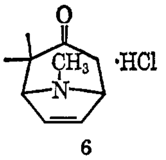
Treatment of **1** with purified N-methylpyrrole resulted in the formation of **4** in approximately 50% yield (nmr). Extraction with 1% aqueous HCl followed by neutralization resulted in the isolation of **4**, purity approximately 90%; nmr (neat), δ 0.87 (s, 3 H), 1.23 (s, 3 H), 2.24 (s, 3 H), 2.37 (AB, 2 H, $\Delta\nu_{AB} = 34.8$ Hz, $J_{AB} = 16$ Hz, high-field half split further, $J = 2$ Hz, low-field half split further, $J = 4.5$ Hz), 3.16 (m, 1 H), 3.50–3.70 (m, 1 H), 5.97–6.25 (m, 2 H) (integration approximate due to impurities); ir, $\lambda_{\max}^{\mathrm{CCl_4}}$ 3.27, 3.61, and 5.86 μ; mass spectrum (75 eV), *m/e* (relative intensity) 165 (10.7 M$^+$), 123 (0.75), 122 (6.2), 95 (36.9), 94 (100). The nmr of **4** is very similar to that of the previously reported **1**–furan adduct.[5]

Treatment of **4** with methanolic HCl was followed by the isolation of the hydrochloride **6**: nmr ($CDCl_3$), δ 1.16 (s, 3 H), 1.79 (s, 3 H), 2.65 (d of d, 1 H, $J = 18$ Hz, $J = 2$ Hz), 3.17 (s, 3 H), 4.05 (d of d, 1 H, $J = 18$ Hz, $J = 4$ Hz), 4.38 (s, 1 H), 4.53–4.75 (m, 1 H), 6.51 (m, 2 H), 11.23–13.06 (1 H); ir, $\lambda_{\max}^{\mathrm{KBr}}$ 5.82 μ; mass spectrum (75 eV), *m/e* (relative intensity) 165 (4.0, M$^+$), 123 (0.67), 122 (3.6), 95 (27.8), 94 (100). *Anal.* Calcd for $C_{10}H_{16}NOCl$: C, 59.55; H, 8.00; N, 6.95; Cl, 17.58. Found: C, 59.31; H, 8.08; N, 6.75; Cl, 17.61.

Compound **4** was subjected to preparative vpc workup under the same conditions used previously.[2] This procedure resulted in the collection of a mixture of **2** and **3** in the ratio **3**:**2** = 6:1 (nmr). The uncorrected vpc yield of **2** and **3** was approximately 50%.

Reduction of **4** (H_2–Pd–C) followed by preparative vpc led to the isolation of 336 mg (31%) of **7**: nmr[6] ($CDCl_3$), δ 1.00 (s, 3 H), 1.29 (s, 3 H), 1.35–2.24 (m, 5 H), 2.35 (s 3 H), 2.58–3.07 (m, 2 H), 3.17–3.48 (m, 1 H); ir, $\lambda_{\max}^{\mathrm{neat}}$ 3.60 μ, 5.86; mass spectrum[7] (75 ev), *m/e* (relative intensity) 167 (19.6, M$^+$), 82 (100). *Anal.* Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.38. Found: C, 71.61; H, 10.38; N, 8.54.



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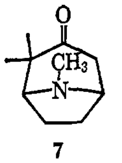

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(5) W. B. Hammond and N. J. Turro, *J. Am. Chem. Soc.*, **88**, 2880 (1966); W. B. Hammond, Ph.D. Dissertation, Columbia University, 1967.

(6) These values are consistent with the values for tropinone: R. J. Bishop, G. Fodor, A. R. Katritzky, F. Soti, L. E. Sutton, and F. J. Swinbourne, *J. Chem. Soc., C*, 74 (1966).

(7) This spectrum correlates with that of tropinone: H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 92.

(8) Alfred P. Sloan Fellow, 1966–1970.

(9) National Science Foundation Predoctoral Trainee, 1965–1966; National Science Foundation Predoctoral Fellow, 1966–present.

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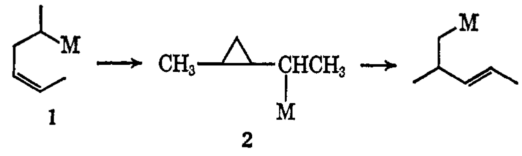
Coordination-Catalyzed Skeletal Rearrangement of *cis*- and *trans*-2-Methylvinylcyclopropanes

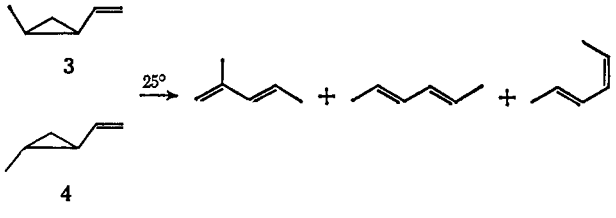
Sir:

We recently reported the skeletal rearrangement of *cis*-1,4-hexadiene to *trans*-2-methyl-1,3-pentadiene by a nickel-based coordination catalyst.[1,2] One possible reaction path for this transformation would involve the intervention of a cyclopropylcarbinylnickel derivative, **2**, derived from rearrangement of **1**.[3] Interaction of *cis*- and *trans*-2-methylvinylcyclopropanes (**3** and **4**) with the catalyst would be expected to generate the respective *cis* and *trans* isomers of **2** if the catalyst is capable of transferring the elements of nickel hydride to olefinic bonds.[1,5] With this in mind, we have examined the behavior of **3** and **4** in the presence of the catalyst.



The methylvinylcyclopropanes were prepared by thermolysis of a 1:1 mixture of *trans*- and *cis*-3-methyl-5-vinylpyrazolines, prepared by reaction of butadiene with diazoethane, using the general procedure reported by Crawford.[6] The resulting 1:1 mixture of *trans*- and *cis*-2-methylvinylcyclopropanes was resolved, and the compounds were collected *via* preparative glpc. Structure assignments were confirmed by comparison of the nmr and infrared spectra with those reported by Roth and König,[7] who synthesized the compounds by a different route.

Addition of diisobutylaluminum chloride to toluene solutions containing *trans*-dichlorobis(tri-*n*-butylphosphine)nickel(II) and either **3** or **4** (olefin:Al:Ni, 18:4.5:1) at 25° results in the formation of *trans*-2-methyl-1,3-pentadiene and *trans,trans*- and *trans,cis*-2,4-hexadienes. *trans*-2-Methyl-1,3-pentadiene is the major isomeric product in each case. At −22°, **3** and **4** remained essentially unchanged during a 3-hr period (<2% conversion) in the presence of the catalyst components. However, the addition of ethylene to the reaction mixtures at −22° has a remarkable effect on the rate of formation of isomeric products. Thus, **3** was converted quantitatively into products within *ca.* 5 min when the above olefin:Al:Ni ratio was employed. The dimerization of ethylene also occurred.



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(1) R. G. Miller, *J. Am. Chem. Soc.*, **89**, 2785 (1967).

(2) Subsequent experiments by Mr. Dennis Baker have uncovered the related conversion of 1,4-pentadiene into 2-methyl-1,3-butadiene and *trans*- and *cis*-1,3-pentadienes.

(3) A large body of evidence supporting the participation of a cyclopropylcarbinyl Grignard reagent in the interconversion of allylcarbinyl Grignards has been obtained by Roberts and coworkers.[4]

(4) (a) M. S. Silver, P. A. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 2646 (1960); (b) D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, **87**, 5144 (1965); M. E. H. Howden, A. Maercker, J. Burdon, and J. D. Roberts, *ibid.*, **88**, 1732 (1966).

(5) R. G. Miller, T. J. Kealy, and A. L Barney, *ibid.*, **89**, 3756 (1967).

(6) R. J. Crawford and D. M. Cameron, *Can. J. Chem.*, **45**, 691 (1967).

(7) W. R. Roth and J. König, *Ann. Chem.*, **688**, 28 (1965). The compounds were first reported by R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 5578 (1964).

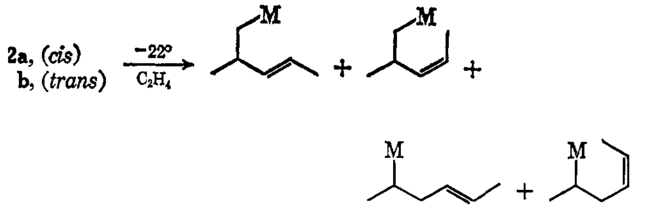
Table I. Rearrangement of *cis*-1,4-Hexadiene and *trans*- and *cis*-2-Methylvinylcyclopropanes[a]

					% of isomer mixture				
					2-Me-1,3-Pd's		2,4-HD's[c]		
Alkene	Time, min	Conditions[b]	Conversion, %	Yield of isomers, %	*trans*	*cis*	*t,t*	*t,c*	*c,c*
cis-1,4-HD	120	A	78	78	79.0			16.4	4.6
cis-1,4-HD + C_2H_4	20	B	67	99	5.7		4.2	64.0	26.1
3	120	A	58	68	79.0		13.4	7.6	
3 + C_2H_4	30	B	64	96	87.0	9.2	1.9	1.9	
4	120	A	68	53	63.4		24.0	12.6	
4 + C_2H_4	4	C	89	90	37.0	36.0	16.0	11.0	
4 + C_2H_4	5	B	51	99	20.3	65.4	4.7	8.6	1.0

[a] Conversions are based on per cent of starting material reacted. Yields are per cent of reacted starting material converted into C-6 isomers. [b] Conditions: A, 25°, 2.4 mmol of Ni in 35 ml of toluene, olefin:Al:Ni, 18:4.5:1; B, −22°, 0.02 mmol of Ni in 35 ml of toluene, olefin:Al:Ni, 211:14:1; C, same as B but at 25°. [c] *t,t*, *t,c*, and *c,c* refer to *trans,trans*, *trans,cis*, and *cis,cis*, respectively.

In order to monitor the formation of products with time, the concentration of the nickel component was decreased tenfold and a 211:14:1 olefin:Al:Ni ratio was used.[8] Under these conditions, 64% of **3** was converted into *trans*- and *cis*-2-methyl-1,3-pentadienes and *trans,trans*- and *trans,cis*-2,4-hexadienes in nearly quantitative yield within 30 min. Particularly noteworthy are the formation of *cis*-2-methyl-1,3-pentadiene and the pronounced change in the methylpentadiene:2,4-hexadiene ratio (Table I). The 2-methyl-1,3-pentadienes composed *ca.* 96% of the product mixture. Introduction of ethylene into toluene solutions of **4** under these same conditions at −22° resulted in the rapid formation of the same four products plus a small amount (1%) of *cis,cis*-2,4-hexadiene, *cis*-2-methyl-1,3-pentadiene composing 65% of the mixture. Control experiments demonstrated that the formation of *cis*-2-methyl-1,3-pentadiene is not a consequence of the higher olefin:Al:Ni ratio used.

The isomeric hydrocarbons formed in these reactions possess carbon skeletons that could be generated from rearrangement of organometallic products **2a** and **2b**, derived from the additive transfer of nickel hydride to the methylvinylcyclopropane double bond.[9] Any speculation regarding the mechanistic relevance of the methylvinylcyclopropane reactions to the *cis*-1,4- hexadiene rearrangement is unwarranted until a number of questions can be answered. Although *cis*-1,4-hexadiene, **3**, and **4** all afford *trans*-2-methyl-1,3-pentadiene as the major isomeric product at 25°, the major 2,4-hexadiene derived from each methylvinylcyclopropane is the *trans,trans* isomer. The only 2,4-hexadienes that are consistently formed in significant quantities from *cis*-1,4-hexadiene are the *trans,cis* and *cis,cis* isomers which may be derived solely or in part from the "direct" migration of the 1,4-hexadiene terminal double bond.[10] Also, the half-life at 25° for the conversion of *cis*-1,4-hexadiene into products, under the conditions listed in Table I, was *ca.* 5 min, whereas the corresponding half-lives for the methylvinylcyclopropanes were *ca.* 60 min. Therefore, the entries in Table I do not accurately reflect the relative rates of conversion into products at 25°. Interestingly, *cis*-1,4-hexadiene, when mixed with the catalyst components at −22°, remains unchanged during a 3-hr period but is rapidly converted to a product mixture containing 64% *trans,cis*- and 26% *cis-cis*-2,4-hexadienes after ethylene is introduced. *trans*-2-Methyl-1,3-pentadiene and *trans,trans*-2,4-hexadiene were minor components of the mixture.



Ethylene may facilitate the transfer of the elements of nickel hydride to and from hydrocarbon substrates. This would explain the rapid double bond migration in *cis*-1,4-hexadiene at −22° which can occur by a metal hydride addition–elimination sequence and the enhanced rates of rearrangement of **3** and **4** if the rate-determining steps involve metal hydride transfer. Apparently the ratios of products derived from the methylvinylcyclopropanes at −22° in the presence of ethylene are regulated mainly by kinetic control. A rapid and irreversible elimination of metal hydride from the organometallic products generated in the ring-opening reactions of **2a** and **2b** would lead to a product mixture with a "kinetically controlled" composition.

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[8] The product mixtures were analyzed by glpc. Products described herein were collected *via* preparative glpc and identified by comparison of infrared and nmr spectra with those of authentic samples. Reaction mixtures and aliquots therefrom were quenched with isopropyl alcohol.

[9] Two diastereomers of **2a** and of **2b** would be expected to result. It is clear that in any concerted ring-opening reaction, the geometry of the internal double bond of the *primary* products will be determined by the configuration at the carbinyl carbon in **2a** and **2b**.

[10] *trans*-1,4-Hexadiene affords *trans,trans* and *trans,cis* isomers as the only 2,4-hexadiene products under similar conditions.

The Structure of Thiepin 1,1-Dioxide

Sir:

The question of π-electron delocalization involving sulfones is an intriguing one.[1] Thiepin 1,1-dioxide (**1**) offers a promising situation for the observation of this

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[1] For a critical summary, see D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 71–84; also D. J. Cram and T. A. Whitney, *J. Am. Chem. Soc.*, **89**, 4651 (1967).