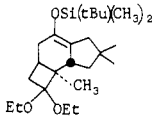
6b with acrylate derivatives, with and without Lewis acid and metal catalysts,[9] failed to produce more than traces of Diels-Alder adducts. This lack of reactivity of diene **6b** was particularly forbidding in light of the tendency of cyclobutene derivatives to rearrange thermally to 1,3-dienes.[10]

However, using the enolsilyl ethers **6c** or **6d**, reaction of **5** proceeded efficiently under minimum temperature conditions (48 °C, 10 days) to produce 1:1 adducts in 70-75% yield and >95% selectivity after purification by column chromatography.[11] Structures **4a** and **4b** were assigned to the adducts based on spectral data.[7] However, the stereochemical assignment was secure only after conversion to illudol, which requires the configuration shown in **4**.

Hydrolysis of **4a** or **4b** under standard conditions (fluoride anion or basic hydrolysis) produced a mixture of the desired cis ring fusion isomer **7** and the corresponding trans isomer, in similar amounts.[12] However, desilylation of **4a** could be achieved under very mild conditions (3-Å molecular sieves, methyl alcohol, 25 °C, 4.5 h) to give exclusively the cis product, **7** (95% yield).[7] This selective hydrolysis could not be obtained from the more stable silyl ether, **4b**. Selective reduction of **7** with lithium triethylborohydride followed by protection of the secondary hydroxyl group as the benzyl ether (to give **10**)[7] allowed application of Ireland's procedure for converting ester units to methyl groups.[13] The lithium metal reduction (Scheme III, step i) also served to remove the benzyl protecting group. Oxidation produced the key intermediate **12a**[7] in 56% overall yield from **4a**.

An alternative preparation of **12** without the use of the benzyl protecting group was developed through application of Ireland's reduction method directly on the *tert*-butyldimethylsilyl ether **4b**. The reduced compound **13** was obtained in 74% yield by using



13

carefully selected conditions.[7,14] Then desilylation with fluoride anion gave a mixture of **12a** and the corresponding trans isomer, **12b**, which were separated by chromatography. Equilibration of the trans isomer in dilute sodium methoxide/methyl alcohol gave a mixture of **12a**/**12b** (60/40) from which **12a** was again isolated. The combined yield of **12a** after two equilibrations was 89%, resulting in an overall yield of **12a** from **4b** of 65%.

Functionalization of C-2 in **12a** was accomplished by carboxylation of the kinetic enolate anion with carbon dioxide and methylation with diazomethane (Scheme III). By means of a selenoxide elimination,[15] the strained double bond exocyclic to the four-membered ring was introduced to give **14** in 37% overall yield from **12a**.[7] Intermediate **14** was used in the earlier synthesis of illudol,[2] and we followed that pathway to produce a sample of (±)-illudol which was identified by comparison with material from nature (Scheme III).[16] Efforts are under way to convert intermediate **4** into fomannosin (**3**).

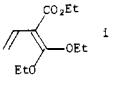
Acknowledgment. We are pleased to acknowledge preliminary work by Dr. Utpal Chakraborty and Professor Leonard Keller (Florida International University) and financial support from the National Institutes of Health. A grant from the National Science Foundation to the Princeton Chemistry Department provided the JEOL-MX90Q NMR spectrometer which was used in this work. S.T. thanks the Ministry of Education (Japanese Government) for financial support.

Supplementary Material Available: Characterization data on all new compounds (5 pages). Ordering formation is given on any current masthead page.

(9) For a review of the role of catalysis in the Diels-Alder reaction, see: J. Sauer, *Angew. Chem., Int. Ed. Eng.*, **6**, 16 (1967).

(10) For discussion and examples, see: R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, 1971, p 48 ff. The cyclobutene derivative **5** has a half-life of ~1 h/90 °C. Cyclobutenes are not common participants in Diels-Alder reactions. For discussion and recent examples, see: V. V. Plemenkov and V. P. Kostin, *J. Org. Chem. USSR (Engl. Transl.)*, **15**, 1086 (1979), and references therein.

(11) The adducts were homogeneous within the limits of ^{13}C NMR analysis. Reaction of **5** at higher temperatures was less efficient, giving a byproduct which has been tentatively characterized as diene i.



i

(12) The cis isomer **7** was converted to a mixture of **7** and the corresponding trans ring fusion isomer (~60:40, favoring **7**) upon treatment with sodium methoxide in methyl alcohol.

(13) R. E. Ireland, D. C. Muchmore, and U. Hengartner, *J. Am. Chem. Soc.*, **94**, 5098 (1972).

(14) The combination of sodium counterion (instead of Li) and 1,2-dimethoxyethane as solvent (instead of tetrahydrofuran) was important in the formation of the phosphorodiamidate, in order to avoid cleavage of the enol silyl ether. Similarly, under the standard[13] conditions (0 °C, Li/$EtNH_2$) for cleavage of primary phosphorodiamidates, substantial desilylation occurred. But at −78 °C, reaction using the same reagents was complete within 2 h with no significant desilylation.

(15) H. J. Reich, F. Chow, and S. K. Shah, *J. Am. Chem. Soc.*, **101**, 6638 (1979), and references therein.

(16) We are grateful to Dr. M. Anchel of the New York Botanical Garden for providing a sample of natural (−)-illudol.

(17) Fellow of the John Simon Guggenheim Foundation, 1978-1979.

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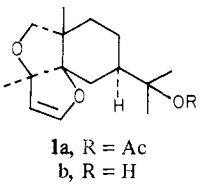
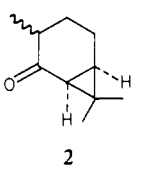
A Convenient, Stereospecific Synthesis of (−)-Phytuberin from (−)-2-Carone[1]

Sir:

\Phytuberin (**1a**) is a sesquiterpene stress metabolite which has been isolated from fungal-infected potato tubers by Coxon and co-workers.[2] Its structure was established by spectroscopic methods and by an X-ray crystallographic structure determination on its 2,3-dihydro derivative. A lengthy biogenetic-like synthesis of **1a** from α-cyperone, which established the absolute stereochemistry of the compound, was reported recently by Masamune and co-workers.[3,4] We wish to report a convenient, seven-step synthesis of **1a** from (−)-2-carone (**2**) which allowed preparation



1a, R = Ac
b, R = H



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of the natural product in 11% overall yield.

The cyclohexanone derivative **3** was obtained in a highly stereospecific manner. Alkylation of the lithium 2,3-enolate of **2** prepared under thermodynamic conditions by using lithium di-

(1) This research was supported by a grant (NSF 7810044) from the National Science Foundation for which we are grateful.

(2) Coxon, D. T.; Price, K. R.; Howard, B.; Curtis, R. F. *J. Chem. Soc., Perkin Trans. 1* **1977**, 53.

(3) Murai, A.; Ono, M.; Abiko, A.; Masamune, T. *J. Am. Chem. Soc.* **1978**, *100*, 7751.

(4) For the proposed biogenetic pathway to phytuberin, see Stossel, A.; Stothers, J. B.; Ward, E. W. B. *Can. J. Chem.* **1978**, *56*, 645.

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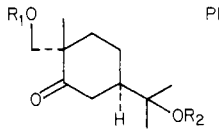
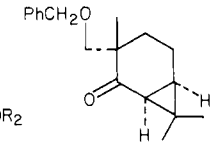
isopropylamide (LDA) as the base in tetrahydrofuran (THF)[5] with chloromethyl benzyl ether gave the bicyclic ketone **4**[6] [65% yield; bp 120–126 °C (0.05 mm); $[\alpha]^{24}_D$ −93.4° (*c* 1.15, EtOH); IR (CCl_4) 1692 cm^{-1} (C=O); NMR (CCl_4) δ 0.91 (s, 3 H), 1.02 (s, 3 H), 1.10 (s, 3 H), 3.17 and 3.49 (AB q, *J* = 8.6 Hz, 2 H, $OCH_2C\lessdot$), 4.42 (s, 2 H, $C_6H_5CH_2O$–), 7.23 (s, 5 H, C_6H_5)] as a single product. The cyclopropane ring in **4** was readily cleaved with aqueous acid to give **3a**. However, to avoid having to protect



3a, $R_1 = CH_2Ph$; $R_2 = H$
b, $R_1 = R_2 = CH_2Ph$



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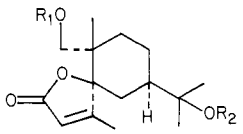
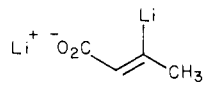


5a, $R_1 = R_2 = CH_2Ph$
b, $R_1 = R_2 = H$



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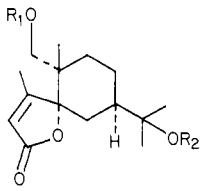
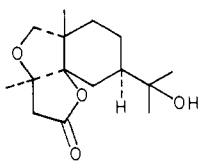


7a, $R_1 = R_2 = CH_2Ph$
b, $R_1 = R_2 = H$



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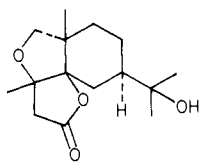

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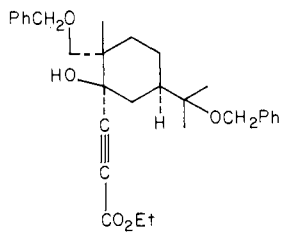

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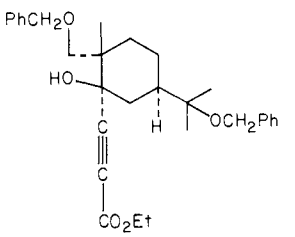

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the tertiary hydroxy group in a separate step, ketone **4** was treated with benzyl alcohol containing a catalytic amount of *p*-toluenesulfonic acid to give directly the dibenzyl derivative **3b**[6] [85% yield; $[\alpha]^{24}_D$ +30° (c 0.75, EtOH); IR (CCl_4) 1710 cm^{-1} (C=O); NMR (CCl_4) δ 1.07 (s, 3 H), 1.25 (s, 6 H), 3.17 and 3.39 (ABq, *J* = 9.2 Hz, 2 H, $-OCH_2C\lessdot$), 4.35 (s, 2 H, $C_6H_5CH_2O$–), 4.44 (s, 2 H, $C_6H_5CH_2O$–), 7.21 (s, 10 H, 2 C_6H_5's)].

We hoped to utilize methodology analogous to that which was reported recently for a direct conversion of ketone **3b** into the β-methyl spirobutenolide **5a**.[7] Thus, **3b** was reacted with the β-lithioacrylate derivative **6** (prepared by treatment of (*Z*)-3-bromobutenoic acid with 2 equiv of *n*-butyllithium in ether at −78 °C) under the conditions described previously for the conversion of ketones into butenolides.[7] This led to the formation of a ~12:88 mixture of the isomeric spirobutenolides **5a** and **7a** in 45–51% yield. The isomers which were separated by chromatography on silica gel exhibited the following spectral properties. **5a**:[6] [IR (CCl_4) 1755 (α,β-unsaturated γ-lactone C=O), 1637 cm^{-1} (conjugated C=C); NMR (CCl_4) δ 1.09 (s, 3 H), 1.19 (s, 6 H), 2.08 (d, *J* = 1.6 Hz, 3 H), 3.18 and 3.41 (AB q, *J* = 9.0 Hz, 2 H), 4.45 (s, 2H), 4.61 (s, 5 H), 7.22 (s, 5 H), 7.27 (s, 5 H). **7a**:[6] IR (CCl_4) 1764 (C=O), 1637 cm^{-1} (C=C); NMR (CCl_4) δ 1.22 (s, 6 H), 1.27 (s, 3 H), 1.98 (d, *J* = 1.8 Hz, 3 H), 2.96 and 3.27 (AB q, *J* = 9.0 Hz, 2 H), 4.25 (s, 2 H), 4.35 (s, 2 H), 5.43 (q, *J* = 1.8 Hz, 1 H), 7.17 (s, 10 H).

Hydrogenation of the minor isomer **5a** in 95% ethanol containing 10% Pd(C) allowed quantitative removal of the benzyl protecting groups without reduction of the conjugated double bond to give the diol **5b**. When **5b** was allowed to stand on basic alumina[8] for 1 h and then eluted with 50% ether–hexane, deacetylphytuberin lactone **8**, which showed spectral properties identical with those of an authentic sample,[2,9] was isolated in 88% yield. Application of a similar sequence to the major butenolide led via **7b** to the tricyclic hydroxylactone **9**[6] [mp 61–62 °C; IR (CCl_4) 3620, 3480 (OH), 1772 (C=O), 1382, 1368, 1117, 1040, 1017, 906 cm^{-1}; NMR ($CDCl_3$) δ 1.23 (s, 9 H), 1.40 (s, 3 H), 2.52 and 2.82 (AB q, *J* = 18 Hz, 2 H), 3.63 (s, 2 H)]. Since the addition of the vinyllithium reagent **6** to the carbonyl group in **3b** occurred predominantly from the undesired equatorial direction, it was clear that a method which would lead to the butenolide **5a** stereoselectively would have to be sought.

It was felt that the addition of a relatively small carbanionic species such as acetylide ion to the carbonyl group in **3b** might occur predominately from the axial direction.[10] In a model study it was found that addition of lithium carboxyethylacetylide[11] to a 4-*tert*-butylcyclohexanone occurred almost exclusively in the axial manner; furthermore, it was observed that the resulting γ-hydroxy acetylenic ester was converted into the corresponding anti β-methyl spirobutenolide by reaction with 2 equiv of lithium dimethylcuprate.[12] Thus it appeared that an analogous two-step process might be applicable to the **3b** → **5a** conversion. Indeed, the first step proceeded readily and the γ-hydroxyacetylenic ester **10**[6] [92% yield; $[\alpha]^{24}_D$ +22° (*c* 1.18, EtOH); IR (CCl_4) 3495 (OH), 2225 (C≡C), 1715 cm^{-1} (C=O); NMR (CCl_4) δ 1.08 (s, 3 H), 1.21 (s, 6 H), 1.30 (t, *J* = 7.4 Hz, 3 H), 3.19 and 3.79 (AB q, *J* = 8.9 Hz, 2 H), 4.18 (q, *J* = 7.4 Hz, 2 H), 4.40 (s, 2 H), 4.56 (s, 2 H), 7.22 (s, 5 H), 7.28 (s, 5 H)] formed by axial addition was obtained when **3b** was reacted with lithium (carboxyethyl)-acetylide in THF at −78 °C for 1.0 h. The stereochemistry of **10** was confirmed by the subsequent transformations. None of the isomeric γ-hydroxy ester which could have resulted from equatorial addition to **3b** was isolated.

Considerable difficulty was encountered in finding proper conditions to effect the **10** → **5a** conversion. When **10** was treated with 2 equiv of lithium dimethylcuprate in THF at ~−10 °C for 3 h under the same conditions which were used to convert the adduct of lithium (carboxyethyl)acetylide and 4-*tert*-butylcyclohexanone into the corresponding *anti*-β-methyl spirobutenolide,[12] only unchanged starting material was recovered. When the cuprate addition was run in THF at 0–25 °C by using 2–10 equiv of reagent, the tertiary alcohol **11**[6] [mp 97.5–98.5 °C; IR(CCl_4) 3620, 3520 (OH), 2230 cm^{-1} (C≡C); NMR (CCl_4) δ 1.10 (s, 3 H), 1.20 (s, 6 H), 1.43 (s, 6 H), 3.16 and 3.78 (AB q, *J* = 8.6 Hz, 2 H), 4.40 (s, 2 H), 4.53 (s, 2 H), 7.23 (s, 5 H), 7.35 (s 5 H)], which resulted from 1,2 addition of the cuprate to the carboxyethyl group, was the only product isolated. When the reaction was carried out at temperatures below −10 °C for extended reaction times using 2 equiv of lithium dimethylcuprate in ether, mixtures of the butenolides **5a**, the acetylenic diol **11**, and the starting material were isolated. However, best results were obtained when **10** was reacted with 1 equiv of lithium dimethylcuprate in ether at −24 °C for 84 h. This led to the formation of a ~3:1:1 mixture of **5a**, **11**, and **10**.[13] Chroma-

(5) Treatment of **2** with LDA in THF at −78 °C under kinetic control followed by addition of methyl chloromethyl ether or benzyl chloromethyl ether gave C-1 rather than C-3 alkylation products.

(6) All new compounds for which spectral data are reported gave correct combustion analyses and/or exact mass data.

(7) Caine, D.; Frobese, A. S. *Tetrahedron Lett.* **1978**, 5167.

(8) Posner, G. H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 487.

(9) We are grateful to Dr. D. T. Coxon for providing us with generous quantities of authentic samples of deacetylphytuberin lactone (**8**) and phytuberin (**1a**).

(10) For an excellent review on the stereochemistry of the addition of organometallic reagents to cyclic ketones, see: Ashby, E. C.; Laemmle, J. T. *Chem. Rev.* **1975**, *75*, 521.

(11) Herrmann, J. L.; Berger, M. H.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1979**, *101*, 1544.

(12) Caine, D.; Smith, T. L., Jr. *Synth. Commun.* **1980**, *10*, 751.

tography of the mixture on silica gel allowed the isolation of **5a** in 60% yield, based on unrecovered starting material.

In order to form the tetrahydro and dihydrofuran rings in phytuberin, diol **5b**, which was prepared by hydrogenolysis of the benzyl groups in **5a**, was reacted with 3.5 equiv of DIBAL-H (−40 °C, 1.0 h; 0 °C, 0.5 H), as described for the reduction of the related formylspirobutenolide.[3] Workup of the mixture with 2 N NaOH gave deacetylphytuberin (**1b**), $[\alpha]^{24}_D$ −34.6° (*c* 0.1, EtOH), in 63% yield. This material exhibited identical spectral properties with those reported previously.[2,3] Acetylation of **1b** (Ac_2O, Et_3N, catalytic amount of 4-*N*,*N*-dimethylaminopyridine[14]) gave 71% of (−)-phytuberin (**1a**), $[\alpha]^{24}_D$ −34.0 ° (*c* 0.25, EtOH), having IR and NMR spectral properties and TLC behavior identical with those of an authentic sample.[9]

(13) Since the best yield of the butenolide was obtained when 1 equiv of lithium dimethylcuprate was used, it is possible that the conjugate addition reaction was effected primarily via the mixed methylalkoxycuprate derived from reaction of lithium dimethylcuprate with the hydroxy group in **10**. For examples of conjugate additions using mixed alkylalkoxycuprates, see Posner, G. H.; Whitten, C. E.; Sterling, J. J. *J. Am. Chem. Soc.* **1973**, *95*, 7788.

(14) Hofle, G.; Steglich, W.; Vorbrüggen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 569.

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Received July 14, 1980

Extension of the Woodward-Hoffmann Rules to Heterocyclic Systems: Stereospecific Thermal Isomerization of 1-Azacyclobutene 1-Oxides

Sir:

In a recent publication Snyder[1] predicts, on the basis of calculated potential surfaces for isomerization of heteracyclobutenes, that 1-azacyclobutenes will undergo ring opening in a conrotatory mode similar to cyclobutenes. This possible extension of the Woodward-Hoffmann rules to the isomerization of heteracyclobutenes has, to our knowledge, hitherto not been confirmed experimentally. A number of 2,3-dihydroazetes are known,[2-6] and Cantrell[4] and recently Harnisch and Szeimies[5] have reported that several derivatives of these heterocycles are thermally unstable. Attempts to isolate the corresponding 2-aza-1,3-butadienes were unsuccessful, probably because of rapid polymerization or hydrolysis if water is present.

We wish to report in this communication the stereospecific thermal isomerization of 2,3-dihydroazete 1-oxides together with the X-ray structure determination of one of the corresponding 2-aza-1,3-butadiene 2-oxides. Recently we have obtained a number of 2,3-dihydroazete 1-oxides from reactions of nitroalkenes and 1-aminoacetylenes (ynamines). The structure of one of these four-membered cyclic nitrones, 2-(*N*,*N*-diethylcarbamoyl)-2,4-dimethyl-3-phenyl-2,3-dihydroazete 1-oxide (**1a**), has been determined by X-ray crystallography.[7] This revealed the stereochemistry of **1a** and showed that the two bulkiest substituents, the phenyl and the *N*,*N*-diethylcarbamoyl group, are on the same side of the almost flat four-membered ring. When a chloroform solution of this 2,3-dihydroazete 1-oxide was heated at reflux, isomerization to *N*-[1-(*N*,*N*-diethylcarbamoyl)-ethylidene]-1-phenyl-1-propen-2-amine *N*-oxide (**2a**) took place as indicated by ^{1}H NMR. After 20 h we isolated **2a** from the reaction mixture as a white crystalline solid (40%):[8,9] mp 117-120 °C; IR (KBr) $\nu_{C=C}$, $\nu_{C=O}$, and $\nu_{C=N}$ 1660, 1650, and 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.98 and 1.23 (t, 6 H, $NCCH_3$), 2.32 (s, 6 H, $=C-CH_3$), 3.34 and 3.39 (q, 4 H, NCH_2-), 6.58 (s, 1 H, C=CH), 7.2-7.4 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 125.1 (=CH-), 142.0 and 143.1 (C=N and =CN), 164.1 (C=O). The structure of **2a** was determined by single-crystal X-ray analysis, and this unambiguously proved the *E*,*E* stereochemistry of **2a**.[11] This means that ring opening has taken place in a conrotatory mode in line with the isomerization of cyclobutenes.

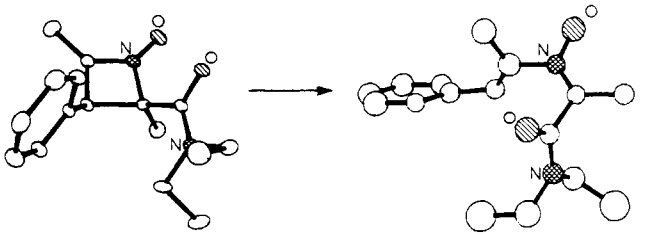


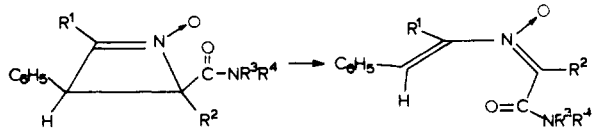
Figure 1. ORTEP drawings of **1a** and **2a**.

Table I. Rate Constants for the Isomerizations of **1** to **2**

	10^5k, s		
temp, °C	1a	1b	1c
51.5	0.48 ± 0.01		
61.1	1.50 ± 0.1	9.60 ± 0.3	77 ± 3
71.9	5.71 ± 0.2		

Orthorhombic crystals of **2a** belong to space group $Pna2_1$ with a = 15.93 (1), b = 8.41 (1), c = 11.74 (1) Å, Z = 4. Intensities were measured with Mo Kα radiation (λ = 0.7107 Å) on a single-crystal diffractometer in ω-2θ scan mode ($3° < \theta < 20°$); 1450 reflections were measured, of which 869 were significant ($I > \sigma(I)$, counting statistics). The structure was solved by direct methods.[12] Full-matrix least-squares refinement[13] of positional and anisotropic parameters of the nonhydrogen atoms resulted in a final R_w factor of 5.5%. The structure of **2a**[14] is given in Figure 1.

The rate of the isomerization of **1a** to **2a** in chloroform was measured by ^{1}H NMR spectroscopy at temperatures of 51.5, 61.1, and 71.9 °C. The rates were calculated from the decrease of the intensity of the singlet at 3.98 ppm corresponding to H-3 in **1a**. The data fitted first-order kinetics, and from a plot of the rates vs. T^{-1}, we obtained the activation parameters of the isomerization reaction ($\Delta H^{\ddagger}$ 27 ± 1 kcal mol^{-1} and $\Delta S^{\ddagger}$ −2 ± 3 eu). The rates of isomerization of two other 2,3-dihydroazete 1-oxides were also determined at 61.1 °C in chloroform (see Table I). The isom-



1 **2**

a R^1=R^2=CH_3, R^3=R^4=CH_2CH_3
b R^1=CH_3, R^2=C_6H_5, R^3R^4= -$(CH_2)_4$-
c R^1=H, R^2=C_6H_5, R^3R^4= -$(CH_2)_4$-

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