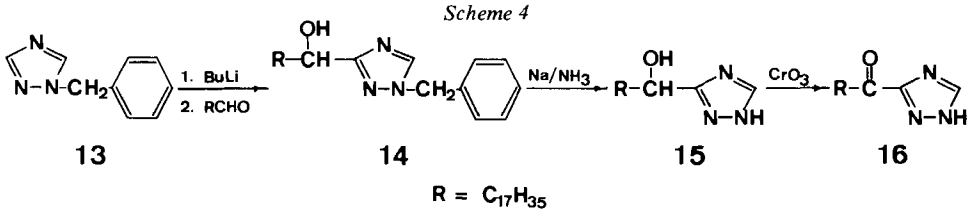
[a]) The values in brackets are the yields calculated from converted **2**.

Scheme 3



The absence of a *C*-acyltriazole among the photoproducts of the above *N*-acyltriazoles prompted us to prepare such a so far unknown *C*-acyl compounds in order to study its photochemical properties. Thus, 3(5)-stearoyl-1,2,4-triazole (**16**) was synthesized as shown in *Scheme 4*, the hydroxyalkylation **13** → **14** being a known procedure for the 2-hydroxyalkylation of 1-alkylimidazoles [3]. On irradiation with > 235 nm light in THF **16** was converted at a rate about six times as fast as the corresponding 2-stearoylimidazole, leading to the Type II fragmentation product **3** in 62% yield. This yield was raised to 70% by irradiating **16** in ethanol using a medium pressure mercury lamp with a pyrex immersion well (> 280 nm light).

Scheme 4



Scheme 5

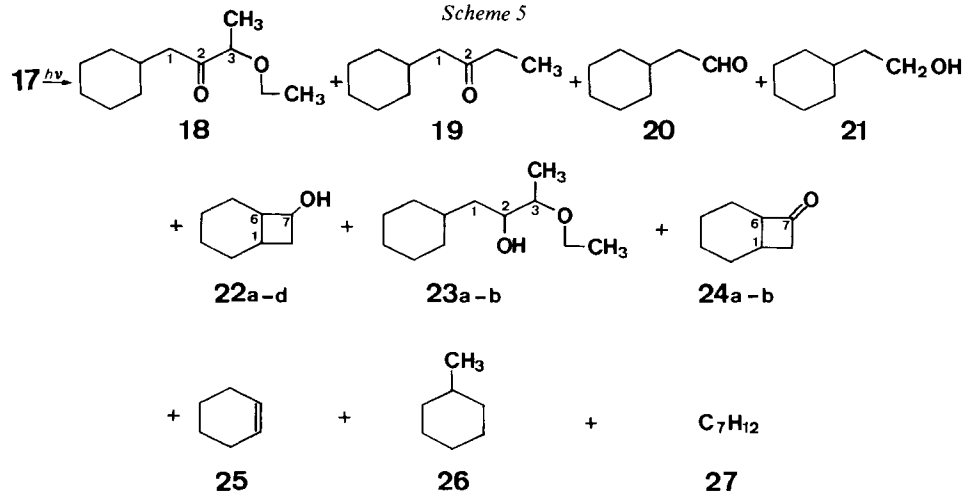


Table 2. *Yields [%] of products from* **17** *and* **20**

Starting material	Product									
	18	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**
17	2.0	8.0	0.3	4.3	6.4	9.5	9.5	12.8	2.0	8.0
20				4.5	13.4	20.8		19.5	4.6	11.6

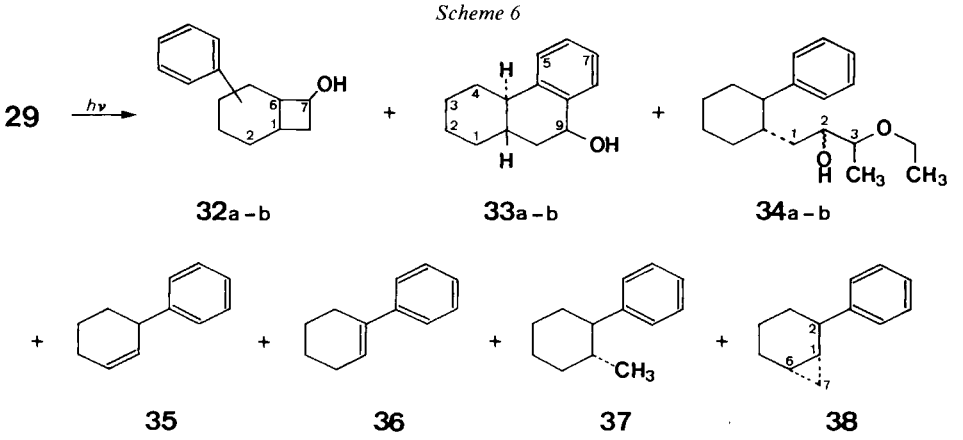
Since there is an obvious difference in the photochemical behaviour of *N*-acylimidazoles and *N*-acyltriazoles, it was decided to study the photoreactivity of the latter in more detail. Irradiation of 1-cyclohexylacetyl-1,2,4-triazole (**17**; *Scheme 1*) with >235 nm light in ether gave a complex mixture of the product **18**–**27** (s. *Scheme 5* and *Table 2*). Among the four possible stereoisomers **22a**–**22d**, **22a** and **22b** were isolated in pure form and **22c** and **22d** were obtained as a mixture. The ratio of these three fractions was found to be 4:3:3.

The diastereomers **23a** and **23b** were formed in a 10:7 ratio and each isolated in pure form. The *cis*/*trans* isomers **24a** and **24b** were obtained as a mixture.

The occasional isolation of aldehydes (*e.g.* **5** from **2**, **20** from **17**, and other aldehydes in unpublished irradiations) suggested the intermediacy of aldehydes in the formation of some of the products observed in the photolysis of *N*-acyltriazoles. Indeed, on irradiation of cyclohexylacetaldehyde (**20**) compounds **21**–**23**, and **25**–**27**, all photoproducts of **17**, were produced (s. *Table 2*). In this case compounds **22a**–**d** were each isolated in pure form, and their formation ratio was about 5.0:4.1:2.5:1.8. The ratio of **23a** and **23b** was about 9:8[4]).

Similar experiments were carried out with 1-(*trans*-2-phenylcyclohexyl)acetyl-1,2,4-triazole (**29**; *Scheme 1*) and (*trans*-2-phenylcyclohexyl)acetaldehyde (**31**; *cf.* below, *Scheme 8*). Irradiation of **29** with >235 nm light in ether gave the products **32**–**38** (s. *Scheme 6* and *Table 3*). The 7-epimers **32a** and **32b**, formed in a 2:3 ratio, were each isolated in pure form. The 9-epimers **33a** and **33b** were obtained as a 1:1 mixture (determined by GC.), and the diastereomers **34a** and **34b**

Scheme 6



[4]) Irradiation of **20** in pentane and in benzene with >235 nm light yielded the mixtures of **22a**–**d** in 34 and 37% yield, respectively.

Table 3. *Yields [%] of products from* **29** *and* **31**

Starting material	Product						
	32	**33**	**34**	**35**	**36**	**37**	**38**
29	9.6	3.7	11.8	4.9	1.4	3.1	16.6
31	10.6	5.9	17.4	15.0	17.2	0.8	

were formed in a 9:4 ratio and each isolated in pure form. Under the same conditions aldehyde **31** gave the expected products **32**–**37** (s. *Table 3*) with the ratios **32a/32b** = 1:1, **33a/33b** = 2:1 and **34a/34b** = 2:1.

B. *N-Acyltetrazoles.* Irradiation of 2-acetyltetrazole (**39**; *Scheme 1*) with >235 nm light gave again no N→C acyl migration product, but 2-methyl-1,3,4-oxadiazole (**40**) as well as one of two possible (1-ethoxyethyl)tetrazoles (**41**) in 16 and 3.5% yield, respectively (s. *Scheme 7*).

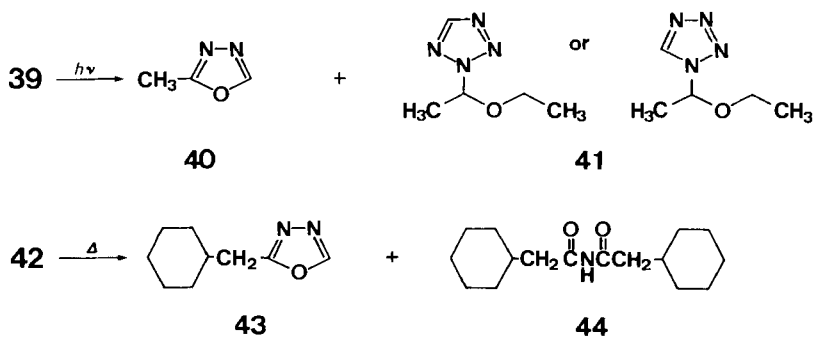
The photoreactivity of *N*(2)-acyltetrazoles as compared with those of *N*-acylimidazoles and *N*-acyltriazoles, emerged in more detail on irradiating 2-(cyclohexylacetyl)tetrazole (**42**; *Scheme 1*), which (in ether) gave compounds **18** (1.5%), **22a–d** (1.8%), **23a/23b** (2.9%), **24a/24b** (2.2%), **25** (13%), **26** (2.5%), **27** (3.4%), **41** (0.3%) and 2-(cyclohexylmethyl)-1,3,4-oxadiazole (**43**; 19.2%).

Since the thermal formation of various 2,5-disubstituted 1,3,4-oxadiazoles from 5-substituted 2-acyltetrazoles has been reported previously [4], compounds **39** and **42** were pyrolyzed in refluxing toluene giving **40** (60%), and **43** (51%) and 2,2′-dicyclohexyldiacetamide (**44**, 12%), respectively.

On irradiation of 2-stearoyltetrazole (**45**; *Scheme 1*) Type II fragmentation occurred to give **3** in only 16% yield, *i.e.* much less than from the corresponding *N*-acylimidazole [2b] and -triazole. In this irradiation the concurrent production of **4** (3.5%) and **6** (1.7%) was also observed, but not the formation of the 1,3,4-oxadiazole derivative.

The photochemical behaviour of 1-acylpyrazoles and of 1-acylbenzimidazoles has been studied. The former appeared to give some of the expected acyl migration product, but the reaction proceeded very slowly, and benzimidazole derivatives were found to be rather stable. 1-Acylpyrroles are known to show photochemical N→C acyl migration [5], but the rearranged product was found to be inert to irradiation with >280 nm light.

Scheme 7



Structure of products. – The structure assignments of the photoproducts obtained from the above reactions are essentially based on their spectroscopic data as well as (for volatile compounds) on their gas chromatographic behaviour.

Products **3**–**8**, **11**, **20**, **21**, **25** and **26** were identified by comparison with authentic samples (spectral and chromatographic comparison; for **6** s. [2c], for **8** and **11** s. [2b]). Spectral and analytical data of **9** and **12** are in agreement with the proposed structures (see exper. part).

Compound **18** was correlated with both **23a** and **23b** by chromic acid oxidation of epimeric alcohols.

Concerning the configuration of the four bicyclo[4.2.0]octan-7-ols **22a**–**d**, the relationships of H–C(1) to H–C(6) and H–C(6) to H–C(7) were tentatively assigned as *trans* and *trans*, *trans* and *cis*, *cis* and *trans*, and *cis* and *cis*, respectively, by comparing their ^{1}H-NMR. spectra and their chromatographic behaviour to the reported data [6] (s. exper. part). Moreover, the epimeric pairs **22a/22b** and **22c/22d**, were correlated to each other by chromic acid oxidation giving the same cyclobutanones **24a** and **24b**, respectively.

trans-Bicyclo[4.2.0]octan-7-one (**24a**) has not been reported, and its IR. spectrum exhibits a broad carbonyl band at 1780 cm^{-1} with many shoulders, whereas the *cis*-isomer **24b** possesses a sharp band at 1780 cm^{-1} (s. also [6]).

The alcohols **32a** and **32b** were shown to be epimeric, since oxidation gave the same cyclobutanone **48**. However, the position of the phenyl substituent as well as the configuration remain unknown. Mechanistic considerations suggest the phenyl substitution to be at C(2) or C(6) (s. discussion).

The mixture **33a/33b** was oxidized to a ketone which was identified as *trans*-1,2,3,4,4a,10a-hexahydro-9(10*H*)-phenanthrone (**52**) by comparison of its ^{1}H-NMR. spectrum with reported data [7].

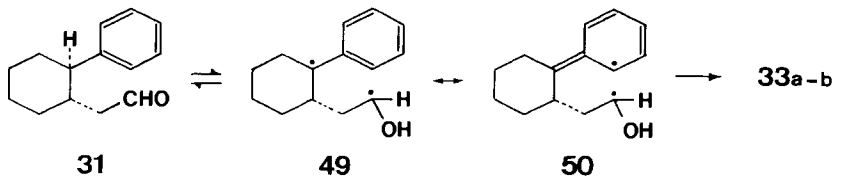
The diastereomers **34a** and **34b** were converted to the same ketone **53** (s. exper. part). Their *trans* configuration at the cyclohexane moiety was deduced from the configurations of their precursors, **29** and **31**.

The spectroscopic and analytical data of **35**–**38** are in accord with the proposed structures and in good agreement with reported data (for **35** and **36** s. [8], for **37** s. [9], and for **38** s. [10]).

The spectroscopic properties of **40** were compared to the reported data [11], and those of **43** were compared with the data of **40**. The ^{1}H-NMR. spectrum of **41** exhibits a one-proton singlet at 8.38 ppm and the signal pattern due to the 1-ethoxyethyl moiety. This fact, together with the other spectral and analytical data, suggest that the tetrazole ring is substituted by the 1-ethoxyethyl group at one of the N-atoms (**41**).

Discussion. – It is now clear that 1-acyl-1,2,4-triazoles behave differently from 1-acylimidazoles on irradiation. Indeed, no N→C acyl migration was observed, but a number of products without the triazole moiety were formed. Irradiation of the *N*-acyltriazoles **2** and **17** led to the aldehydes **5** and **20**, respectively, in varying amounts depending on the conditions; their yield (based on converted starting material), was found to be higher at lower conversion of starting material, *i.e.* at early stages of the photolysis. On the other hand it was demonstrated in the

Scheme 8



irradiations of the *N*-acyltriazoles **17** and **29** that many of the photoproducts were also photoproducts of the aldehydes **20** and **31**, respectively (see *Tables 2* and *3*). These facts indicate the important role of the aldehydes as intermediates in the photolysis of *N*-acyltriazoles.

The structure of ketone **18** suggests it to be the coupling product of a cyclohexylacetyl radical, formed from **17** by a photochemical CO,N-bond fission, with an 1-ethoxyethyl radical generated from the solvent (ether). This mechanistic pathway is partly supported by the fact that **18** was not produced on irradiation of aldehyde **20**. Ketone **19** could presumably originate from **18** by a *Norrish* Type II elimination.

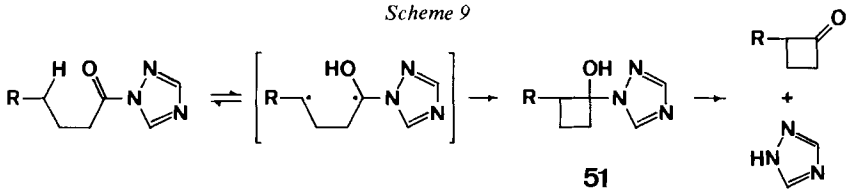
In the alcohols **32a** and **32b** the position of the phenyl substituent could not be determined; however, assuming a mechanism of formation which involves γ-hydrogen abstraction by the carbonyl group the position of the phenyl group is restricted to C(2) or C(6).

The pathway leading to products **33a** and **33b** from **31** can be assumed to have a biradical intermediate **50**, the mesomeric form of another biradical intermediate **49**, which could arise from **31** by an intramolecular hydrogen abstraction by the carbonyl group as shown in *Scheme 8*. Thus, we suggest the formation of **33a** and **33b** in the irradiation of **29** to proceed *via* an aldehyde.

It is of interest to consider the mechanism leading to cyclobutanone derivatives **6** and **24a/24b** by irradiation of **2** and **17**, respectively[5]). One possible route may involve intramolecular hydrogen abstraction by the acyl carbonyl group of 1-acyltriazoles followed by cyclization to give unstable 1-(1-triazolyl)cyclobutanol derivatives such as **51** (*Scheme 9*) which might be expected to decompose very easily into cyclobutanones and triazole. However, attempts to confirm such a mechanism have so far been unsuccessful.

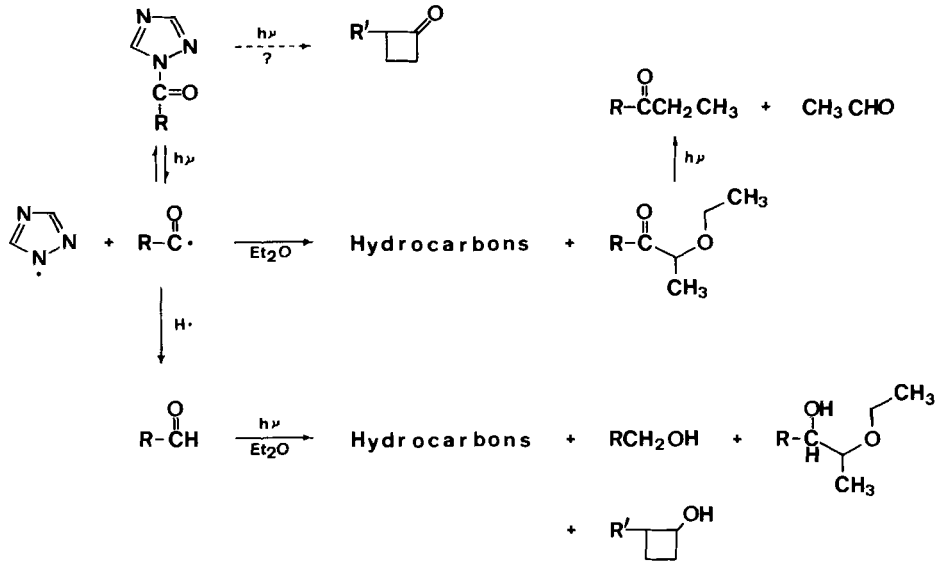
A further possibility of cyclobutanone formation, the photochemical oxidation of cyclobutanol derivatives by radicals generated in this process, was also examined. Thus, a mixture of **22a–d** was irradiated in ether in the presence of

Scheme 9



[5]) On irradiation **29** also occasionally gave the corresponding cyclobutanone derivative (IR. evidence), but it was not obtained pure enough for complete characterization.

Scheme 10



1-acyl-1,2,4-triazole (**1**), a mixture in which acetyl, triazolyl and 1-ethoxyethyl radicals might be expected to be produced. The cyclobutanols **22a–d** were, however, recovered unchanged.

Most of the hydrocarbons produced in the irradiation of *N*-acyltriazoles might arise from intermediate aldehydes by *Norrish* Type I and Type II processes, but products such as **4**, **9**, **12**, **26**, **27**, and **37** as well as **38** might also have been formed by decarbonylation of the respective intermediate acyl radicals (s. *Scheme 10*).

Since the cyclopropane derivative **38**, the product from **29**, was not produced by irradiation of aldehyde **31**, a (2-phenylcyclohexyl)methyl radical derived from a (2-phenylcyclohexyl)acetyl radical might be an intermediate. The formation of **38** *via* a 3-phenylcycloheptene seems to be a likely mechanism [10].

The suggestive routes for product formation in the photolysis of 1-acyl-1,2,4-triazoles are summarized in *Scheme 10*.

The reaction mode of 2-acyltetrazoles on irradiation appears to be partially the same as that of 1-acyl-1,2,4-triazoles, but the former undergoes an additional reaction leading to 1,3,4-oxadiazole derivatives. The corresponding mechanistic path can be considered to be the same as that of the thermal transformation of 3-substituted 2-acyltetrazoles which involves N_2-elimination followed by an intramolecular 1,3-dipolar addition [4].

As we have so far demonstrated there are marked differences in the photoreactivities of 1-acylpyrroles, 1-acylimidazoles, 1-acyl-1,2,4-triazoles and 2-acyltetrazoles: The former two can undergo efficient photo-*Fries* type rearrangements leading to their *C*-acyl derivatives, but not the latter two. The difference may be due to different electron densities on the C-atoms of the respective intermediate azolyl radicals; in triazolyl and tetrazolyl radicals the electron density on the C-

atoms should conceivably be too low to enable them to couple with their counterparts (acyl radicals)[6]).

Financial support by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and *Ciba-Geigy AG*, Basel, are gratefully acknowledged. The authors wish to thank Prof. *H.J. Eli Loewenthal*, Israel, Institute of Technology, Haifa, Israel, for his helpful advice in the preparation of the manuscript.

Experimental Part

General. S. [2c]. Columns used for GLC. were 5% SE-30 on *Chromosorb* W (60/80 AW/DMCS) and 20% *Carbowax* 20M (60/80 AW/DMCS). RT. = room temperature.

Preparation of the 1-acyl-1,2,4-triazoles 1, 2, 7, 10, 17 and 29, and of the 2-acyltetrazoles 39, 42 and 45. – *1-Acetyl-1,2,4-triazole* (**1**). To 3.5 g (0.05 mol) of triazole and 4.1 g (0.05 mol) of 1-methylimidazole in 150 ml of dry benzene were added 4 g (0.05 mol) of acetyl chloride in 50 ml of dry benzene. The mixture was stirred for 48 h at RT. After filtration of 1-methylimidazole hydrochloride the filtrate was evaporated i.V. to give an oily residue (about 1 g) which solidified on standing in the refrigerator. Sublimation i.HV. of the solid gave crystals, m.p. 37–39° ([13]: 40–42°). – UV. (THF): 224 (6700). – IR. (CCl_4): 3500*w*, 3140*w*, 1763*s*, 1510*m*, 1390*s*, 1380*s*, 1367*s*, 1280*s*, 1245*m*, 1205*s*, 1130*m*, 1098*w*, 1037*w*, 1000*w*, 950*s*, 875*m*. – ^{1}H-NMR. ($CDCl_3$): 8.85 (*s*, H–C(5)); 8.02 (*s*, H–C(3)); 2.74 (*s*, CH_3CO). – MS.: 111 (M^+, $C_4H_5N_3O$, 21), 83 (24), 70 (26), 60 (3), 56 (1), 43 (*100*).

All the other 1-acyl-1,2,4-triazoles were prepared in the same way as **1** from the corresponding acid chlorid (obtained from the respective acid with thionyl chloride).

1-Stearoyl-1,2,4-triazole (**2**): m.p. 74–75° (from acetonitrile). – UV. (THF): 227 (7600). – IR. (CCl_4): 3140*w*, 2925*s*, 2855*s*, 1757*s*, 1510*w*, 1470*m*, 1390*s*, 1380*s*, 1278*s*, 1182*s*, 1120*m*, 951*m*, 875*w*. – ^{1}H-NMR. ($CDCl_3$): 8.86 (*s*, H–C(5)); 7.99 (*s*, H–C(3)); 3.12 (*t*, J = 7.0, CH_2CO); 1.81 (*m*, CH_2CH_2CO); 1.60–1.10 (*m*, 28 H); 0.88 (*t*, J = 6.0, terminal CH_3). – MS.: 335 (M^+, $C_{20}H_{37}N_3O$, 2), 334 (2), 318 (1), 307 (1), 306 (1), 292 (1), 278 (1), 267 (8), 250 (1), 238 (1), 237 (1), 236 (1), 224 (1), 223 (1), 222 (1), 210 (1), 196 (1), 182 (1), 167 (2), 149 (3), 138 (2), 111 (7), 98 (20), 84 (13), 70 (*100*), 57 (24), 55 (24), 43 (22).

$C_{20}H_{37}N_3O$ (335.52) Calc. C 71.59 H 11.12 N 12.52% Found C 71.54 H 11.08 N 12.51%

1-(4'-Methylstearoyl)-1,2,4-triazole (**7**): m.p. 46–47° (from acetonitrile). – UV. (THF): 225 (7500). – IR. (CCl_4): 3140*w*, 2920*s*, 2850*s*, 1753*s*, 1510*m*, 1467*m*, 1390*s*, 1375*s*, 1277*s*, 1180*s*, 1120*s*, 952*m*, 942*m*, 875*m*, 663*m*. – ^{1}H-NMR. ($CDCl_3$): 8.86 (*s*, H–C(5)); 8.00 (*s*, H–C(3)); 3.12 (*t*, J = 7.0, CH_2CO); 1.99–1.62 (*m*, CH_2CH_2CO); 1.60–1.10 (*m*, 27 H); 0.94 (*d*, J = 6.0, H_3C–C(4')); 0.88 (*t*, J = 6.0, terminal CH_3). – MS.: 349 (M^+, $C_{21}H_{39}N_3O$, 1), 332 (1), 320 (1), 306 (1), 281 (5), 265 (3), 250 (1), 194 (1), 181 (1), 167 (2), 153 (6), 125 (4), 111 (21), 98 (12), 83 (8), 70 (*100*), 55 (26), 43 (26).

$C_{21}H_{39}N_3O$ (349.54) Calc. C 72.15 H 11.25 N 12.02% Found C 72.23 H 11.20 N 11.87%

1-(3'β-Acetoxy-5'-cholen-24'-oyl)-1,2,4-triazole (**10**): m.p. 185–190° (from CH_2Cl_2/acetonitrile). – UV. (THF): 222 (7400). – IR. ($CHCl_3$): 3145*w*, 2945*s*, 2910*m*, 2875*m*, 1750*s*, 1722*s*, 1510*w*, 1375*s*, 1250*s*, 1120*m*, 1030*m*, 955*m*, 947*m*, 870*w*. – ^{1}H-NMR. ($CDCl_3$): 8.98 (*s*, H–C(5)); 8.00 (*s*, H–C(3)); 5.34 (br.*d*, J = 4.0, H–C(5')); 4.60 (*m*, $w_{1/2}$ = 20, H–C(3')); 3.20–2.90 (*m*, 2 H–C(23')); 2.40–2.20 (br.*d*, 3 H); 2.00 (*s*, CH_3COO); 2.00–0.80 (*m*, 20 H); 1.00 (*s*, H_3C(18')); 0.97 (*d*, J = 6.0, H_3C(21')); 0.68 (*s*, H_3C(19')). – MS.: 407 ($M^+ - 60$, 11), 370 (11), 356 (17), 338 (11), 323 (3), 310 (5), 295 (2), 277 (25), 256 (8), 213 (11), 199 (10), 159 (11), 145 (19), 105 (23), 97 (29), 95 (30), 83 (38), 81 (38), 69 (*100*), 55 (76), 43 (88).

$C_{28}H_{41}N_3O$ (467.63) Calc. C 71.91 H 8.84 N 8.99% Found C 72.30 H 8.99 N 8.70%

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[6]) A similar explanation was given for enethiol esters which failed to give photo-*Fries* products [12].

1-Cyclohexylacetyl-1,2,4-triazole (**17**): m.p. 58–58.5° (from heptane). – UV. (THF): 223 (8600). – IR. (CCl_4): 3150*w*, 2930*s*, 2858*m*, 1755*s*, 1510*m*, 1450*m*, 1370*s*, 1275*s*, 1210*m*, 1180*s*, 1120*m*, 974*m*, 945*m*, 878*w*, 668*m*. – ^{1}H-NMR. ($CDCl_3$): 9.00 (*s*, H–C(5)); 8.09 (*s*, H–C(3)); 2.99 (*d*, J=7.0, CH_2CO); 2.20–0.80 (*m*, 11 H). – MS.: 193 (M^+, $C_{10}H_{15}N_3O$, 8), 192 (30), 125 (45), 112 (83), 111 (27), 97 (67), 83 (46), 81 (25), 70 (75), 67 (37), 60 (10), 55 (*100*), 41 (52).

$C_{10}H_{15}N_3O$ (193.32) Calc. C 62.15 H 7.82 N 21.75% Found C 61.99 H 7.69 N 21.63%

trans-*(2-Phenylcyclohexyl)acetic acid* (**28**) [14]. To a dark blue solution of 950 mg of lithium (135 mmol) in liquid ammonia were added 7.32 g (33.9 mmol) of (2-phenylcyclohexylidene)acetic acid [15] in 200 ml of dry ether, under stirring and in an argon atmosphere. After 1 h stirring at −28° the reaction was quenched by gradual addition of 20 g of ammonium chloride, ammonia was evaporated, the mixture acidified with hydrochloric acid and extracted with ethyl acetate. The extract was washed with water and dried ($MgSO_4$). Solvent removal and recrystallization from heptane yielded 6.36 g of **28** as colorless flakes, m.p. 110.5–111° ([14]: 112–114°). – IR. ($CHCl_3$): 3400–2400br., 3085*m*, 3065*m*, 3030*m*, 2930*s*, 2860*s*, 1708*s*, 1602*w*, 1492*m*, 1445*m*, 1410*m*, 1300*m*, 1250*m*, 1192*w*, 1180*m*, 1100*w*, 1074*w*, 1030*w*, 932*m*, 909*m*, 702*s*. – ^{1}H-NMR. ($CDCl_3$): 11.0 (br. *s*, COOH); 7.4–7.0 (*m*, C_6H_5); 2.4–1.0 (*m*, 12 H). – MS.: 218 (M^+, $C_{14}H_{18}O_2$, 11), 158 (*100*), 149 (3), 143 (10), 130 (15), 117 (20), 104 (15), 91 (28), 77 (4), 67 (4), 65 (4), 55 (2), 51 (2), 41 (4).

$C_{14}H_{18}O_2$ (218.28) Calc. C 77.03 H 8.13% Found C 76.94 H 8.39%

*1-((*trans*-2'-Phenylcyclohexyl)acetyl)-1,2,4-triazole* (**29**): m.p. 106–107° (from heptane). – UV. (THF): 217 (10,800), sh. 280 (6040). – IR. (CCl_4): 3140*w*, 3000*w*, 2930*s*, 2860*m*, 1750*s*, 1600*w*, 1515*w*, 1490*w*, 1445*w*, 1375*s*, 1277*m*, 1175*s*, 1120*m*, 968*s*, 942*s*, 880*w*. – ^{1}H-NMR. ($CDCl_3$): 8.64 (*s*, H–C(5)); 7.88 (*s*, H–C(3)); 7.16 (*s*, C_6H_5); 4.00–3.60 (*m*, CH_2CO); 2.4–1.1 (*m*, 10 H). – MS.: 269 (M^+, $C_{16}H_{19}N_3O$, 2), 218 (3), 200 (28), 158 (*100*), 143 (12), 130 (14), 117 (9), 115 (8), 91 (26), 81 (5), 77 (7), 70 (7), 41 (6).

$C_{16}H_{19}N_3O$ (269.34) Calc. C 71.34 H 7.11 N 15.60% Found C 71.00 H 6.81 N 15.66%

*2-(*trans*-2'-Phenylcyclohexyl)ethanol* (**30**). To a stirred suspension of 0.57 g (15 mmol) of lithium aluminium hydride in 40 ml of dry THF was added dropwise a solution of 2.69 g (10 mmol) of **29** in 50 ml of dry THF at 0° and the whole was heated under reflux for 3 h. The reaction was quenched with sat. aqueous ammonium chloride-solution. After dilution with ethyl acetate, inorganic salts were filtered off. Work-up of the filtrate and evaporation of the solvent i.V. afforded 1.58 g of crude alcohol, which was purified by distillation, yielding 1.30 g of pure **30** as a colorless oil, b.p. 150°/0.03 Torr. – IR. (CCl_4): 3630*m*, 3085*w*, 3065*w*, 3030*m*, 2930*s*, 2855*s*, 1600*w*, 1492*m*, 1447*m*, 1384*w*, 1083*w*, 1045*m*, 1031*m*, 995*m*, 970*w*, 906*w*, 887*w*, 868*w*. – ^{1}H-NMR. (CCl_4): 7.28–6.90 (*m*, C_6H_5); 3.23 (*d*×*d*, J_1=8.0, J_2=6.0, CH_2O); 1.68 (*s*, HO); 2.28–0.85 (*m*, 12 H). – MS.: 204 (M^+, $C_{14}H_{20}O$, 43), 186 (29), 158 (*100*), 143 (25), 129 (26), 117 (45), 115 (21), 104 (98), 95 (17), 91 (83), 78 (11), 67 (12), 55 (10), 41 (12).

$C_{14}H_{20}O$ (204.30) Calc. C 82.30 H 9.8% Found C 82.20 H 10.02%

*(*trans*-2-Phenylcyclohexyl)acetaldehyde* (**31**). With *Sarett* reagent (prepared *in situ* from 3.60 g (36 mmol) of chromic anhydride and 5.69 g (72 mmol) of pyridine in 100 ml of dry CH_2Cl_2) 1.20 g (5.9 mmol) of **30** were oxidized. After the reaction 100 ml of ether were added and then the solution was decanted from the black residue, which was washed with ether. The combined organic solution was washed successively with dil. NaOH-, dil. HCl-solution and water, dried ($MgSO_4$) and evaporated to give 1.30 g of crude aldehyde. Distillation afforded 0.95 g of pure **31** as colorless oil, b.p. 115°/0.03 Torr. – IR. (CCl_4): 3085*w*, 3065*w*, 3030*m*, 2930*s*, 2855*s*, 2818*m*, 2715*m*, 1725*s*, 1602*w*, 1494*m*, 1448*m*, 1409*w*, 1360*w*, 1340*w*, 1294*w*, 1280*w*, 1250*w*, 1185*w*, 1134*m*, 1080*m*, 1020*m*, 900*w*, 703*s*. – ^{1}H-NMR. (CCl_4): 9.38 (*d*, J=2.0, CHO); 7.30–6.90 (*m*, C_6H_5); 2.40–0.90 (*m*, 12 H). – MS.: 202 (M^+, $C_{14}H_{18}O$, 1), 158 (*100*), 143 (24), 130 (24), 117 (19), 115 (13), 104 (21), 91 (33), 77 (6), 67 (5), 55 (5), 41 (7).

$C_{14}H_{18}O$ (202.28) Calc. C 83.12 H 8.97% Found C 83.06 H 8.95%

2-Acetyltetrazole (**39**) [13]. To 2.10 g (30 mmol) of tetrazole[7]) and 2.71 g (33 mmol) of 1-methylimidazole in 75 ml of dry benzene were added 2.34 ml (33 mmol) of acetylchloride with cooling in an ice-bath. The mixture was stirred for 48 h at about 40°. 1-Methylimidazole-hydrochloride was filtered off and the filtrate evaporated i.V. to give a colorless solid which was purified by sublimation (about 110°/0.5 Torr) affording 1.17 g of colorless prisms, m.p. 54–56°. – UV. (THF): 218 (5200). – IR. ($CHCl_3$): 3155*w*, 1775*s*, 1465*w*, 1382*s*, 1360*m*, 1296*w*, 1180*m*, 1124*w*, 1090*w*, 1072*s*, 1035*w*, 1001*w*, 957*s*, 916*w*, 879*w*. – ^{1}H-NMR. ($CDCl_3$): 9.24 (*s*, H–C(5)); 2.90 (*s*, CH_3CO). – MS.: 113 ($M^+ + 1$, 3), 112 (M^+, 0), 69 (3), 55 (5), 43 (*100*), 42 (24), 41 (11).

$C_3H_4N_4O$ (112.09) Calc. C 32.14 H 3.60 N 49.99% Found C 31.88 H 3.63 N 49.9%

All the other 2-acyltetrazoles were prepared similarly from the corresponding acid chlorides and tetrazole.

2-Cyclohexylacetyltetrazole (**42**): m.p. 69.5–70.5° (from hexane). – UV. (THF): 213 (8000). – IR. (CCl_4): 3160*m*, 2930*s*, 2860*s*, 1772*s*, 1465*m*, 1450*m*, 1402*m*, 1377*s*, 1352*m*, 1304*m*, 1282*w*, 1267*w*, 1180*m*, 1150*s*, 1130*m*, 1123*m*, 1076*s*, 1035*w*, 981*s*, 955*s*, 920*w*, 896*w*, 882*w*. – ^{1}H-NMR. ($CDCl_3$): 9.22 (*s*, H–C(5)); 3.11 (*d*, J=7.0, CH_2CO); 2.4–1.0 (*m*, 11 H). – MS.: 194 (M^+, $C_9H_{14}N_4O$, 1), 165 (2), 152 (4), 149 (6), 125 (61), 113 (67), 97 (37), 84 (31), 82 (36), 71 (31), 67 (31), 55 (*100*), 41 (46).

$C_9H_{14}N_4O$ (194.23) Calc. C 55.65 H 7.27 N 28.85% Found C 55.46 H 7.26 N 28.80%

2-Stearoyltetrazole (**45**): m.p. 64–65° (from hexane). – UV. (THF): 214 (6600). – IR. (CCl_4): 3160*w*, 2930*s*, 2855*s*, 1773*s*, 1466*s*, 1407*w*, 1380*s*, 1350*w*, 1300*w*, 1234*w*, 1190*w*, 1164*m*, 1120*w*, 1075*m*, 960*m*, 915*w*, 877*w*. – ^{1}H-NMR. (CCl_4): 9.10 (*s*, H–C(5)); 3.24 (*t*, J=7.0, CH_2CO); 2.0–1.1 (*m*, 30 H); 0.89 (*t*, J=6.0, terminal CH_3). – MS.: 308 ($M^+ - 28$, 13), 267 (59). 237 (6), 224 (11), 223 (10), 210 (18), 196 (20), 182 (20), 168 (19), 154 (17), 140 (18), 126 (16), 112 (32), 98 (*100*), 84 (52), 71 (35), 69 (39), 55 (63), 43 (90), 41 (60).

$C_{19}H_{36}N_4O$ (336.51) Calc. C 67.81 H 10.78 N 16.65% Found C 67.78 H 10.85 N 16.70%

Preparation of 3(5)-stearoyl-1,2,4-triazole (16). – *1-Benzyl-3-(1-hydroxy-octadecyl)-1,2,4-triazole* (**14**) was prepared following the known procedure for hydroxyalkylation of imidazole [3]: To a solution of 3.60 g of 1-benzyl-1,2,4-triazole (**13**) in 200 ml of abs. ether were added dropwise 12.4 ml of butyllithium solution (about 2M, *Fluka AG, pract.*) while cooling (ice/salt bath). After 1 h stirring at RT. 7.10 g of octadecanal in 40 ml abs. ether were added under ice cooling and stirring at RT. was continued for 3 h. Water was added and the mixture extracted with ether. The ether layer was separated, washed with water and dried ($MgSO_4$). Evaporation of the solvent gave crude product which was purified by silicagel column chromatography. Recrystallization of the eluted product from acetonitrile afforded 8.3 g of **14**. Its further recrystallization from acetone gave colorless needles, m.p. 97–99°. – IR. (CCl_4): 2920*s*, 2855*s*, 1500*w*, 1470*m*, 1460*m*, 1275*w*, 1180*w*, 880*w*. – ^{1}H-NMR. ($CDCl_3$): 7.76 (*s*, H–C(5)); 7.4–7.1 (*m*, C_6H_5); 5.42 (br. *s*, $C_6H_5CH_2$); 4.78 (*t*, J=7.0, CH(OH)); 1.95–1.50 (*m*, 3 H); 1.50–1.00 (*m*, 29 H); 0.89 (*t*, J=6.0, terminal CH_3). – MS.: 427 (M^+, $C_{27}H_{45}N_3O$, 13), 409 (4), 383 (3), 378 (3), 368 (3), 336 (10), 258 (3), 244 (6), 202 (9), 189 (74), 173 (5), 158 (4), 91 (*100*), 83 (5), 70 (6), 57 (16), 43 (32),

$C_{27}H_{45}N_3O$ (427.65) Calc. C 75.83 H 10.61 N 9.83% Found C 75.81 H 10.58 N 9.67%

3(5)-(1-Hydroxyoctadecyl)-1,2,4-triazole (**15**). To 2.0 g of **14** in 250 ml of abs. THF were given about 300 ml of liquid ammonia while cooling with CO_2/2-propanol. To this solution were added 2 g of sodium metal and the whole was stirred for 10 h under ice-water cooling, after which the reaction was quenched by gradual addition of 5 g of ammonium chloride. After evaporation of ammonia and addition of water the product was extracted with chloroform. The extract was washed with water and dried ($MgSO_4$). Solvent removal gave 1.51 g of crude **15** which was purified by silicagel column chromatography and subsequent recrystallization from carbon tetrachloride to give 1.2 g of **15**, m.p. 97–98°. – IR. (KBr): 3600–2500 br.*s*, 2920*s*, 2860*s*, 1500*w*, 1470*s*, 1315*w*, 1270*m*,

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[7]) Commercial tetrazole (*Fluka AG, purum*, containing 10% of water) was dissolved in methanol/benzene and the solvent was evaporated i.V., this was repeated several times to remove water azeotropically. The remaining crystalline product was dried i.HV. overnight.

1260*m*, 1180*w*, 1125*w*, 1085*m*, 1040*m*, 980*m*, 880*w*, 715*m*, 693*w*. – ^{1}H-NMR. (CD_3COOD): 9.63 (*s*, H–C(5 or 3)); 6.34 (*t*, J=7.0, C*H*(OH)); 2.5–2.2 (*m*, 3 H); 1.8–1.2 (*m*, 29 H); 0.93 (*t*, J=6.0, terminal CH_3). – MS.: 337 (M^+, $C_{20}H_{39}N_3O$, 47), 319 (6), 292 (16), 278 (10), 262 (4), 250 (4), 236 (4), 224 (4), 220 (4), 210 (4), 206 (4), 196 (4), 192 (4), 178 (4), 168 (12), 154 (37), 141 (6), 136 (8), 122 (8), 112 (45), 98 (*100*), 83 (22), 70 (22), 57 (31), 43 (59).

$C_{20}H_{39}N_3O$ (337.54) Calc. C 71.16 H 11.65 N 12.45% Found C 71.08 H 11.59 N 12.50%

3(5)-Stearoyl-1,2,4-triazole (**16**). To a chromium oxide-pyridine complex prepared from 6 g of chromium oxide and 50 ml of pyridine were added 3.0 g of **15** in 250 ml of pyridine under ice cooling. The whole was kept in the refrigerator for 48 h. After addition of water the mixture was extracted with chloroform, the extract washed with dilute hydrochloric acid and with water, and dried ($MgSO_4$). Evaporation of the solvent afforded 3.1 g of crude mixture which was separated by a silicagel column chromatography to give 1.68 g of crude **16**. Recrystallization from chloroform gave 1.2 g of colorless needles, m.p. 135.5–138°. – UV. (THF): 240 (5240). – IR. (KBr): 3400*m*, 2920*s*, 2850*s*, 1700*s*, 1520*w*, 1470*m*, 1445*m*, 1400*w*, 1273*m*, 1265*m*, 1080*w*, 985*m*, 887*w*, 775*w*, 715*w*. – ^{1}H-NMR. (CF_3COOD): 9.78 (br. *s*, H–C(5 or 3)); 3.33 (*t*, J=7.0, CH_2CO); 2.3–1.7 (*m*, 3 H); 1.7–1.2 (*m*, 29 H); 0.93 (*t*, J=6.0, terminal CH_3). – MS.: 335 (M^+, $C_{20}H_{37}N_3O$, *100*), 318 (4), 307 (11), 292 (4), 278 (5), 264 (11), 251 (4), 250 (4), 236 (10), 222 (5), 208 (8), 194 (8), 180 (8), 166 (8), 152 (18), 138 (18), 124 (24), 112 (61), 111 (47), 96 (34), 83 (42), 70 (55), 57 (34), 55 (36), 43 (71).

$C_{20}H_{37}N_3O$ (335.52) Calc. C 71.59 H 11.12 N 12.53% Found C 71.45 H 11.00 N 12.41%

Photolysis of the 1-acyl-1,2,4-triazoles 1, 2, 7, 10, 17 and 29, and of the 2-acyltetrazoles 39, 42 and 45. – *General.* A low pressure mercury lamp (TMN 15132, *Quarzlampen GmbH*; Hanau; lamp A) or a 125 W medium pressure mercury lamp (QM 125, *Meda-Licht AG*, Basel; lamp B) were used. Irradiation conditions: Lamp A with quartz immersion well = 254 nm light, lamp B with quartz immersion well = > 235 nm light, and lamp B with pyrex immersion well = > 280 nm light.

Photolysis of **2**. 1) In 400 ml of ether 1.8 g of **2** were irradiated with 254 nm light for 10 h. The residue obtained after solvent removal was chromatographed on 90 g of silicagel. Elution with benzene gave 115 mg of **3/4** and 274 mg of **5/6**, and elution with $CHCl_3$/MeOH 10:1 1.4 g of starting material. Each fraction was further resolved by repeated column chromatography to give **3/4** (103 mg, about 4.5:1) which were separated by GLC., and **5** (232 mg) and **6** [2c] (23 mg), with the recovery of stearic acid (820 mg).

2) In 400 ml of ether 1.8 g of **2** were irradiated with 254 nm light for 24 h. The mixture was separated as described above to give **3/4** (228 mg, about 4.5:1), **5** (305 mg) and **6** (40 mg), with the recovery of stearic acid (130 mg).

3) In 400 ml of ether 2.0 g of **2** were irradiated with > 235 nm light for 48 h. The mixture obtained was separated as described above to give **3/4** (584 mg, about 4.5:1).

Photolysis of **7**. A solution of 1.5 g of **7** in 350 ml of ether was irradiated with > 235 nm light for 10 h. The mixture obtained was separated by column chromatography affording **8** [2b]/**9** (600 mg, about 11:1) which were separated by GLC. *3-Methylheptadecane* (**9**): liquid. – IR. (CCl_4): 2960*s*, 2930*s*, 2860*s*, 1460*m*, 1378*w*. – ^{1}H-NMR. (CCl_4): 2.0–1.5 (*m*, 1 H); 1.5–1.0 (*m*, 28 H); 1.0–0.7 (*m*, 3 CH_3). – MS.: 254 (M^+, $C_{18}H_{38}$, 1), 239 (2), 225 (22), 211 (*1*), 197 (3), 183 (3), 169 (7), 155 (10), 141 (13), 127 (15), 113 (20), 99 (24), 85 (72), 71 (*100*), 57 (58), 43 (84).

Photolysis of **10**. A solution of 945 mg of **10** in 150 ml of THF was irradiated with > 235 nm light. The mixture obtained was chromatographed on 50 g of silicagel. Elution with hexane/ether 4:1 gave **11/12** (about 4:1, determined by ^{1}H-NMR.). This mixture was rechromatographed to give pure **11** and **12**. *20-Methylidene-5-pregnen-3β-ol acetate* (**11**): see [2b].

20-Ethyl-5-pregnen-3β-ol acetate (**12**): m.p. 132–133° (from $CHCl_3$/MeOH). – IR. (CCl_4): 2970*s*, 2945*s*, 2910*s*, 2875*s*, 2860*s*, 1732*s*, 1465*m*, 1458*m*, 1440*m*, 1374*s*, 1367*s*, 1332*w*, 1314*w*, 1242*s*, 1200*w*, 1165*w*, 1138*w*, 1090*w*, 1034*s*, 994*w*, 980*w*, 959*w*, 940*w*, 928*w*, 918*w*, 905*w*, 890*w*, 880*w*, 845*w*. – ^{1}H-NMR. (CCl_4): 5.31 (br. *d*, J=4.5, H–C(5)); 4.48 (*m*, $w_{1/2}$=18, H–C(3)); 2.40–0.62 (*m*, 29 H); 1.91 (*s*, CH_3CO); 0.99 (*s*, H_3C(19)); 0.66 (*s*, H_3C(18)). – MS.: 312 (M^+-60, *100*), 297 (33), 255 (24), 228 (6), 213 (19), 204 (29), 191 (55), 173 (8), 159 (19), 145 (41), 133 (19), 121 (25), 105 (39), 95 (33), 81 (43), 67 (22), 55 (27), 41 (24).

$C_{25}H_{40}O_2$ (372.57) Calc. C 80.59 H 10.82% Found C 80.59 H 10.83%

Photolysis of **17**. 1) A solution of 3.86 g of **17** in 400 ml of ether was irradiated with >235 nm light for 8 h. The mixture obtained after solvent removal was separated by a combination of column chromatography and GLC. affording **18–24**.

2) A solution of 770 mg of **17** in 200 ml of ether was irradiated with >235 nm light for 2 h and the mixture was analyzed by GLC. using both SE-30 and *Carbowax* 20M columns. The peaks of cyclohexene (**25**) and methylcyclohexane (**26**) were identified with authentic samples, and yields were determined as 13 and 2%, respectively. GLC./MS. analysis of this mixture (on *Varian* apparatus, model MAT-111, SE-30 (5%) on *Chromosorb* W) showed another peak to be due to compound **27** with C_7H_{12} ($M^+ = 96$), and its yield was determined as about 8%. After solvent removal the mixture was dissolved in methanol and heated under reflux for 2 h to convent unreacted **17** into methyl cyclohexylacetate. After evaporation of methanol the mixture was again analyzed by GLC. using both SE-30 and *Carbowax* 20M columns at several oven temp., and yields of the other products were determined as follows: **18** (2%), **19** (8%), **20** (0.3%), **21** (4.3%), **22a** (2.6%), **22b** (2.0%), **22c/22d** (1.8%), **23a** (5.6%), **23b** (3.9%), **24a/24b** (9.5%). The ratio **22c/22d** has not yet been determined. *1-Cyclohexyl-3-ethoxy-2-butanone* (**18**): liquid. – IR. (CCl_4): 2985*s*, 2930*s*, 2860*s*, 1720*s*, 1450*s*, 1400*m*, 1372*s*, 1323*m*, 1288*m*, 1250*w*, 1220*m*, 1130*s*, 1110*s*, 1030*w*, 990*w*, 927*w*, 900*w*, 860*w*. – ^{1}H-NMR. (CCl_4): 3.80 (*qa*, $J = 7.0$, H–C(3)); 3.48 (*qa*, $J = 7.0$, CH_3CH_2O); 2.40 (*m*, 2 H–C(1)); 1.22 (*t*, $J = 7.0$, CH_3CH_2O). – MS.: 154 ($M^+ - 40$, 3), 125 (2), 97 (7), 83 (3), 74 (7), 73 (*100*), 55 (14), 45 (66), 41 (9).

$C_{12}H_{22}O_2$ (198.30) Calc. C 72.68 H 11.18% Found C 72.58 H 11.37%

1-Cyclohexyl-2-butanone (**19**): liquid. – IR. (CCl_4): 2922*s*, 2850*s*, 1713*s*, 1447*m*, 1410*w*, 1377*w*, 1355*w*, 1108*w*, 1020*w*, 953*w*. – ^{1}H-NMR. (CCl_4): 2.29 (*qa*, $J = 7.0$, 2 H–C(3)); 2.17 (*d*, $J = 7.0$, 2 H–C(1)); 2.1–0.6 (*m*, 11 H of cyclohexyl); 0.97 (*t*, $J = 7.0$, 3 H–C(4)). – MS.: 154 (M^+, $C_{10}H_{18}O$, 2), 124 (3), 99 (7), 83 (*100*), 82 (79), 67 (50), 60 (86), 55 (71), 41 (34).

(1R,6S*,7S*)-Bicyclo[4.2.0]octan-7-ol* (**22a**): liquid. – IR. (CCl_4): 3625*m*, 2930*s*, 2845*s*, 1440*m*, 1405*w*, 1368*w*, 1300*w*, 1265*w*, 1180*m*, 1156*m*, 1054*s*, 974*w*, 945*w*, 918*w*, 880*w*. – ^{1}H-NMR. (CCl_4): 3.80–3.46 (*m*, H–C(7)); 1.40–1.16 (*sept.*-like *m*, 1 H); 1.16–0.60 (*m*, 12 H). – MS.: 126 (M^+, $C_{18}H_{14}O$, 1), 108 (6), 98 (9), 97 (11), 93 (16), 82 (98), 79 (17), 70 (16), 67 (*100*), 57 (40), 55 (36), 54 (41), 41 (34).

$C_{18}H_{14}O$ (126.19) Calc. C 76.14 H 11.18% Found C 76.08 H 11.03%

Acetylation of **22a** with acetic anhydride in pyridine afforded *(1R*,6S*,7S*)-bicyclo[4.2.0]oct-7-yl acetate* (**45**) [6], liquid. – IR. (CCl_4): 2935*s*, 2860*s*, 1736*s*, 1444*m*, 1370*m*, 1240*s*, 1153*w*, 1132*m*, 1042*s*, 950*w*. – ^{1}H-NMR. (CCl_4): 4.58–4.30 (*qa*-like *m*, H–C(7)); 1.48–1.23 (*sept.*-like *m*, 1 H); 1.89 (*s*, CH_3CO); 1.89–0.80 (*m*, 11 H). – MS.: 168 (M^+, $C_{10}H_{16}O_2$, < 1), 149 (1), 124 (9), 108 (28), 93 (15), 87 (63), 82 (70), 79 (25), 67 (77), 55 (25), 43 (*100*).

$C_{10}H_{16}O_2$ (168.23) Calc. C 71.39 H 9.59% Found C 71.23 H 9.40%

Oxidation of **22a** (33 mg) with the chromium oxide-pyridine complex in methylene chloride gave trans-*bicyclo[4.2.0]octan-7-one* (**24a**): 25 mg, liquid. – IR. (CCl_4): 2938*s*, 2860*s*, 1780*s*, 1445*m*, 1415*w*, 1400*w*, 1374*w*, 1364*w*, 1310*w*, 1295*w*, 1250*w*, 1235*w*, 1207*w*, 1193*w*, 1170*m*, 1125*m*, 1105*w*, 1090*m*, 1065*w*, 1038*m*. – ^{13}C-NMR. (CCl_3): 202.6 (*s*), 65.7 (*d*), 50.1 (*t*), 32.8 (*t*), 32.2 (*t*), 27.0 (*t*), 26.5 (*t*), 25.7 (*t*).

$C_8H_{12}O$ (124.18) Calc. C 77.37 H 9.74% Found C 77.40 H 9.74%

(1R,6S*,7R*)-Bicyclo[4.2.0]octan-7-ol* (**22b**) [6]: liquid. – IR. (CCl_4): 3620*m*, 2928*s*, 2850*s*, 1450*m*, 1440*m*, 1285*w*, 1200*w*, 1132*m*, 1014*m*, 960*w*, 917*w*, 665*w*. – ^{1}H-NMR. (CCl_4): 4.20 (br. *s*, $w_{1/2} = 8$, H–C(7)); 2.6–0.8 (*m*, 13 H). – MS.: 126 (M^+, $C_8H_{14}O$, 1), 108 (6), 93 (13), 82 (69), 67 (*100*), 57 (35), 55 (44), 41 (35).

$C_8H_{14}O$ (126.19) Calc. C 76.14 H 11.18% Found C 76.07 H 11.08%

Acetylation of **22b** with acetic anhydride in pyridine gave *(1R*,6S*,7R*)-bicyclo[4.2.0]oct-7-yl acetate* (**46**) [6], liquid. – IR. (CCl_4): 2980*m*, 2935*s*, 2860*s*, 1740*s*, 1445*w*, 1372*m*, 1243*s*, 1122*m*, 1024*m*, 960*w*, 920*w*. – ^{1}H-NMR. ($CDCl_3$): 5.06–4.92 (*qi*-like *m*, H–C(7)); 1.97 (*s*, CH_3CO); 1.9–0.8 (*m*, 12 H). – MS.: 168 (M^+, $C_{10}H_{16}O_2$, 1), 149 (1), 124 (4), 108 (13), 93 (6), 87 (40), 82 (36), 67 (28), 55 (10), 43 (*100*).

$C_{10}H_{16}O_2$ (168.23) Calc. C 71.39 H 9.58% Found C 71.38 H 9.57%

The isomer **22b** (70 mg) was oxidized by the chromium oxide-pyridine complex in methylene chloride to give **24a** (40 mg).

(1R,6R*,7R*)-Bicyclo[4.2.0]octan-7-ol* (**22c**)[8]) [6]: liquid. – IR. (CCl_4): 3622*m*, 3320br.*m*, 2930*s*, 2850*s*, 1447*m*, 1395*w*, 1287*w*, 1228*w*, 1190*w*, 1116*m*, 1094*m*, 1069*m*, 1050*m*, 1034*m*, 993*w*, 910*w*. – ^{1}H-NMR. (CCl_4): 4.24–3.90 (*qa*-like *m*, H–C(7)); 2.4–0.6 (*m*, 13 H). – MS.: 126 (M^+, $C_8H_{14}O$, 1), 108 (5), 97 (6), 93 (8), 82 (90), 67 (*100*), 57 (22), 54 (42), 41 (27).

$C_8H_{14}O$ (126.19) Calc. C 76.14 H 11.18% Found C 75.90 H 11.38%

(1R,6R*,7S*)-Bicyclo[4.2.0]octan-7-ol* (**22d**)[8]) [6]: liquid. – IR. (CCl_4): 3630*m*, 2935*s*, 2860*s*, 1465*m*, 1453*m*, 1400*w*, 1360*w*, 1224*m*, 1150*s*, 1080*s*, 1000*w*, 980*w*. – ^{1}H-NMR. (CCl_4): 4.20–3.80 (*m*, H–C(7)); 2.6–0.6 (*m*, 13 H). – MS.: 126 (M^+, $C_8H_{14}O$, 1), 108 (5), 98 (6), 93 (8), 82 (*100*), 67 (91), 57 (18), 55 (76), 41 (24).

$C_8H_{14}O$ (126.19) Calc. C 76.14 H 11.18% Found C 76.05 H 11.22%

A mixture **22c/22d** (45 mg) was oxidized with the chromium oxide-pyridine complex in methylene chloride to give *cis-bicyclo[4.2.0]octan-7-one* (**24b**) [6]: 35 mg, liquid. – IR. (CCl_4): 2935*s*, 2860*s*, 1780*s*, 1458*m*, 1447*m*, 1400*w*, 1350*w*, 1306*w*, 1277*w*, 1255*w*, 1206*w*, 1194*m*, 1162*w*, 1141*w*, 1108*w*, 1092*m*, 1058*m*, 1039*m*, 1014*w*, 992*w*, 927*m*, 915*w*, 898*m*, 890*w*, 848*w*. – ^{1}H-NMR. (CCl_4): 3.30–2.84 (*m*, 2 H); 2.60–1.80 (*m*, 4 H); 1.70–0.90 (*m*, 6 H). – ^{13}C-NMR. ($CDCl_3$): 210.0 (*s*), 56.6 (*d*), 52.2 (*t*), 29.5 (*t*), 22.8 (*d*), 22.6 (*t*), 22.4 (*t*), 21.2 (*t*). – MS.: 124 (M^+, $C_8H_{12}O$, 10), 95 (3), 82 (50), 67 (*100*), 54 (27), 41 (13).

$C_8H_{12}O$ (124.18) Calc. C 77.37 H 9.74% Found C 77.21 H 9.84%

1-Cyclohexyl-3-ethoxy-2-butanol (**23a**): liquid. – IR. (CCl_4): 3590*m*, 3490br.*m*, 2980*s*, 2930*s*, 2858*s*, 1485*w*, 1450*s*, 1385*s*, 1318*m*, 1310*m*, 1290*m*, 1264*w*, 1243*w*, 1200*w*, 1175*w*, 1160*w*, 1105*s*, 1090*s*, 1045*m*, 1020*m*, 980*m*, 965*w*, 907*w*, 815*w*. – ^{1}H-NMR. (CCl_4): 3.86 (*m*, H–C(2)); 3.52 (*m*, CH_3CH_2O); 3.36 (*m*, H–C(3)); 2.90 (br. *s*, HO); 1.96–0.80 (*m*, 2 H–C(1) and 11 H of cyclohexyl); 1.18 (*t*, J=7.0, CH_3CH_2O); 1.07 (*d*, J=6.5, 3 H–C(4)). – MS.: 200 (M^+, $C_{12}H_{24}O_2$, 0.5), 171 (2), 127 (6), 109 (10), 95 (2), 83 (12), 81 (3), 73 (*100*), 67 (4), 57 (6), 55 (16), 45 (70), 41 (12).

$C_{12}H_{24}O_2$ (200.31) Calc. C 71.95 H 12.08% Found C 71.08 H 11.84%

Oxidation of **23a** (169 mg) with the chromium oxide-pyridine complex in methylene chloride gave **18** (160 mg).

1-Cyclohexyl-3-ethoxy-2-butanol (**23b**): liquid. – IR. (CCl_4): 3950*m*, 2980*s*, 2930*s*, 2860*s*, 1485*w*, 1450*s*, 1405*m*, 1375*m*, 1330*w*, 1285*m*, 1245*w*, 1140*m*, 1105*s*, 1090*s*, 1075*m*, 1050*m*, 1035*m*, 990*w*, 963*w*, 910*w*, 898*w*. – ^{1}H-NMR. (CCl_4): 3.65 (*m*, H–C(2)); 3.46 (*m*, CH_3CH_2O); 3.18 (*m*, H–C(3)); 2.67 (br. *s*, HO); 2.00–0.70 (*m*, 2 H–C(1) and 11 H of cyclohexyl); 1.19 (*t*, J=7.0, CH_3CH_2O); 1.09 (*d*, J=6.0, 3 H–C(4)). – MS.: 200 (M^+, $C_{12}H_{24}O_2$, <1), 171 (1), 127 (5), 126 (4), 109 (10), 83 (12), 73 (*100*), 67 (4), 55 (13), 45 (47), 41 (8).

$C_{12}H_{24}O_2$ (200.31) Calc. C 71.95 H 12.08% Found C 72.09 H 11.55%

Oxidation of **23b** (119 mg) with the chromium oxide-pyridine complex in methylene chloride gave **18** (102 mg).

Photolysis of 1-cyclohexylacetaldehyde (**20**). 1) A solution of 2.03 g of **20** in 200 ml of ether was irradiated with >235 nm light for 7 h. The mixture obtained after solvent removal was separated by column chromatography on 100 g of silicagel. Elution with ether/hexane 1:2 afforded **23a** (350 mg), **23b** (310 mg) and a mixture **21/22a/22b/22c/22d** (510 mg). The yields of the latter were determined by GLC. to be 4.5, 5.0, 4.1, 2.5 and 1.8%, respectively. Each component was isolated in pure form by GLC.

2) A solution of 3 mg of **20** in 0.5 ml of ether was irradiated in a quartz tube with >235 nm light for 5 min, and the mixture analyzed by GLC. using both SE-30 and *Carbowax* 20M columns. Yields of **25**, **26** and **27** were determined to be 19.5, 4.6 and 11.6%, respectively.

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[8]) This isomer was obtained in pure form from the irradiation mixture of cyclohexylacetaldehyde (**20**).

Photolysis of **29**. A solution of 538 mg of **29** in 200 ml of ether was irradiated with >235 nm light for 24 h. The mixture obtained was separated by silicagel column chromatography. Elution with ether/hexane 1:2 afforded **35/36/37/38** (88 mg), **34a** (20 mg), **34b** (40 mg), **33a/33b** (15 mg), **32a** (16 mg) and **32b** (23 mg). Yields of each of **35–38** were determined by GLC. to be 4.9, 1.4, 3.1 and 16.6%, respectively, and they were isolated in pure form by GLC. *2(or 6)-Phenylbicyclo[4.2.0]octan-7-ols* (**32a** and **32b**). **32a**: m.p. 84–84.5° (from hexane). – IR. (CCl_4): 3620*m*, 3085*w*, 3060*w*, 3025*m*, 2930*s*, 2855*s*, 1600*w*, 1492*w*, 1450*w*, 1442*m*, 1410*w*, 1375*w*, 1288*w*, 1190*w*, 1157*m*, 1138*m*, 1097*m*, 1080*w*, 1052*s*, 1040*m*, 960*w*, 893*w*, 700*s*. – ^{1}H-NMR. (CCl_4): 7.30–6.90 (*m*, C_6H_5); 3.76 (*qa*, J=7.0, H–C(7)); 2.72–2.42 (*m*, 1 H); 2.30 (*sept.*-like *m*, 1 H); 1.76 (*s*, HO); 2.08–0.90 (*m*, 9 H). – MS.: 202 (M^+, $C_{14}H_{18}O$, 1), 184 (2), 158 (*100*), 143 (27), 130 (36), 117 (36), 115 (21), 104 (16), 91 (33), 80 (5), 67 (6), 57 (5), 41 (9).

$C_{14}H_{18}O$ (202.28) Calc. C 83.12 H 8.97% Found C 82.96 H 9.04%

32b: m.p. 76–78° (from hexane). – IR. (CCl_4): 3625*m*, 3615*m*, 3320br.*m*, 3085*w*, 3065*w*, 3030*m*, 2970*m*, 2930*s*, 2855*s*, 1602*w*, 1492*m*, 1451*m*, 1445*m*, 1438*w*, 1398*w*, 1290*w*, 1280*w*, 1194*w*, 1168*w*, 1156*w*, 1136*m*, 1090*s*, 1070*m*, 1033*m*, 976*w*, 912*w*, 878*w*, 700*s*. – ^{1}H-NMR. (CCl_4): 7.26–6.90 (*m*, C_6H_5); 4.18 (*qa*, J=7.5, H–C(7)); 1.39 (*s*, HO); 2.42–1.08 (*m*, 11 H). – MS.: 202 (M^+, $C_{14}H_{18}O$, <1), 158 (*100*), 143 (25), 130 (34), 117 (28), 115 (19), 104 (13), 91 (25), 80 (6), 67 (5), 57 (4), 41 (5).

$C_{14}H_{18}O$ (202.28) Calc. C 83.12 H 8.97% Found C 83.00 H 8.85%

Oxidation of **32a** (29 mg) by the chromium oxide-pyridine complex in methylene chloride; and distillation of the reaction product afforded *2(or 6)-phenylbicyclo[4.2.0]octan-7-one* (**48**); (18 mg) as colorless oil. Oxidation of the other isomer **32b** in the same way gave the same ketone **48**. – IR. (CCl_4): 3085*w*, 3060*w*, 3030*m*, 2930*s*, 2860*m*, 2850*m*, 1780*s*, 1600*w*, 1494*w*, 1450*m*, 1445*m*, 1412*w*, 1400*w*, 1178*w*, 1156*w*, 1122*w*, 1090*w*, 1070*w*, 1060*w*, 1032*w*, 984*w*, 920*w*, 875*w*, 700*s*. – ^{1}H-NMR. (CCl_4): 7.30–6.95 (*m*, C_6H_5); 3.40–1.20 (*m*, 11 H). – MS.: 200 (M^+, $C_{14}H_{16}O$, 3), 158 (*100*), 143 (18), 130 (44), 117 (24), 115 (19), 104 (16), 91 (18), 77 (7), 67 (4), 51 (5), 41 (4).

$C_{14}H_{16}O$ (200.27) Calc. C 83.96 H 8.05% Found C 83.50 H 8.33%

trans-*1,2,3,4,4a,9,10,10a-Octahydrophenanthren-9-ol* (**33a/33b**) [16–18]: m.p. 85.5–86.5° (from hexane). – IR. (CCl_4): 3610*m*, 3070*w*, 3030*w*, 2930*s*, 2858*s*, 1604*w*, 1485*m*, 1448*m*, 1378*m*, 1272*w*, 1235*w* 1182*w*, 1142*w*, 1093*w*, 1068*m*, 1046*m*, 1026*m*, 1000*m*, 978*m*, 964*w*, 933*w*, 894*m*, 860*w*, 845*w*. – ^{1}H-NMR. (CCl_4): 7.46–6.90 (*m*, H–C(5), H–C(6), H–C(7), H–C(8)); 4.56 (*m*, $w_{1/2}$=16, H–C(9)); 1.96 (*s*, HO); 2.50–0.90 (*m*, 12 H). – MS.: 202 (M^+, $C_{14}H_{18}O$, 27), 184 (*100*), 169 (8), 158 (11), 155 (17), 141 (82), 120 (84), 115 (31), 105 (20), 91 (27), 77 (16), 65 (9), 55 (7), 41 (8).

$C_{14}H_{18}O$ (202.28) Calc. C 83.12 H 8.97% Found C 83.00 H 9.00%

Oxidation of **33a/33b** (27 mg) gave 28 mg of crude product; recrystallization from hexane afforded *1,2,3,4,4a,10a-hexahydro-9(10H)-phenanthrone* (**52**, 23 mg) as colorless, fine needles, m.p. 93° ([7a]: 95°; [7b]: 95–96°). – UV. (EtOH): 244 (12,000), 280 (1000). – IR. (CCl_4): 3065*w*, 3030*w*, 2930*s*, 2855*m*, 1688*s*, 1600*m*, 1475*w*, 1450*m*, 1445*m*, 1410*w*, 1342*w*, 1314*w*, 1286*s*, 1250*m*, 1155*w*, 1090*w*, 1045*w*, 1030*m*, 960*w*, 934*w*, 980*w*, 863*w*. – ^{1}H-NMR. (CCl_4): 7.95 (*m*, H–C(8)); 7.5–7.1 (*m*, H–C(5), H–C(6), H–C(7)); 2.64–2.42 (*m*, H–C(4a)); 2.58 (*d*×*d*, J_1=16.0, J_2=3.5, 1 H–C(10)); 2.22 (*d*×*d*, J_1=16.0, J_2=12.0, 1 H–C(10)); 2.0–1.0 (*m*, 9 H). – MS.: 200 (M^+, $C_{14}H_{16}O$, 92), 185 (56), 182 (32), 171 (23), 167 (23), 158 (*100*), 144 (19), 131 (70), 115 (65), 105 (37), 103 (30), 91 (20), 77 (35), 63 (9), 51 (11), 41 (14).

$C_{14}H_{16}O$ (200.27) Calc. C 83.96 H 8.05% Found C 83.48 H 8.17%

*3-Ethoxy-1-(*trans-*2-phenylcyclohexyl)-2-butanols* (**34a** and **34b**). **34a**: liquid. – IR. (CCl_4): 3580*m*, 3080*w*, 3060*w*, 3025*m*, 2975*s*, 2930*s*, 2855*s*, 1600*w*, 1491*m*, 1445*s*, 1402*m*, 1373*m*, 1329*m*, 1285*m*, 1278*m*, 1250*w*, 1152*m*, 1120*s*, 1097*s*, 1086*s*, 1065*m*, 1050*m*, 1030*m*, 1002*w*, 990*w*, 960*w*, 935*w*, 912*w*, 890*w*, 868*w*, 858*w*, 842*w*, 700*s*. – ^{1}H-NMR. (CCl_4): 7.30–6.90 (*m*, C_6H_5); 3.46 (*m*, $w_{1/2}$=22.0, H–C(2)); 3.24 (*m*, $w_{1/2}$=21.0, 2 H–C(1)); 2.83 (*m*, $w_{1/2}$=13.0, H–C(3)); 2.17 (*s*, HO); 2.22–1.10 (*m*, 12 H); 1.08 (*t*, J=6.0, CH_3CH_2O); 0.86 (*d*, J=6.0, 3 H–C(4)). – MS.: 276 (M^+, $C_{18}H_{28}O_2$, 1), 230 (7), 212

(4), 202 (15), 185 (57), 158 (62), 149 (8), 143 (11), 129 (12), 117 (24), 107 (17), 91 (48), 81 (15), 73 (*100*), 67 (5), 57 (7), 45 (50).

$C_{18}H_{28}O_2$ (276.40) Calc. C 78.21 H 10.21% Found C 78.12 H 10.25%

34b: liquid. – IR. (CCl_4): 3585*m*, 3085*w*, 3065*w*, 3030*m*, 2980*s*, 2930*s*, 2855*s*, 1600*w*, 1492*w*, 1446*s*, 1385*m*, 1374*m*, 1334*w*, 1300*w*, 1245*w*, 1200*w*, 1150*w*, 1133*m*, 1100*s*, 1044*w*, 1032*w*, 1020*w*, 985*w*, 964*w*, 946*w*, 912*w*, 702*s*. – ^{1}H-NMR. (CCl_4): 7.31–6.90 (*m*, C_6H_5); 3.56 (*m*, $w_{1/2}$ = 13.0, H–C(2)); 3.34 (*m*, $w_{1/2}$ = 16.0, 2 H–C(1)); 3.02 (*m*, H–C(3)); 2.20–1.10 (*m*, 12 H); 1.47 (*d*, *J* = 4.0, HO); 1.08 (*t*, *J* = 6.0, CH_3CH_2O); 0.81 (*d*, *J* = 6.0, 3 H–C(4)). – MS.: 276 (M^+, $C_{18}H_{28}O_2$, 1), 230 (4), 212 (3), 202 (12), 185 (54), 158 (56), 149 (11), 143 (10), 129 (12), 117 (23), 107 (18), 91 (45), 81 (15), 73 (*100*), 67 (5), 57 (6), 45 (57).

$C_{18}H_{28}O_2$ (276.40) Calc. C 78.21 H 10.12% Found C 78.53 H 10.17%

Oxidation of **34a** (8.3 mg) with the chromium oxide-pyridine complex in methylene chloride gave 8.3 mg of crude product. GLC. purification gave liquid *3-ethoxy-(*trans*-2-phenylcyclohexyl)-2-butanone* (**53**). Oxidation of **34b** in the same way and distillation of the crude product (145°/0.04 Torr) led to the same ketone. – IR. (CCl_4): 3090*w*, 3067*w*, 3035*w*, 2985*s*, 2860*s*, 1713*s*, 1600*w*, 1490*w*, 1445*m*, 1400*w*, 1370*m*, 1323*w*, 1110*s*, 1030*w*, 990*w*, 955*w*, 930*w*, 880*w*, 703*s*. – MS.: 274 (M^+, $C_{18}H_{26}O_2$, < 1), 256 (5), 201 (20), 183 (3), 158 (38), 117 (6), 115 (6), 105 (9), 91 (25), 73 (*100*), 45 (53).

3-Phenylcyclohexene (**35**) [8]: liquid. – UV. (pentane): 249 (930). – IR. (CCl_4): 3085*m*, 3065*m*, 3030*s*, 2930*s*, 2860*s*, 2840*s*, 1647*w*, 1600*m*, 1492*s*, 1448*s*, 1434*m*, 1375*w*, 1334*w*, 1321*w*, 1300*w*, 1360*w*, 1245*w*, 1136*m*, 1077*m*, 1040*w*, 1030*m*, 1005*w*, 985*w*, 912*m*, 898*m*, 882*m*, 847*w*, 720*m*, 701*s*. – ^{1}H-NMR. (CCl_4): 7.30–6.90 (*m*, C_6H_5); 5.92–5.54 (*m*, H–C(1) and H–C(2)); 3.29 (*m*, $w_{1/2}$ = 15.0, H–C(3)); 2.20–1.20 (*m*, 6 H). – MS.: 158 (M^+, $C_{12}H_{14}$, *100*), 143 (50), 130 (69), 129 (81), 117 (31), 115 (50), 104 (50), 91 (38), 77 (19), 57 (13), 41 (6).

$C_{12}H_{14}$ (158.23) Calc. C 91.08 H 8.92% Found C 91.03 H 8.92%

1-Phenylcyclohexene (**36**) [8]: liquid. – UV. (pentane): 246 (13,000). – IR. (CCl_4): 3085*m*, 3060*m*, 3030*m*, 2930*s*, 2860*s*, 2835*s*, 1643*w*, 1600*m*, 1492*m*, 1446*m*, 1438*m*, 1350*w*, 1276*w*, 1242*w*, 1139*m*, 1075*m*, 1060*m*, 1022*w*, 1006*w*, 920*m*, 904*w*, 847*m*, 696*s*. – ^{1}H-NMR. (CCl_4): 7.40–6.90 (*m*, C_6H_5); 5.98 (*m*, $w_{1/2}$ = 8.0, H–C(2)); 2.60–2.00 (*m*, 2 H–C(3) and 2 H–C(6)); 1.96–1.40 (*m*, 2 H–C(4) and 2 H–C(5)). – MS.: 158 (M^+, $C_{12}H_{14}$, *100*), 143 (56), 130 (71), 129 (86), 115 (58), 104 (27), 91 (32), 80 (10), 77 (18), 67 (10), 51 (12), 41 (5).

$C_{12}H_{14}$ (158.23) Calc. C 91.08 H 8.92% Found C 90.95 H 8.98%

trans-*1-Methyl-2-phenylcyclohexane* (**37**) [9]: liquid. – UV. (pentane): 260 (552). – IR. (CCl_4): 3085*m*, 3065*m*, 3030*s*, 2925*s*, 2870*s*, 2855*s*, 1600*m*, 1491*m*, 1452*s*, 1448*s*, 1375*m*, 1300*w*, 1250*w*, 1150*w*, 1139*w*, 1080*m*, 1068*w*, 1029*w*, 987*w*, 968*w*, 956*w*, 913*w*, 880*w*, 975*w*, 864*w*, 700*s*. – ^{1}H-NMR. (CCl_4): 7.30–6.90 (*m*, C_6H_5); 2.20–1.00 (*m*, 10 H); 0.63 (*d*, *J* = 6.0, H_3C–C(1)). – MS.: 174 (M^+, $C_{13}H_{18}$, 51), 158 (12), 143 (6), 131 (10), 129 (14), 117 (51), 104 (*100*), 91 (42), 78 (7), 77 (8), 67 (6), 55 (9), 41 (7).

$C_{13}H_{18}$ (174.27) Calc. C 89.59 H 10.41% Found C 89.40 H 10.27%

trans-*2-Phenylbicyclo[4.1.0]heptane* (**38**) [10]: liquid. – UV. (pentane): 259 (473). – IR. (CCl_4): 3080*m*, 3060*s*, 3025*s*, 3000*s*, 2925*s*, 2855*s*, 1600*m*, 1490*s*, 1461*s*, 1450*s*, 1380*w*, 1363*w*, 1346*w*, 1335*w*, 1323*w*, 1300*w*, 1291*w*, 1260*w*, 1164*w*, 1142*w*, 1131*w*, 1113*w*, 1090*m*, 1078*m*, 1063*m*, 1030*m*, 1015*s*, 972*w*, 945*w*, 910*w*, 890*m*, 876*w*, 846*w*, 830*w*, 700*s*. – ^{1}H-NMR. (CCl_4): 7.30–6.94 (*m*, C_6H_5); 2.77 (*m*, $w_{1/2}$ = 11.0, H–C(2)); 1.98–0.88 (*m*, 8 H); 0.65 (*m*, $w_{1/2}$ = 13.0, H–C(7)); 0.15 (*qa*, *J* = 5.0, H–C(7)). – ^{13}C-NMR. ($CDCl_3$): 149.2 (*s*), 128.2 (2*d*), 127.6 (2*d*), 125.7 (*d*), 42.3 (*d*), 31.9 (*t*), 23.2 (*t*), 18.7 (*t*), 16.2 (*d*), 10.6 (*d*), 10.44 (*t*). – MS.: 172 (M^+, $C_{13}H_{16}$, 41), 158 (13), 144 (64), 129 (76), 117 (85), 115 (50), 104 (*100*), 91 (59), 81 (25), 77 (19), 65 (13), 51 (11), 39 (13).

$C_{13}H_{16}$ (172.26) Calc. C 90.64 H 9.36% Found C 90.51 H 9.46%

Photolysis of **31**. A solution of 830 mg of **31** in 200 ml of ether was irradiated with > 235 nm light for 2.5 h. The mixture obtained was separated by silicagel column chromatography. Elution with ether/hexane 1:10 gave **35**/**36**/**37** (210 mg) in 15, 17 and 0.8% yield (GLC.), respectively. They

were isolated in pure form by GLC. Elution with ether/hexane 1:2 afforded **32a** (44 mg), **32b** (43 mg), **33a/33b** (48 mg), **34a** (63 mg) and **34b** (133 mg).

Photolysis of **16**. 1) A THF solution of **16** (0.03 M) was irradiated with >235 nm light and the yield of *1-hexadecene* (**3**) determined by GLC. to be 62%.

2) An ethanol solution of **16** (750 mg) was irradiated with >280 nm light for 16 h. The mixture obtained was chromatographed on 20 g of silicagel. Elution with hexane/benzene 2:1 gave 350 mg of **3**.

Photolysis of **39**. A solution of **39** (1.02 g) in 200 ml of ether was irradiated with >235 nm light. The mixture obtained after 95% conversion of **39** was separated by a combination of GLC. and column chromatography giving **40** (120 mg) and **41** (45 mg) in pure form. Many other products were also detected on TLC. but could not be isolated in pure form. *2-Methyl-1,3,4-oxadiazol* (**40**) [11]: liquid. – UV. (MeOH): 206 (421). – IR. (CCl_4): 3160*w*, 3080*w*, 2980*w*, 2940*w*, 1640*w*, 1584*s*, 1560*m*, 1522*m*, 1510*m*, 1442*m*, 1389*m*, 1352*w*, 1337*w*, 1305*s*, 1275*w*, 1214*s*, 1097*s*, 1045*w*, 1027*m*, 953*m*, 928*s*, 835*m*, 680*m*, 639*s*. – ^{1}H-NMR. ($CDCl_3$): 8.33 (*s*, H–C(5)); 2.54 (*s*, CH_3). – MS.: 84 (M^+, $C_3H_4N_2O$, *100*), 73 (5), 56 (15), 55 (30), 45 (8), 43 (53), 41 (12).

$C_3H_4N_2O$ (84.08) Calc. C 42.85 H 4.80 N 33.32% Found C 42.67 H 4.85 N 33.12%

1(or 2)-(1'-Ethoxyethyl)tetrazole (**41**): liquid. – UV. (pentane): 203 (4400). – IR. (CCl_4): 2985*m*, 2945*m*, 2925*m*, 2885*w*, 1480*w*, 1444*m*, 1385*m*, 1376*m*, 1365*w*, 1337*m*, 1315*s*, 1282*s*, 1272*w*, 1220*w*, 1174*m*, 1165*m*, 1155*m*, 1135*s*, 1120*s*, 1096*w*, 1066*m*, 1027*m*, 1018*m*, 1001*m*, 949*m*, 853*w*, 708*m*. – ^{1}H-NMR. (CCl_4): 8.38 (*s*, H–C(5)); 5.98 (*qa*, J=6.0, H–C(1')); 3.70–3.14 (*m*, CH_3CH_2O); 1.82 (*d*, J=6.0, 3 H–C(2')); 1.13 (*t*, J=7.0, CH_3CH_2O). – MS.: 141 (M^+-1, 2), 73 (89), 69 (7), 57 (4), 45 (*100*), 43 (34), 41 (9).

$C_5H_{10}N_4O$ (142.16) Calc. C 42.24 H 7.09 N 39.41% Found C 42.21 H 7.07 N 39.41%

Photolysis of **42**. A solution of **42** (2.34 g) in ether was irradiated with >235 nm light for 48 h. Solvent and volatile hydrocarbons were distilled off carefully under atmospheric pressure using a *Vigreux*-column; the distillate was analyzed by GLC. (SE-30): **25** (13%), **26** (2.2%) and **27** (3.4%) were identified. The residual oil of the distillation was separated by a combination of column chromatography and GLC. giving **18**, **22a**, **22b**, **22c/22d**, **23a/23b**, **24a/24b/41** and 383 mg of **43**. The yields were determined by GLC. (SE-30 and *Carbowax* 20M) as follows: **18** (1.5%), **22a** (0.6%), **22b** (0.4%), **22c/22d** (0.7%), **23a/23b** (2.9%), **24a/24b** (2.2%) and **41** (0.3%). *2-Cyclohexylmethyl-1,3,4-oxadiazole* (**43**). m.p. 61–62° (from hexane). – UV. (MeOH): 209 (751). – IR. (CCl_4): 3160*w*, 3000*m*, 2930*s*, 2860*s*, 1574*s*, 1525*w*, 1510*w*, 1450*s*, 1102*s*, 980*m*, 960*m*, 930*w*, 897*w*, 844*m*, 640*m*. – ^{1}H-NMR. ($CDCl_3$): 8.30 (*s*, H–C(5)); 2.76 (*d*, J=7.0, $C_6H_{11}CH_2$); 2.10–0.80 (*m*, 11 H). – ^{13}C-NMR. ($CDCl_3$): 166.1 (*s*), 153.3 (*d*), 36.2 (*d*), 32.8 (2*t*), 32.5 (*t*), 26.0 (*t*), 25.9 (2*t*). – MS.: 166 (M^+, $C_9H_{14}N_2O$, 1), 165 (1), 149 (7), 123 (2), 84 (*100*), 67 (2), 55 (16), 41 (11).

$C_9H_{14}N_2O$ (166.22) Calc. C 65.03 H 8.49 N 16.85% Found C 64.80 H 8.55 N 16.77%

Photolysis of **45**. A solution of **45** (3.65 g) in 400 ml of THF was irradiated with >235 nm light for 24 h. After evaporation the residue was chromatographed on 200 g of silicagel. Elution with hexane/ether 8:1 afforded **3/4** (440 mg) and **6** (46 mg). The ratio **3/4** was about 4.6:1 (GLC.).

Irradiation of 22 in the presence of 1-acetyl-1,2,4-triazole (1). – A mixture of 11.1 mg of **1** and 12.6 mg of an isomeric mixture of bicyclo[4.2.0]octan-7-ols (**22**) was irradiated with >235 nm light both in 4 ml of dry ether and in 1 ml of dry THF. The reaction was followed by GLC. (*Carbowax* 20M). Conversion of **22** into bicyclooctanone **24** was not observed.

Pyrolysis of 39 and 42. – A solution of **39** (314 mg) in 0.5 ml of dry toluene was heated under reflux for 20 h and the product was separated by column chromatography on 5 g of alumina. Elution with pentane/ether 5:1 afforded 140 mg (60%) of **40**.

A solution of **42** (137 mg) in 5 ml of dry toluene was heated under reflux for 2 days. After evaporation of the solvent i.V. the residue was chromatographed on 20 g of silicagel. Elution with hexane/ether 1:1 gave 55 mg (51%) of **43**, 11.3 mg (12%) of **44** and 4.5 mg of unknown product. *2,2'-Dicyclohexyldiacetamide* (**44**): m.p. 161° (from methanol). – IR. ($CHCl_3$): 3400*m*, 3260*w*, 3210*w*, 3150*w*, 2935*s*, 2850*s*, 1730*s*, 1695*s*, 1604*w*, 1490*m*, 1460*s*, 1449*s*, 1380*m*, 1363*m*, 1318*m*, 1295*s*, 1262*m*, 1181*m*, 1164*s*, 1138*m*, 1120*m*, 1065*w*, 1052*w*, 1000*w*, 972*w*, 960*w*, 937*w*, 914*w*, 899*w*. – ^{1}H-NMR.

($CDCl_3$): 8.26–8.04 (br. *s*, HN); 2.44 (*d*, $J = 7.0$, 2 CH_2CO); 2.00–0.80 (*m*, 22 H). – MS.: 265 (M^+, $C_{16}H_{27}NO_2$, 28), 183 (*100*), 168 (7), 155 (9), 149 (31), 142 (63), 141 (49), 125 (63), 101 (33), 97 (58), 81 (32), 60 (56), 59 (60), 55 (88), 41 (44).

$C_{16}H_{27}NO_2$ (265.38) Calc. C 72.41 H 10.26 N 5.28% Found C 72.51 H 10.29 N 5.32%

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