Original Scientific Paper

# Diallylic and Diallenic Dyotropic Rearrangements*

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A previously unexamined approach to dyotropic rearrangements involving only atoms from the first row is tested with four substrates. Both migrating groups contain π orbitals, either allylic or allenic. We have prepared 3,6-dimethyl-1,7-octadiene, 1,2-bis(vinyloxy)ethane, ethylene diisocyanate, and ethylene dithiocyanate to test this approach. All four substrates were pyrolyzed in a sealed tube and in a flash system. Products of ene reactions, diradical rearrangements, cycloaddition, and polymerization were observed, but the dyotropic rearrangements did not take place.

A dyotropic rearrangement is defined as an uncatalyzed valence isomerization in which two σ bonds migrate simultaneously and intramolecularly. In the Type I variety, the two σ bonds simply exchange places.[2] When the groups migrate with retention, the reaction is $[\sigma_a^2 + \sigma_a^2]$ and is thermally forbidden. This forbiddenness is easily seen in the orbital depiction for the dyotropic exchange of hydrogen in ethane (**1**), in which inversion occurs at each carbon atom (antarafacial). In the Dewar-Evans description, the transition state has two nodes (Hückel) but four electrons and so is forbidden. The


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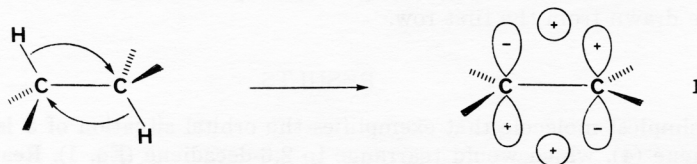
rearrangement can become thermally allowed in a number of ways, for example by migration of one group with inversion, $[\sigma_s^2 + \sigma_a^2]$, thereby making the system a uninodal (Möbius), four-electron ribbon. Alternatively, use of allyl for one migrating group

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* Dedicated to Profesor Dionis E. Sunko on the occasion of his seventieth birthday.
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changes the number of electrons by two and renders the reaction allowed.[2] The forbidden transition state **1** also may be stabilized by secondary orbital interactions, as provided by d orbitals in **2**. Reetz has exploited these approaches, primarily with migrating silyl groups, to uncover numerous examples of dyotropic rearrangements.[2,3] To date, no uncatalyzed Type I dyotropic rearrangement has been reported that does not involve migrating atoms that possess d orbitals.
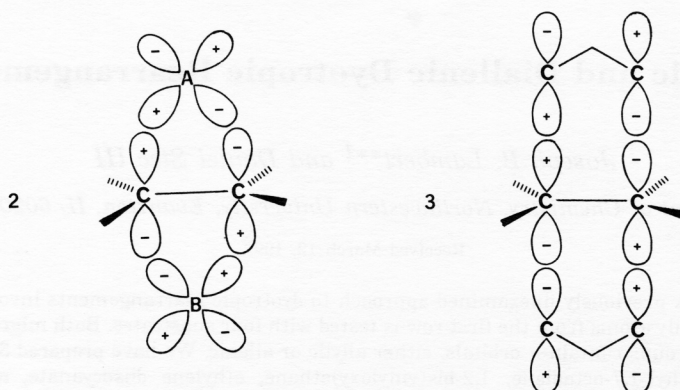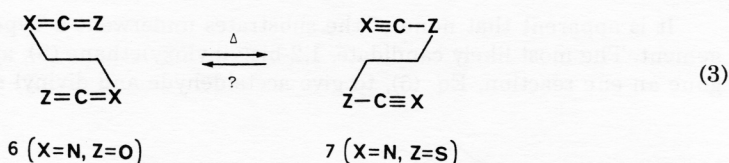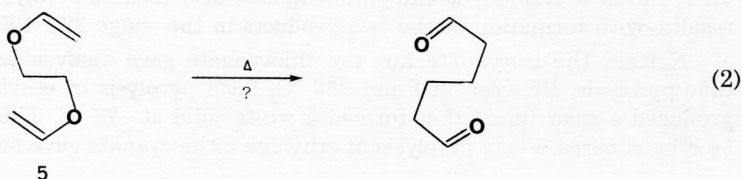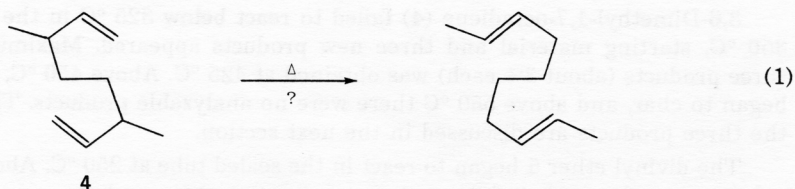

In the present study, we investigated systems in which two groups may migrate that both contain π orbitals: $(CH_2=CH-CH_2-CH_2)_2$ in its simplest expression. This arrangement has eight electrons, two each from the π bonds and two each from the σ bonds that are broken. With inversion at each central carbon atom and suprafacial migration over the allyl systems, the reaction is $[\sigma_a^2 + \pi_s^2 + \sigma_a^2 + \pi_s^2]$. If the HOMO of the allyl system is used (other choices give the same results), the orbital picture is given by **3**, in which orbital symmetry appears to be conserved, as in **2**, *i.e.*, bonding relationships are replaced with bonding relationships. The number of nodes on the electron ribbon of **3**, however, is even (two), so the system is Hückel and the reaction apparently is forbidden for the eight electrons. Because the diallylic dyotropic rearrangement has not previously been examined experimentally and it contains interesting electronic distinctions from other dyotropic systems, we have prepared several molecules that incorporate the requisite electronic structure. We report herein the thermolysis of four candidates for this new variety of dyotropic rearrangement, in which all key atoms are drawn from the first row.

RESULTS

The simplest molecule that exemplifies the orbital situation of **3** is 3,6-dimethyl-1,7-octadiene (**4**), which would rearrange to 2,6-decadiene (Eq. 1). Rearrangement of one allyl group along with a 1,2 shift of the other with retention would give 3-methyl-1,9-nonadiene. The methyl groups serve as the label to indicate the mode of rearrangement and as a source of thermodynamic stability for the right side. Stronger thermodynamic driving force is available from divinyl ethers, such as **5**, in which the double vinyl ether would be converted to a double carbonyl (Eq. 2).

A distinctly different version of the double π system involves the use of allenic rather than allylic structures. For this purpose, we prepared ethylene diisocyanate (**6**) and ethylene dithiocyanate (**7**). Isocyanate to cyanate rearrangements are well known,

$$\mathbf{4} \xrightarrow[?]{\Delta} \qquad\qquad (1)$$

$$\mathbf{5} \xrightarrow[?]{\Delta} \qquad\qquad (2)$$

$$\begin{array}{c} X=C=Z \\ | \\ Z=C=X \end{array} \xrightleftharpoons[?]{\Delta} \begin{array}{c} X\equiv C-Z \\ | \\ Z-C\equiv X \end{array} \qquad (3)$$

$$\mathbf{6}\,(X=N,\,Z=O) \qquad\qquad \mathbf{7}\,(X=N,\,Z=S)$$

but the double rearrangement has not previously been examined (Eq. 3, **6**). Although **7** possesses a second row element, the d orbitals of sulfur are not necessary for the process.

Consequently, for this study we required compounds **4-7**. The hydrocarbon **4** had previously been prepared by Fabricius,[4] through addition of vinylmagnesium chloride to 2,5-dibromohexane. We found that reaction with 2,5-bis-[p-(tosyloxy)]hexane gave a better yield of **4**, which was obtained as an approximately equal mixture of the *dl* and *meso* forms. 1,2-Bis(vinyloxy)ethane (**5**) was obtained by reaction of paraldehyde with dry ethylene glycol and hydrogen chloride gas; the resulting 1,2-bis(1-chloroethoxy)ethane was dehydrochlorinated with N,N-diethylaniline (Eq. 4). The synthesis of ethylene diisocyanate **6** was patterned after that of Ruden and Bonjouklian.[5] Succinyl chloride was allowed to react with sodium azide in acetonitrile; Curtius rearrangement[6] of the resulting diazide in ethanol-free chloroform produced **6**. Ethylene dithiocyanate **7** was prepared by the method of Söderbäch.[7]

$$HOCH_2CH_2OH + (CH_3CHO)_3 \xrightarrow{HCl} CH_3CHClOCH_2CH_2OCHClCH_3 \xrightarrow{-2HCl} \mathbf{5} \qquad (4)$$
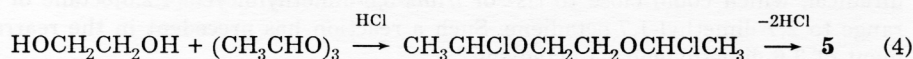
Pyrolyses were carried out both by sealed tube and by flash methods. Details are given in the Experimental Section. Both methods involve reactions in the vapor phase under reduced pressure. Reaction in a sealed tube is carried out for longer periods of time (minutes to hours) at lower temperatures and can give the thermodynamic products. The flash method uses a short residence time (seconds) at higher temperatures and can give the kinetic products.

3,6-Dimethyl-1,7-octadiene (4) failed to react below 325 °C in the sealed tube. At 350 °C, starting material and three new products appeared. Maximum yield of the three products (about 3% each) was obtained at 425 °C. Above 450 °C, the compounds began to char, and above 550 °C there were no analyzable products. The structures of the three products are discussed in the next section.

The divinyl ether 5 began to react in the sealed tube at 250 °C. Above 400 °C, only polymer was observed. At intermediate temperatures two products were obtained, which proved to be acetaldehyde and paraldehyde. Flash vacuum pyrolysis produces the same results, with formation of the two products in the range 325–490 °C.

Neither the isocyanate nor the thiocyanate gave analyzable products by sealed tube pyrolysis. Between 200 and 350 °C, flash pyrolysis of ethylene diisocyanate (6) produced a clear liquid that formed a white solid at −78 °C. This material proved to be ethyleneurea. Flash pyrolysis of ethylene dithiocyanate gave no analyzable product.

DISCUSSION

It is apparent that none of the substrates underwent a Type I dyotropic rearrangement. The most likely candidate, 1,2-bis(vinyloxy)ethane (5), appears to have undergone an ene reaction, Eq. (5), to give acetaldehyde and divinyl ether.

$$\tag{5}$$
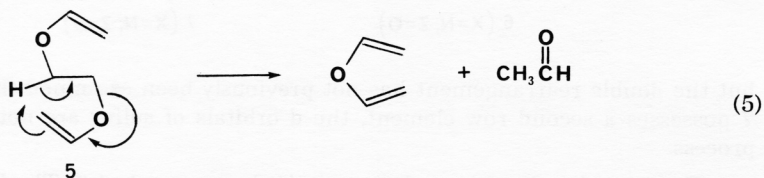
Such a process has precedent in the chemistry of alkyl vinyl ethers.[8] Our pyrolysis mixtures contained only starting material, acetaldehyde, and its trimer, paraldehyde. It is possible that the divinyl ether underwent a further ene reaction to give another molecule of acetaldehyde and acetylene. We did not analyze for acetylene.

The three products of 3,6-dimethyl-1,7-octadiene (4) were formed in too small a yield for isolation, but we were able to obtain their mass spectra. One of two products with earlier retention times than that of the starting material probably is 1,6-dimethyl-cyclooctene, from an ene reaction (Eq. 6). The mass spectrum of this compound proved to be almost identical to that of the starting materials. A McLafferty rearrangement of 1,6-dimethylcyclooctene indeed can give the parent ion from 4. Structures of the remaining products are uncertain. One possibility is that 4 cyclizes to a cyclooctadiyl diradical, which could close to cis- or trans-5,8-dimethylbicyclo[4.2.0]octane or rearrange to 2,7-dimethyl-1,7-octadiene. Such a reaction has precedent in the rearrangement of 3,6-dimethylene-1,7-octadiene.[9]

$$\tag{6}$$
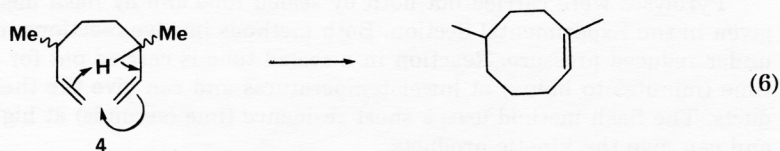
The pyrolytic properties of cyanates, thiocyanates, isocyanates, and isothiocyanates have been studied thoroughly by Barroeta,[10] who found that alkyl cyanates were thermally unstable and eluded useful interpretation. The other compounds frequently underwent elimination to form alkenes and hydrocyanic acids. The only reaction we observed for ethylene diisocyanate was production of ethyleneurea, which could result from dimerization of the two isocyanate groups and loss of carbon monoxide. From ethylene dithiocyanate, we obtained only polymeric material. Mass spectral analysis showed the product mixture to contain dimer, trimer, and higher polymer.

The failure to observe dyotropic reactions in any of these systems suggests that the electron ribbon is indeed Hückel (two nodes in **3**). Such a reaction is forbidden for eight electrons, despite the apparent bonding conservation in **3**. Alternatively, the high steric organization required in the transition state **3** for Eqs. (1)–(3) may lead to highly unfavorable entropy requirements. The allenic-type structures **6** and **7** introduce further angle strain, despite the possibility of secondary orbital interactions. We conclude that the diallylic or diallenic dyotropic rearrangement is not observed on account of a combination of unfavorable steric and orbital interactions.

EXPERIMENTAL

2,5-Dibromohexane was prepared by the addition of phosphorus tribromide to 2,5-hexanediol in 81% yield.[11]

2,5-Bis(tosyloxy)hexane was prepared by the reaction of *p*-toluenesulfonyl chloride with 2,5-hexanediol in 65% yield.[12]

Vinylmagnesium bromide was prepared from magnesium metal, ethyl bromide, and vinyl chloride in 95% yield.[13] A modified Gilman titration indicated that the solution in tetrahydrofuran was 1.5 M.

3,6-Dimethyl-1,7-octadiene (4). First method. To 2,5-dibromo-hexane (4.8 g, 0.02 mol) in 150 mL of dry tetrahydrofuran was added 33 mL of vinylmagnesium chloride solution (0.05 mol of the Grignard reagent). Boiling chips were added to ensure smooth boiling. The mixture was stirred at reflux under a N_2 atmosphere for 52 h. The reaction was cooled to room temperature, and saturated NH_4Cl solution (40 mL), diethyl ether (20 mL), and H_2O (20 mL) were added. The mixture was stirred at room temperature for 90 min. The layers were separated, and the aqueous layer was extracted three times with diethyl ether (50 mL). The combined organic layers were washed three times with saturated NaCl solution (200 mL), dried ($MgSO_4$), and filtered, and the solvent was distilled off at atmospheric pressure. The residue was distilled under reduced pressure. The fraction boiling between 50 and 96 °C at 8–12 mm was collected: crude yield 1.3 g (47%), 60% pure by gas chromatography. The mixture of stereoisomers (*dl* and *meso*) was purified by gas chromatography: ^{1}H NMR (CCl4) δ 5.45 (m, 2, CH2 = CH), 4.8 (m, 4, CH2 = CH), 0.95 (m, 10, alkyls).

Second method. To a stirred solution of 2,5-bis(tosyloxy)hexane (8 g, 17.4 mmol) in 10 mL of dry tetrahydrofuran, under a N_2 atmosphere, was added vinylmagnesium chloride in tetrahydrofuran (40 mmol) over a 60 min period. The reaction was stirred at room temperature for 6 h after complete addition of the Grignard reagent. The reaction was then heated at 50 °C for 2 h. After the reaction had cooled to room temperature, a workup as described in the first method was performed. Yield after distillation: 1.7 g (70%), 83% pure by gas chromatography.

Paraldehyde (2,4,6-trimethyl-1,3,5-trioxane).[14] Acetaldehyde was condensed into a flask containing three drops of concentrated H_2SO_4. The resulting liquid was washed with 10% aqueous Na_2CO_3 and saturated NaCl solution, was dried over $MgSO_4$, and was distilled to give a 95% yield of the trimer.

1,2-Bis(1-chloroethoxy)ethane.[15] Ethylene glycol (15.5 g, 13.9 mL, 0.25 mol) and paraldehyde (22.0 g, 22.2 mL, 0.167 mol) were cooled to 5 °C. Dry HCl gas was bubbled into the mixture for 20 min with stirring. The reaction was cooled to –45 °C, and the bubbling of HCl was continued

for 2 h. The reaction was cooled to −78°C, and two layers formed. The upper layer was poured off and dried twice in a freezer over CaCl$_2$. The compound was used without further purification: 27.8 g (59%), ^{1}H NMR (CDCl$_3$) δ 5.6 (q, 2, J = 5.4 Hz, OCClH), 4.1–3.4 (m, 4, CH$_2$CH$_2$), 1.7 (d, 6, J = 5.4 Hz, CH$_3$).

1,2-Bis(vinyloxy)ethane (5).[15] The ether (27.8 g, 0.148 mol) was stirred at 0 °C under reduced pressure for 1 h to remove any dissolved HCl. To this material was added dry *N,N*-diethylaniline (45.6 g, 48.9 mL, 0.304 mol). The flask was fitted with a reflux condenser connected to an aspirator through a −78 °C cold finger and collection flask. The mixture was stirred at room temperature and atmospheric pressure for 2 h. The system was placed under reduced pressure (8.9 mm Hg), and the reaction was heated at 80 °C in an oil bath for 90 min. The collection flask was cooled in an ice-methanol bath. A clear liquid began to distill. The oil bath temperature was raised to 125 °C, and the reaction was heated until *N,N*-diethylaniline began to distill over. The collected product was distilled from K$_2$CO$_3$ through a Vigreux column and showed contamination by paraldehyde and acetaldehyde ethylene glycol acetal. The ether was purified by gas chromatography: 6.7 g, ^{1}H NMR δ 6.4 (X of ABX, 2, =C(O)H), 4.3–3.5 (m, 8, =CH$_2$ and CH$_2$CH$_2$); MS (25 eV) *m/z* (relative intensity) 114 (12).

Ethylene diisocyanate (6)[5,6]*(Caution:* the intermediate diacyl azide is potentially explosive. Carry out all reactions and solvent removal behind a safety shield. Do not heat the concentrated sample). Succinyl chloride (9.52 g, 6.0 mL, 0.055 mol) was added to a suspension of activated NaN$_3$ (14.3 g, 0.22 mol) in 150 mL of dry acetonitrile. (The NaN$_3$ (20 g) was activated by trituration with 2 mL of hydrazine hydrate. The hydrazine was evaporated off overnight in a hood. The NaN$_3$ was then dissolved in a minimum amount of H$_2$O, reprecipitated with acetone, suction filtered, washed consecutively with methanol and ether, dried in vacuo, and used immediately). The reaction mixture was stirred at room temperature under an atmosphere of N$_2$ gas for 1 h. The excess NaN$_3$ was filtered off through a pad of Celite. Acetonitrile was removed at room temperature in vacuo. Ethanol-free CHCl$_3$ (60 mL) was added to the resulting brown oil. The solution was stirred overnight at room temperature under an atmosphere of N$_2$ gas, then heated for 2 h at 60 °C. The solvent was removed by distillation at atmospheric pressure, and the product was isolated by bulb-to-bulb distillation under reduced pressure (Kügelrohr): 3.7 g (60%), bp 57 °C (8–10 mm), IR (thin film) 2290 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.38 (s, 4, CH$_2$CH$_2$).

Ethylene dithiocyanate (7)[7,16] was prepared from ethylene and thiocyanogen in quantitative yield: mp 89.5–91 °C (lit[16] 90 °C), IR (KBr) 2158 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.3 (s, 4, CH$_2$CH$_2$).

Sealed Tube Pyrolysis. For sealed tube pyrolyses, 5, 10, or 24 μL of a liquid sample, or 5, 10 or 25 mg of the dithiocyanate was added to a Pyrex pyrolysis tube. Tube volumes ranged from 80 to 175 ml. The solid was dissolved in diethyl ether and added to the pyrolysis tube, and the solvent was removed in vacuo. The sample tube was evacuated and flushed with N$_2$ gas three times. Liquids were degassed by the freeze-pump-thaw method. Samples were sealed under a pressure of about 5×10^{-2} mm. The tubes were placed in a preheated tube furnace of local design. The temperature of the sample was measured by a thermocouple placed inside the furnace near the tube. After the sample was heated for 12 h, the tube was removed from the furnace. The tip of the tube was cooled at −78 °C to condense any sample and product vapors. The tip was removed, and the condensate was analyzed by gas chromatography.

Flash Vacuum Pyrolysis. The flash apparatus consisted of a flask from which the sample was vaporized, a horizontal quartz pyrolysis tube externally heated by a tube furnace, and a trap cooled at −78 °C. The set-up was kept under a N$_2$ atmosphere when not under vacuum. Sample was added to a sample flask (25 μL for liquids, 25 mg for solids), the system was evacuated, and the sample was degassed by the freeze-pump-thaw method. The sample was vaporized and allowed to flow down the pyrolysis tube. Effluent was trapped at −78 °C upon emerging from the tube. Portions of the pyrolysis tube exposed to the atmosphere were heated with heating tapes. The system was then flooded with N$_2$ gas, and the trapped effluent was warmed to room temperature. Each pyrolysis was run at a pressure of about 5×10^{-2} mm. Residence time in the pyrolysis tube was under 1 s. Temperatures were measured with a thermocouple placed in a channel through the center of the pyrolysis tube. Flash pyrolyses were performed both with an empty tube and with the tube filled with Pyrex 3/8 in. helices.

REFERENCES

1. This work was supported by the National Science Foundation Grant No. CHE-8910841.
2. M. T. Reetz, *Advan. Organomet. Chem.* **16** (1977) 33-65; M. T. Reetz, *Angew. Chem., Int. Ed. Enlg.* **11** (1972) 129-130; M. T. Reetz, *Tetrahedron* **29** (1973) 2189-2194.
3. M. T. Reetz, M. Kliment, and M. Plachky, *Angew. Chem., Int. Ed. Engl.* **13** (1974) 813-814.; M. T. Reetz, *ibid.* **13** (1974) 402-403; M. T. Reetz, and M. Kliment, *Tetrahedron Lett.* (1975) 2909-1910;. M. T. Reetz. M. Kliment, and M. Plachky, *Chem. Ber.* **109** (1976) 2716-2727; M. T. Reetz, M. Kliment, M. Plachky, and N. Greif, *ibid.* **109** (1976) 2728-2742; M. T. Reetz, *Tetrahedron Lett.* (1976) 817-820;. M. T. Reetz, *Chem. Ber.* **110** (1977) 954-964, 965-978.
4. D. M. Fabricius, unpublished results; see D. M. Fabricius, Ph.D. Dissertation, Northwestern University, 1977.
5. R. A. Ruden, and R. Bonjouklian, *J. Amer. Chem. Soc.* **97** (1975) 6892-6893.; R. Bonjouklian and R. A. Ruden, *J. Org. Chem.* **42** (1977) 4095-4103.
6. T. Curtius and W. Hechtenberg, *J. Prakt. Chem.* **105** (1922) 289-318.
7. E. Söderbäch, *Justus Liebigs Ann. Chem.* **443** (1925) 142-161.
8. G. G. Smith, and F. W. Kelly, *Progr. Phys. Org. Chem.* **8** (1971) 75-234, W. J. Bailey and J. Di Petro, *J. Org. Chem.* **42** (1977) 3899-3902.
9. K. J. Shea and S. Wise, *Tetrahedron Lett.* (1978) 2283-2286.
10. N. Barroeta, in: *The Chemistry of Cyanates and Their Thio Derivatives*, Part I, S,. Patai, Ed., Wiley-Interscience: New York, 1977. pp. 549-567 and references therein.
11. N. Kornblum and J. H. Eicher, *J. Amer. Chem. Soc.* **71** (1949) 2259-2260.
12. R. M. Dodson, and V. C. Nelson, *J. Org. Chem.* **33** (1968) 3966-3968.
13. H. E. Ramsden, J. R. Leebrick, S. D. Rosenberg, E. H. Miller, J. J. Walburn, A. E. Balint, and R. Cserr, *J. Org. Chem.* **22** (1957) 1602-1605.
14. A. Kekule and T. Zincke, *Justus Liebigs Ann. Chem.* **162** (1872) 125-150.
15. J. R. Nooi, and J. F. Arens, *Rec. Trav. Chim. Pays-Bas* **81** (1962) 517-532.
16. J. L. Wood, *Org. React.* **3** (1946) 240-266.

SAŽETAK

Dialilne i dialenske diotropne pregradnje

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Ispitana je mogućnost diotropne pregradnje 3,6-dimetil-1,7-oktadiena, 1,2-bis(viniloksi)etana, etilen-diizocijanata i etilen-ditioizocijanata u uvjetima pirolize u vakuumu bljeskom (flash vacumm pyrolysis). Analizom sastava produkata zaključeno je da niti jedan od ispitanih prekursora u navedenim uvjetima ne podliježe diotropnoj pregradnji.