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Azimines. VIII[1]. Contribution to the Preparation and Thermolysis of Alkyl (2Z)-2,3-Diisopropyl-azimine-1-carboxylates[+]

Hans Hilpert, Lienhard Hoesch and André S. Dreiding*

Organisch-Chemisches Institut der Universität Zürich, Winterthurerstr. 190, CH-8057 Zürich, Switzerland

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After improving the preparation of the azimines *9* (*a* = methyl, *b* = ethyl ester), we reinvestigated the mild thermolysis of *9* to *13* in $CDCl_3$: Unlike previously postulated, the azimines *9* first undergo a 1,4-H migration to the triazones *14* (step a), which suffer an elimination to yield the diazenes *16* (step b), which, in turn, are finally transformed by a 1,3-H migration to the carbazates *13* (step c). Step a is base catalyzed while step b is not (or less), so that *14*, example of a relatively rare class of compounds, could be isolated after thermolysis of *9* in *t*-butylamine. During the thermolyses of pure *14* in $CDCl_3$, the diazenes *16* accumulated transiently (step b) before passing to *13*. This accumulation of *16* was less (10%, as compared to 40%) when starting with 10% (as compared to 1%) solution of *14*, which suggest that the conversion of *16* to *13* (step c) is catalyzed by *14*. With pure *16*, prepared in another way, step c occured in a 1% $CDCl_3$ solution at 50 °C with $t_{1/2} = \sim 21$ hrs. Step c also proved to be catalyzed by silica.

INTRODUCTION

Alkyl azimine-1-carboxylates as the (2Z)- and (2E)-stereoisomers *6* and *7* have been prepared[2] in modest yields by the stereospecific addition of alkoxycarbonyl-nitrenes *3*, generated by base promoted 1,1-hydro-sulfonyloxy--elimination** from alkyl *N*-[(4-nitrophenyl)sulfonyloxy]carbamates *2*, to (E)- and (Z)-azo compounds *4* and *5*. We have now improved these preparations by using the alkyl *N*-[(2-nitrophenyl)sulfonyloxy]carbamates *1*[4] instead of their 4-nitro isomers *2* for the nitrene generation, otherwise keeping the conditions as described before.[2]

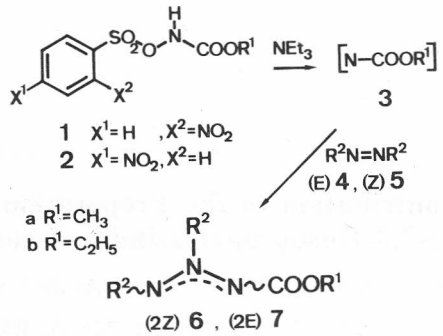
In this way *1a, b* was reacted with (E)-1, 1'-dimethylazoethane (*8*) to yield methyl and ethyl (2Z)-2,3-diisopropyl-azimine-1-carboxylate (*9a* and *9b*, 25% and 49%).

[+] Dedicated to Professor Mihailo Lj. Mihailović on the occasion of his 60th birthday.

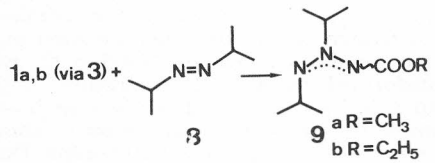
* Present address: Institut für Pflanzenbiologie, Universität Zürich, Zollikerstr. 107, CH-8008 Zürich, Switzerland.

** Term according to »IUPAC Provisional Nomenclature for Straightforward Transformations«.[3]

Scheme 1



Scheme 2



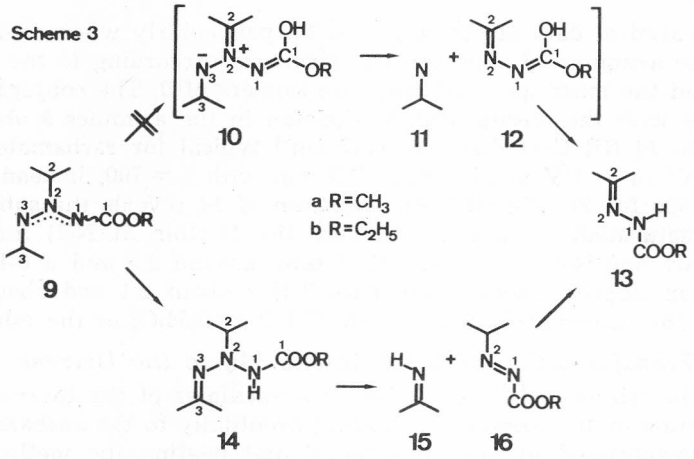
This higher yield access (improvement by a factor of 1.3—1.9) to the (2Z)--diisopropyl-azimines *9* was of help when we set out to identify still unknown by-products and intermediates which had been observed in the thermolysis[2] (and photolysis[5]) of *9*.

Mild thermolysis (62 °C) of ethyl (2Z)-2,3-diisopropyl-azimine-1-carboxylate (*9b*) in $CDCl_3$ had previously been shown[2] to lead to ethyl 2-isopropylidene-diazane-1-carboxylate (*13b*, 83%), carbazate. In order to explain the formation of a double bond between (2) and N(2) in the carbazate *13b*, we had at the time considered an initial 1,5-H migration of H—C(2) to the carbonyl O-atom of the azimine (*9* → *10*) together with an elimination of the nitrene *11* to generate the enol *12* of the final product *13* (top of Scheme 3). In the following we report that the conversion of the azimine *9* to the carbazate *13* is, in fact, initiated by a 1,4-H migration of H—C(3) to N(1) (*9* → *14*), then passes *via* the diazene *16* to the final product *13*, which implies elimination of isopropylideneamine *15* (bottom of Scheme 3).

Thermal Transformation of the (2Z)-Azimines 9a *and* 9b *to the Triazones* 14a *and* 14b

The new reaction course (*9* → *14* → *16* → *13*) was first discovered when the thermolysis of the azimines *9* was performed under somewhat milder conditions, namely at 45 °C instead of 62 °C, in $CDCl_3$: By monitoring the course of the reaction with ^{1}H-NMR, we found the transient appearance of alkyl 2-isopropyl-3-isopropylidene-triazane-1-carboxylates *14*. These products are new examples of alkylidene derivatives of triazanes, which have so far

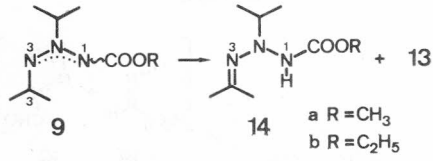
Scheme 3



been met with only rarely*. They might be called triazones in analogy with the term hydrazones as applied to alkylidene derivatives of hydrazines. Evidence for the structure of *14a, b* will be given below, after their preparative isolation has been described.

Two modes of 1,4-migration of H—C(3) to N(1) might be considered for the isomerization of the azimine *9* to the triazone *14*, either an intramolecular (non-catalyzed)** or an intermolecular (potentially base or acid catalyzed) process. In order to test this alternative, we performed the thermolyses of *9a* and *9b* in *t*-butylamine instead of $CDCl_3$ until the ^{1}H-NMR signals of the starting azimines[2] (those of the two methine H-atoms and of the OCH_3 or OCH_2CH_3) group had disappeared. After that it was possible to isolate the triazones *14a* (72%) and *14b* (65%), together with the carbazates *13a* (10%) and *13b* (9%), respectively (Scheme 4). In *t*-butylamine the disappearance of the azimine *9a* was about *45* times as fast as in $CDCl_3$. This means that the isomerization of *9* to *14* is a base catalyzed process. Furthermore, since *14* had accumulated to a greater extent (allowing isolation) in *t*-butylamine than in $CDCl_3$, the fragmentation of the triazone *14*, leading eventually to the carbazate *13*, is not equally enhanced by the basic medium.

Scheme 4



* Known are two examples of 1-acyl-3-benzylidene-2-phenyl-triazanes[6] (such as *17*), two examples of 1,2-diacyl-3-benzylidene-triazanes,[7] 1,1-diethyl-2-trifluoromethyl-3-difluoromethylidene-triazane[8] and 3-bisanilinomethylene-1,1-diethyl-2-trifluoromethyl-triazane.[8]

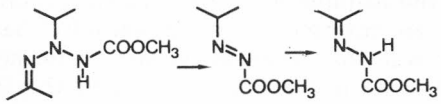
** A remotely related case might be the sigmatropic [1,4] shift of an alkyl group in the rearrangment of 2-alkoxypyridine-*N*-oxides to *N*-alkoxy-2-pyridones.[9]

The analytical data of the triazones *14*, particularly when compared with those of the azimines *9*,[2] support their structure. According to the elementary analysis and the mass spectrum they are isomers of *9*. The conjugation of the ester group with the unsaturated N_3-skeleton in the azimines *9* obviously has been lost in *14* (IR C=O-band at 1745 cm^{-1} typical for carbamates,[10] instead of 1675 cm^{-1} in *9*; UV maximum at 255 nm with $\varepsilon = 700$, instead of 285 nm with $\varepsilon = 7500$ for *9*). The ^{1}H-NMR spectrum of *14* reveals the substituents of the (now saturated) N_3-skeleton, namely the H-atom at N(1) (br. s around 6 ppm), only one isopropyl group (1-H sept. around 2.9 and a 6-H d around 1.1 ppm), an isopropylidene group (two 3-H s about 2.1 and about 2.0 ppm) as well as the respective alkoxy group (CH_3O or C_2H_5O) of the ester function.

Thermal Transformation of the Triazone 14a *to the Diazene* 16a

That the triazones 14 are, in fact, intermediates of the thermal fragmentation reaction of the azimines *9*, leading eventually to the carbazates *13*, was further substantiated by the observation that heating the methyl ester *14a* in $CDCl_3$ at 50 °C for a longer time (12—25 hrs., depending on the concentration) yielded *13a* (70%). But even this reaction proceeds *via* a further intermediate, namely methyl 2-isopropyl-diazene-1-carboxylate (*16a*), the known[11] ^{1}H-NMR signals of which appeared transiently.

Scheme 5



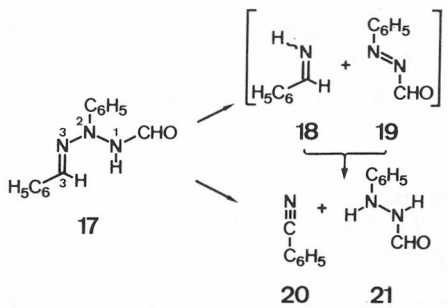
14a **16a** **13a**

We assume that the diazenes *16* are formed from the triazones *14* by a 1,2-hydro-imino-elimination*. The second product of this reaction, the known[12] isopropylideneamine (*15*), was not identified; it might be the origin of the polymeric material mentioned in ref.[2]

Interpretation of the N,N*-Cleavage of Another Triazone*

One of the other examples of triazones (see above) in the literature,[6] 3-benzylidene-2-phenyl-triazane-1-carbaldehyde (*17*), is also reported[6] to be thermally unstable; upon melting (188 °C) it yields benzonitrile (*20*, 70%) and 1-formyl-2-phenylhydrazine (*21*, 80%).

Scheme 6



17 **18** **19** **20** **21**

* See footnote on page 559.

As a rational for this conversion in the light of the present results one might consider two possibilities: a) a 1,3-migration of the vinyl H-atom from C(3) to N(2) with accompanying N(2), N(3) bond cleavage (an intramolecular 1,2-hydro-hydrazino-elimination*), leading directly to *20* and *21*, or b) a 1,2--hydro-imino-elimination* to benzylideneamine (*18*) and 2-phenyl-diazene-1--carbaldehyde (*19*) (in analogy to the thermal decomposition of the triazones *14* to the diazenes *16*), followed by an intermolecular redox reaction (since *19*, unlike *16*, cannot undergo an azo-hydrazone rearrangment,[11,13] see below) to the ultimate products *20* and *21*.

Transformation of the Diazene 16a *to the Carbazate* 13a

Attempts to isolate the (previously known[11]) diazene *16a* from the thermolysis of *14a* by chromatography of the reaction mixture on silica yielded only the carbazate *13a*, presumably as the result of an acid catalyzed isomerization of *16a*. This conversion is an example of the well known[13] azo--hydrazone-rearrangement; it has already been observed earlier[11] with *16a*, namely under base catalysis or upon storage. We found the conversion to *13a* also on tlc of authentic[11] *16a* with silica.

Under the thermolysis conditions of the triazones *14*, the isomerization of *16* to *13* seems to be catalyzed by the disappearing *14*. This follows from two observations, namely a) that the thermolysis of a 1% solution of *14a* in $CDCl_3$ at 50 °C led to an intermediate accumulation of up to 40% of *16a*, while a 10% solution of *14a* permitted an accumulation of only 10% of *16a*, and b) that the thermolysis of the 1% solution of *14a* reached a thermally stable situation with *13a* as the major product (70%) already after 25 hrs. at 50 °C, whereas a 1% solution of authentic[11] *16a* under about the same conditions was isomerized to *13a* only to an extent of about 50%.

Acknowledgment. — This work was supported by the Swiss National Science Foundation and by Sandoz AG, Basel.

EXPERIMENTAL

General

See[14]. The interpretations of the mass spectra are hypothetical; no high resolution spectra were measured.

Improved Synthesis of Methyl and Ethyl (2Z)-2,3-Diisopropyl-azimine--carboxylate (9a and 9b)

Methyl and Ethyl N-*[(2-Nitrophenyl)sulfonyloxy]carbamate* (1a and 1b)

The procedure described[4] for *1b* was modified as follows: In order to obtain *1a* a solution of 115.6 g (1.27 mol) methyl *N*-hydroxycarbamate (prepared according to[15] and used as a crude product after drying at 35 °C/0.1 Torr for 7 hrs.) in 500 ml Et_2O was added to a stirred suspension of 47.0 g (1.125 mol) 55—60% NaH-dispersion in mineral oil (washed 3times with pentane) in 3200 ml Et_2O over a period of 30 min. After stirring for another 50 min. at r. t. and 40 min. under reflux, the reaction mixture was cooled to 10 °C, treated with a solution of 249.3 g (1.125 mol) 2-nitrobenzenesulfonyl chloride (Fluka pract., dried at 35 °C/0.5 Torr for 6 hrs.) in 750 ml Et_2O and stirred at 10—15 °C for 60 min. After filtering and washing the residue twice with 300 ml Et_2O each, the filtrate was evaporated and its residue dried at 22 °C/0.2 Torr, affording 268 g crude *1a* as a yellow solid, m. p. 80—100 °C. Crystallization of 67 g of this crude product from 450 ml $CHCl_3$ at −20 °C yielded

* See footnote on page 559.

56 g (72%) purified *1a* as a beige powder, m. p. 114—116 °C, which decomposed slowly upon storage at r. t. For the elemental and spectral analysis, 100 mg crude *1a* were recrystallized 3times from $CHCl_3$ to give 72 mg pure *1a* as beige globules, m. p. 115—116 °C. UV (EtOH): 274 sh (1610), 266 sh (1680), 205 (13150). IR ($CHCl_3$): 3360w, 3030w, 1785m, 1755m, 1555s, 1450m, 1405s, 1365m, 1130w, 1085w, 1065m, 855w. ^{1}H-NMR (60 MHz, d_6-acetone): 10.33/br. s, 1H (NH); 8.3—7.8/m, 4 H (aryl-H); 3.66/s, 3 H (OCH_3). MS (70 eV): 187/11, 186/100 ($C_6H_4NO_4S^+$), 76/12, 59/10, 51/16, 50/16, 39/11.

Anal. $C_8H_8N_2O_7S$ (276.23) calc'd.: C 34.78; H 2.92; N 10.14%
found: C 34.43; H 2.99; N 9.69%

The preparation of *1b* from 45.5 g (0.433 mol) ethyl *N*-hydroxycarbamate (prepared in the same manner as the corresponding methyl carbamate[15] and used as a crude product after drying at 40 °C/0.1 Torr for 3 hrs.), 15.7 g (0.38 mol) NaH-dispersion (3times washed with pentane) and 83.1 g (0.38 mol) 2-nitrobenzenesulfonyl chloride was accomplished in the same manner as described above for *1a* to yield 62.1 g (57%) *1b* after crystallization from toluene as a beige powder, m. p. 75—83 °C. For the elemental and spectral analysis 500 mg crude *1b* were recrystallized 4times from toluene to afford 401 mg pure *1b* as beige needles, m. p. 85—85.5 °C (ref.[4]. 87—89 °C). UV (EtOH): 274 sh (1510), 266 sh (1680), 204 (13530). IR ($CHCl_3$: 3360w, 3030w, 1780m, 1745m, 1550s, 1470w, 1445m, 1405s, 1380m, 1370m, 1330m, 1130w, 1100w, 1080w, 1060w, 855w. ^{1}H-NMR (60 MHz, $CDCl_3$): 8.43/s, 1 H (NH); 8.3—7.5/m, 4 H (aryl-H); 4.06/q, $J = 7$, 2 H (OCH_2CH_3); 1.15/t, $J = 7$, 3 H (CH_3CH_2). MS (70 eV): 187/9, 186/100 ($C_6H_4NO_4S^+$), 92/24, 91/26, 77/14, 51/15, 50/15, 39/14.

Anal. $C_9H_{10}N_2O_7S$ (290.26) calc'd.: C 37.24; H 3.47; N 9.65%
found: C 37.36; H 3.49; N 9.87%

Thermolysis of Methyl and Ethyl (2Z)-2,3-Diisopropyl-azimine-1-carboxylate (9a and 9b)

A solution of 1.52 g (15 mmol) Et_3N in 15 ml CH_2Cl_2 was added dropwise within 20 min. to a stirred and cooled (15 °C) suspension of 4.15 g (15 mmol) *1a*, or of 4.35 g (15 mmol) *1b*, and 15.0 g (132 mmol) (E)-1,1'-dimethylazoethane (*8*) in 15 ml CH_2Cl_2. After stirring at r. t. for 60 min., the yellow solution in each case was evaporated to dryness at 22 °C/11 Torr and the residue treated with 50 ml Et_2O. The insoluble part was filtered off and washed several times with Et_2O. The filtrate and the washing solutions were evaporated and the residue after prep. LOBAR-LC (hexane/AcOEt 7 : 3, 10 ml/min., column B) yielded 0.72 g (25%) *9a*, or 1.48 g (49%) *9b*, respectively, as slightly yellow oils, which by ^{1}H-NMR were identical with the products described in literature.[2]

Methyl and Ethyl (2Z)-2,3-Diisopropyl-azimine-1-carboxylate (9a and 9b)

Thermolysis of 9a *in* $CDCl_3$

A solution of 103 mg *9a* in 0.5 ml $CDCl_3$ was kept at 45 ± 0.1 °C and monitored from time to time by ^{1}H-NMR (90 MHz). The transient appearance of methyl 2-isopropyl-3-isopropylidene-triazane-1-carboxylate (*14a*) was noted by the signals described in Experimental. After 7 hrs. a 4 : 1-mixture of *9a* and *14a* (ratio determined by means of the OCH_3 signals) represented the state of highest accumulation of *14a*. After 37 hrs. the signals of *9a*, *14a* and of methyl 2-isopropylidene-diazane-1-carboxylate (*13a*)[16] were found in a ratio of 3 : 1 : 4 (according to the OCH_3 signals), along with a number of unidentified signals, making up about 30% of the total integration.

Thermolysis of 9a *in* t-*Butylamine*

A solution of 107.1 mg (0.57 mmol) *9a* in 0.5 ml *t*-butylamine was kept at 45 ± 0.1 °C and monitored from time to time by ^{1}H-NMR (90 MHz). Within the first 10 min. a 4 : 1 ratio of *9a* and *14a* was observed (ratio determined by means of the OCH_3 signals). After 3.5 hrs. the methine and OCH_3 signals of *9a* had disappeared completely, while the signals (OCH_3) of *13a* had appeared only to a minor extent. The solution was evaporated to dryness at 22 °C/11 Torr and the residue fractionated by prep. LOBAR-LC (hexane/AcOEt/MeOH 16 : 6 : 1, 10 ml/min., column A).

The first fraction contained 76.7 mg (72%) ^{1}H-NMR pure methyl 2-isopropyl--3-isopropylidene-triazane-1-carboxylate (*14a*) as a colorless oil which, after two crystallizations from hexane at —25 °C, yielded 58 mg (54%) analytically pure *14a* as beige rosettes, m. p. 54.5—55.5 °C. UV (EtOH): 255 (730). IR ($CHCl_3$): 3350w (NH), 2970m, 1745s (C=O), 1715m, sh 1650w, 1500m, 1460m, 1435m, 1375m, 1365m, 1340w. ^{1}H-NMR (90 MHz, $CDCl_3$): 5.95/br. s, 1 H (HN(1)); 3.68/s, 3 H (OCH_3); 2.92/sept., J = 7, 1 H ($(CH_3)_2CHN(2)$); 2.13 and 1.95/each s, each 3 H ($(CH_3)_2C{=}N(3)$); 1.07/d, J = 7, 6 H ($(CH_3)_2CHN(2)$). MS (70 eV): 187/12 (M^+), 131/32, 116/23, 99/100, 89/18, 76/16, 73/31, 72/12, 71/17, 70/12.

Anal. $C_8H_{17}N_3O_2$ (187.25) calc'd.: C 51.31; H 9.15; N 22.45%
found: C 51.40; H 8.95; N 22.54%

From the second fraction was isolated, after trituration with pentane 7.6 mg (10%) methyl 2-isopropylidene-diazane-1-carboxylate (*13a*) as colorless needles, m. p. 89—91 °C (ref.[16]: 90—92 °C).

Thermolysis of 9b *in* t-*Butylamine*

A solution of 114.5 mg (0.57 mmol) *9b* in 0.5 ml *t*-butylamine was kept at 45 ± 1 °C and monitored by ^{1}H-NMR (60 MHz). After 2 hrs. the methine and OCH_2CH_3 signals of *9b* had completely disappeared, while the signals ($(CH_3)_2C{=}$) of *13b* had appeared only to a minor extent. The solution was evaporated to dryness at 22 °C/11 Torr and the residue fractionated by prep. Lobar-LC (hexane/AcOEt/MeOH 24 : 6 : 1, 8 ml/min., column A).

The first fraction contained 75 mg (65%) ^{1}H-NMR pure ethyl 2-isopropyl-3--isopropylidene-triazane-1-carboxylate (*14b*) as a colorless oil which, after crystallization from hexane at —25 °C, yielded analytically pure *14b* as colorless microcrystals, m. p. 35.5—36.5 °C. UV (EtOH): 255 (710). IR ($CHCl_3$): 3350w (NH), 2990m, 1745s (C=O), 1715m sh, 1650w, 1500m, 1470m, 1450m, 1385m, 1370m, 1335m. ^{1}H-NMR (90 MHz, $CDCl_3$): 5.85/br. s, 1 H (HN(1)); 4.12/q, J = 7, 2 H (OCH_2CH_3); 2.94/sept., J = 6.5, 1 H ($(CH_3)_2CHN(2)$); 2.14 and 1.98/each s, each 3 H ($(CH_3)_2C{=}N(3)$); 1.24/t, J = 7, 3 H (CH_3CH_2); 1.07/d, J = 6.5, 6 H ($(CH_3)_2CHN(2)$). MS (70 eV): 201/8 (M^+), 145/21, 87/36, 86/16, 73/100, 72/21, 71/36, 70/22, 62/80.

Anal. $C_9H_{19}N_3O_2$ (201.28) calc'd.: C 53.71; H 9.51; N 20.88%
found: C 53.85; H 9.59; N 21.13%

From the second fraction was isolated, after solidification at —25 °C, 7 mg (9%) ethyl 2-isopropylidene-diazane-1-carboxylate (*13b*) as colorless microcrystals, m. p. 58—65 °C (ref.[17]: 72—73 °C); ^{1}H-NMR (90 MHz, $CDCl_3$) as reported.[2]

Thermolysis of Methyl 2-Isopropyl-3-isopropylidene-triazane-1--carboxylate (14a)

At 1% Concentration in $CDCl_3$

A solution of 5 mg *14a* in 0.5 ml $CDCl_3$ was kept at 50 ± 1 °C and monitored from time to time by ^{1}H-NMR (90 HMz). After 5 hrs. the OCH_3 signals showed the presence of a 3 : 2 mixture of *14a* and methyl 2-isopropylidene-diazene-1-carboxylate (*16a*, ^{1}H-NMR as reported in ref.[11]), which represents the state of highest relative concentration of *16a*. After 25 hrs. a thermally stable mixture of ca. 70% methyl 2-isopropylidene-diazane-1-carboxylate (*13a*, ^{1}H-NMR as reported[16]) and about 30% signal intensity of several unidentified products was found.

At 10% Concentration in $CDCl_3$

A solution of 50 mg *14a* in 0.5 ml $CDCl_3$ was kept at 50 ± 1 °C and monitored by ^{1}H-NMR (90 MHz). After 3 hrs. the OCH_3 signals showed the presence of a 76 : 11 : 13 mixture of *14a*, *16a* and *13a*, representing the state of highest relative concentration of *16a*, together with several unidentified signals accounting for about 15% of the total integration. After 12 hrs. a thermally stable mixture had evolved which contained the same composition as in experiment at 1% concentration in $CDCl_3$.

Isomerization of Methyl 2-Isopropyl-diazene-1-carboxylate (16a) *to Methyl 2-Isopropylidene-diazane-1-carboxylate* (13a)

On Silica

Thin layer chromatograms of *16a*, prepared according to[11], on silica (POLYGRAM Sil N-HR/UV 254 Macherey-Nagel) in hexane/AcOEt 4 : 1 showed two spots at R_f 0.67 (*16a*) and 0.04 (*13a*). The relative intensity of these spots depended on the time interval between the application of 0.5 µl of a 50% solution of *16a* in $CDCl_3$ on the TLC plate and the start of the chromatogram. When this interval exceeded 1.5 hrs., only the spot R_f 0.04 of *13a* was present.

In $CDCl_3$ at 50 °C

A solution of 5 mg *16a* in 0.5 ml $CDCl_3$ was kept at 50 ± 1 °C and monitored from time to time by ^{1}H-NMR (90 MHz), using the OCH_3-signals for the determination of the ratio of *16a : 13a*. This ratio amounted to 6 : 4 after 15 hrs., to 1 : 1 after 21 hrs., to 35 : 65 after 38 hrs., to 27 : 73 after 47 hrs., and to 18 : 82 alfter 62 hrs.

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SAŽETAK

Azimini. VIII. Priprava i termička pregradnja alkil(2Z)-2,3-diisopropilazimin-1-karboksilata

Hans Hilpert, Lienhard Hoesch i André S. Dreiding

Poboljšan je postupak priprave metil- i etil-(2Z)-2,3-diisopropilazimin-1-karboksilata (*9a* i *9b*) i proučavana njihova termička pregradnja u odgovarajuće alkil-2-isopropilidendiazin-1-karboksilate (*13a* i *13b*). Utvrđeno je da se reakcija odvija u tri stupnja. U prvom stupnju reakcije azimin *9* se 1,4-pomakom vodika pregrađuje u triazin *14*, koji u slijedećem stupnju eliminacijom 1,2-hidroimina daje diazin *16*. 1,3-pomakom vodika *16* se pregrađuje u *13*. Detaljno je raspravljen mehanizam reakcije.