(3) S. S. Hecht, M. Loy, R. R. Maronpot, and D. Hoffmann, *Cancer Lett.*, **1,** 147 (1976).

(4) M. M. Coombs, C. Dixon, and A. M. Kossonerghis, *Cancer Res.*, **36,** 4525 (1976).

(5) (a) M. Newman, *J. Am. Chem. Soc.*, **62,** 870 (1940); (b) L. Fieser and L. Joshel, *ibid.*, **62,** 1211 (1940); (c) W. Bachmann and R. O. Edgerton, *ibid.*, **62,** 2550 (1940); (d) Subsequent to the submission of this paper, the photocyclization of a mixture of **4** and **5** to **1** was reported in 65% yield by D. L. Nagel, R. Kupper, K. Antonson, and L. Wallcave, *J. Org. Chem.*, **42,** 3626 (1977).

(6) See, for example: (a) P. Hugelshofer, J. Kalvoda, and K. Schaffner, *Helv. Chim. Acta*, **43,** 1322 (1960); (b) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29,** 3373 (1964); (c) E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc.*, 163 (1970); (d) C. C. Leznoff and R. J. Hayward, *Can. J. Chem.*, **50,** 528 (1971).

(7) (a) J. W. Cook and R. A. F. Galley, *J. Chem. Soc.*, 2012 (1931). These authors reported mp 139 °C for **4** and/or **5**, but their later work (cf. ref 7b) indicated that impure materials had been used. We suggest that their product was actually 2-(2-naphthyl)-1-phenylpropene, mp 139 °C (cf. ref 7c below); (b) J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 365 (1934); (c) W. Carruthers, *J. Chem. Soc.*, 1525 (1967).

(8) GC analyses were done on a Hewlett-Packard 5750 instrument with dual flame ionization detectors using an 8-ft × 0.25-in. copper column packed with 5% UC W-98 coated on 80–100 mesh AW DMCS-treated Chromosorb G at 230 °C. The retention times for **1**, **3**, **4**, **5**, and **6** were: 47, 21, 17, 10.5, and 11.5 min, respectively.

(9) Amberlyst-15 resin is a sulfonic acid resin available from Rohm and Haas Company, Philadelphia, Pa. We are grateful for a research sample.

(10) Beyond this reaction time, GC showed the appearance of three new products with slightly longer retention times. These new products are possibly cyclized materials. Use of *p*-toluenesulfonic acid in the place of A-15 decreased the reaction times but gave similar results.

(11) J. March, "Advanced Organic Chemistry", McGraw-Hill, New York, N.Y., 1977, Chapter 17.

(12) For a review of peri interactions in naphthalene compounds, see V. Balasubramaniyan, *Chem. Rev.*, **66,** 567 (1966).

(13) W. P. Duncan, E. J. Eisenbraun, and P. W. Flanagan, *Chem. Ind.* (*London*), 78 (1972).

(14) The assignment of erythro and threo was obtained through application of rules developed by R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5,** 385, 511 (1966).

(15) (a) H. Lund and A. D. Thomas, *Acta Chem. Scand.*, **23,** 2567, 3582 (1961); (b) J. Wiemann, G. Dana, Sa-Le-Thi-Thuan, and M. Brami, *C. R. Hebd. Seances Acad. Sci.*, **258,** 3724 (1964); (c) J. H. Stocker, D. W. Kern, and R. M. Jenevein, *J. Org. Chem.*, **33,** 412 (1968); (d) J. H. Stocker, *J. Am. Chem. Soc.*, **88,** 2878 (1966); (e) H. Agahigian, J. F. Moraveck, and H. Gauthier, *Can. J. Chem.*, **41,** 194 (1963); (f) J. Grimshaw, J. T. Grimshaw, and E. J. F. Rea, *J. Chem. Soc.*, 683 (1971).

(16) The IR spectra of the diols (dilute carbon tetrachloride solution) appeared to confirm **9** as the erythro isomer since the intramolecular hydrogen-bonded hydroxyl absorption appeared at lower frequency in **9** (3500 cm^{-1}) than for **7** (3570 cm^{-1}). The tendency for intramolecular hydroxyl absorptions to appear at lower frequency in meso diols has previously been observed; see W. A. Mosher and N. Heidel, *J. Org. Chem.*, **28,** 2154 (1963).

(17) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy", 2nd ed, Pergamon Press, London, 1969, p 224.

(18) (a) Attempts to use (*E*)- and (*Z*)-1,2-diphenylpropene as model compounds for **4** and **5** were unsatisfactory. The UV spectra of the 1,2-diphenylpropenes show significant differences[18b] (*E* isomer, λ 2700, log $\epsilon = 4.3$; *Z* isomer, λ 2600, log $\epsilon = 4.1$). The ^1H NMR spectra of 1,2-diphenylpropenes show an upfield shift of aromatic protons in the *Z* isomer[18c] (7.12 vs. 7.25 δ for the *E* isomer) but the vinyl proton occurs at lower field in the *E* isomer[18c] (6.75 vs. 6.39 δ for the *Z* isomer). These compounds lack the significant interaction between the peri hydrogen of the naphthyl ring and the methyl group present in **4** and **5**. We thank a referee for helpful comments concerning the use of model compounds: (b) D. J. Cram and F. A. Abdelhafez, *J. Am. Chem. Soc.*, **74,** 5828 (1952); (c) M. Michman and H. H. Zeiss, *J. Organomet. Chem.*, **15,** 139 (1968).

(19) (a) H. Gusten and M. Salzwedel, *Tetrahedron*, **23,** 173, 187 (1967); (b) A. F. Casey, A. Parulkar, and P. Pocha, *ibid.*, **24,** 3031 (1968); (c) C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49,** 164 (1966).

(20) For reviews, see: (a) F. R. Stermitz, "Organic Photochemistry", Vol. I, E. D. Chapman, Ed., Marcel Dekker, New York, N.Y., 1967; (b) D. O. Cowan and R. L. Drisko, "Elements of Organic Photochemistry", Plenum Press, New York, N.Y., 1976, Chapter 9; (c) E. V. Blackburn and C. J. Timmons, *Q. Rev., Chem. Soc.*, **23,** 482 (1969).

(21) D. J. Collins and H. J. Hobbs, *Chem. Ind.* (*London*), 1725 (1965).

(22) (a) IR spectra were obtained on a Beckman IR5A, ^1H NMR on a Varian XL-100, and UV on a Cary 14 spectrometer. Mass spectra were obtained on a CEC 21-110B instrument at 70 eV. We thank the National Science Foundation for Grants GP17641 and CHE76-5571 which enabled purchase of the NMR instrument and FT accessory; (b) melting points are not corrected; (c) Phillips Chemical Co., commercial isohexane, bp 55–60 °C.

(23) C. E. Browne, W. L. Buchanan, and E. J. Eisenbraun, *Chem. Ind.* (*London*), 35 (1977).

Isomerization of 2- and 3-Carene Oxides over Solid Acids and Bases[1]

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The reaction of 3-carene oxide catalyzed by solid acids and bases gave ten compounds and several unidentified products. The main products were carbonyl compounds (IV, VI, and VII) and allylic alcohols (IX and X) with a three-membered ring except for the case of H_2SO_4/SiO_2, which gave a large amount of III, V, and VIII. The carbonyl compounds were predominantly formed over SiO_2–Al_2O_3, Al_2O_3 A and $FeSO_4$, while the allylic alcohols were preferentially formed over Al_2O_3 C and TiO_2–ZrO_2. The reactivity of 2-carene oxide over solid acids and bases was exceedingly high in comparison with that of 3-carene oxide, and eight compounds and several unidentified products were observed. All the products were the three-membered ring-opened ones. The formation of allylic alcohols with the hydroxyl group rearranged to the 3 or 8 position was also observed. A large amount of III and XIII was formed. TiO_2–ZrO_2 showed 100% selectivity for the formation of XIII at 30 °C. It is significant that the breaking of the C(3)–O bond of oxygen is much more favorable with 3-carene oxide, while the C(2)–O bond is broken with 2-carene oxide.

Introduction

Among many studies on the rearrangement of α-pinene, limonene, caryophyllene and other terpene epoxides,[2-8] there are some studies dealing with the carene oxides. In the presence of zinc bromide, 3-carene oxide rearranged mainly to the ring-contracted aldehyde and to the ketones with retention of the three-membered ring.[9-11] Joshi and co-workers reported that passing the epoxide over active alumina yielded bicyclic unsaturated alcohols together with some by-products.[11] As for 2-carene oxide, allylic alcohols with the three-membered ring intact were predominantly formed with lithium diethylamide, a strong base,[12] while the three-membered ring was

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Table I. Isomerization of 3-Carene Oxide[d] at 80 °C for 75 min

Catalyst[a]	Catalyst amount, g	Conversion, %	Selectivity, % I	II	III	IV	V	VI	VII	VIII	IX	X	Others
SiO_2–Al_2O_3[b]	0.16	100	1	2	9	52	1	11	14	0.2	1		10
H_2SO_4/SiO_2	0.24	100	2		24		15	10	4	23			23
H_2SO_4/SiO_2[b]	0.24	100	2	4	16	12	5	6	29	10	4	4	10
Al_2O_3 A	0.22	70	10	5	4	46		3	13		6	12	1
$FeSO_4$ (500 °C)	0.48	94	1	3	8	23		5	36		4	8	13
$FeSO_4$ (700 °C)	0.32	95	0.4	2	4	23		4	36	2	3	7	17
SiO_2–TiO_2	0.26	92	6	13	8	33		2	6		14	16	2
$NiSO_4$ (350 °C)	0.28	88	2	10	5	13		6	34		7	18	5
Al_2O_3 C	0.27	37	4	1	1	17		3	3		15	54	1
TiO_2	0.28	42	13	8	2	19		3	1		28	27	
TiO_2–ZrO_2[c]	0.24	61	12	10	2	11		1	2		41	19	2
Al_2O_3 B	0.20	76	11	3	0.4	29		2	5		7	42	2

[a] Figures in parentheses show calcination temperatures. [b] 10 min. [c] 90 °C. [d] Registry no.: 21218-11-1; I, 3479-89-8; II, 21195-59-5; III, 99-87-6; IV, 19534-12-4; V, 31507-62-7; VI, 43124-59-0; VII, 43124-60-3; VIII, 499-74-1; IX, 62532-46-1; X, 22626-38-6.

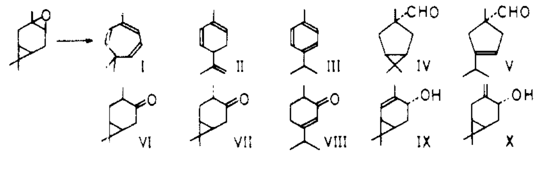
opened to the diene alcohol, *cis*-isolimonenol, on reaction with metatitanic acid.[13]

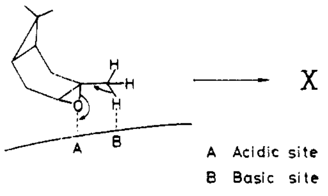
As part of a series on dealing with the rearrangement of epoxides over heterogeneous acid and base catalysts, we have already studied the *d*-limonene and carvomenthene oxides.[14–16] In order to examine the change in catalytic action due to the effect of the three-membered ring as a substituent group, we have now carried out the isomerization of the 2- and 3-carene oxides over several solid acid and base catalysts.

Results and Discussion

Isomerization of 3-Carene Oxide. The reaction of 3-carene oxide catalyzed by solid acid and base catalysts gave the following products: 3,7,7-trimethyltropilidene (I), 1,5,8(9)-*p*-menthatriene (II), *p*-cymene (III), 3,6,6-trimethylbicyclo[3.1.0]hexane-3-carboxaldehyde (IV), 1-methyl-1-formyl-3-isopropyl-3-cyclopentene (V), isocaranone (VI), caranone (VII), carvenone (VIII), *trans*-2-caren-4-ol (IX), *trans*-3(10)-caren-4-ol (X), and unidentified products.

The catalytic activity and selectivity of several solid acid and base catalysts in 75 min at 80 °C are shown in Table I. Catalysts were chosen from those studied in isomerizations of *d*-limonene[14,15] and carvomenthene[16] oxides on the basis of their activities and selectivities. SiO_2–Al_2O_3 and H_2SO_4/SiO_2 are most active for the isomerization. The high activity of SiO_2–Al_2O_3 is considered to be based on its high acidity on the surface.[17,18] The main products with various catalysts were carbonyl compounds (IV, VI, and VII) and allylic alcohols (IX and X) with a three-membered ring except for the case of H_2SO_4/SiO_2, which gave a large amount of III, V, and VIII. Carbonyl compounds were formed predominantly over SiO_2–Al_2O_3, Al_2O_3 A and $FeSO_4$, while allylic alcohols were formed preferentially by Al_2O_3 C and TiO_2–ZrO_2, the selectivities being more than 60%.





Most of the products with H_2SO_4/SiO_2 resulted from opening of the three-membered ring. This is in contrast to the results with the other catalysts. It appears likely that sulfuric acid supported on SiO_2 partially dissolves in the medium and that cleavage of the epoxide and the cyclopropane rings is the result of acid catalysis. In the case of the other catalysts which gave products with the three-membered ring intact, it is thought that the oxygen atom of oxide is adsorbed on the catalyst surface without there being an interaction between the three-membered ring and the surface.

The formation of a large amount of cymene (III) and carvenone over H_2SO_4/SiO_2 was also observed in the isomerization of *d*-limonene oxide.[14] Cymene formation is interpreted as a Bronsted acid-catalyzed dehydration of the reactant to form II with a subsequent shift of the double bond of the isopropenyl group of II to the six-membered ring. Carvenone is probably formed from VI and VII.[19] Compound V was reported in the literature[11] to form by isomerization of 3-carene oxide with silica gel. Its formation is considered due to the very acidic H_2SO_4/SiO_2 catalyst which causes isomerization of the cyclopropane ring in compound IV.

In our previous paper,[20] it was concluded that strong acids on the catalyst surface cause preferential formation of carbonyl compounds. That aldehyde is formed in larger amount than ketone over SiO_2–Al_2O_3, Al_2O_3 A and SiO_2–TiO_2 is ascribed to the extremely high acid strength of these catalysts, as was explained previously.[16] As for the ketones, the more stable caranone (VII) rather than the less stable isocaranone (VI) was formed predominantly.

As discussed in a previous paper,[20] opening of the epoxide ring to form the allylic alcohol can be interpreted by an acid–base bifunctional mechanism, where an oxygen atom of the oxide is adsorbed on an acidic site of the catalyst surface, while a hydrogen atom of the methyl or methylene group is adsorbed on a basic site.

IX was formed predominantly over TiO_2–ZrO_2, while X was formed over Al_2O_3 B and C. TiO_2 produced the same amount of both. TiO_2–ZrO_2 is supposed to have acidic and basic properties which are different from those of the aluminas. It is of interest that Al_2O_3 A showed high selectivity for the formation of carbonyl compounds, while Al_2O_3 B and C yielded the allylic alcohols selectively. The reaction scheme over each catalyst is summarized in Scheme I.

Isomerization of 2-Carene Oxide. The products of the isomerization of 2-carene oxide were *p*-cymene (III), 1(7),2,8(9)-*p*-menthatriene (XI), α,*p*-dimethylstyrene (XII),

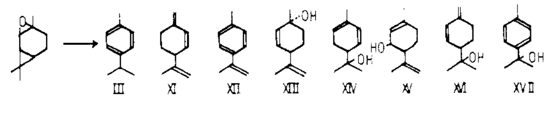


Table II. Isomerization of 2-Carene Oxide[f] at 80 °C for 10 min

Catalyst[a]	Catalyst amount, g	Conversion, %	Selectivity, % III	XI	XII	XIII	XIV	XV	XVI	XVII	Others
SiO_2–Al_2O_3	0.12	100	43	6	7		5				28
HCl/SiO_2	0.16	61	58		3	13	2			2	22
$NiSO_4$ (250 °C)[c]	0.35	51	21	4		24	5	4			32
Al_2O_3 A[b]	0.12	54	21			43	4	3	4		25
$FeSO_4$ (700 °C)	0.23	45	24	1		45	5				24
$FeSO_4$ (900 °C)[c]	0.21	4									
Al_2O_3 C	0.30	53	14	3		36	7	8			31
TiO_2–ZrO_2	0.19	77	11		2	75	4	2		3	3
TiO_2–ZrO_2[d]	0.25	20				100					
TiO_2–ZrO_2[b,e]	0.23	100	22		11	16		10		19	7
TiO_2 (500 °C)	0.19	55	21			49	3	2		4	21
TiO_2 (900 °C)[c]	0.32	4									
CaO[c]	0.10	2									

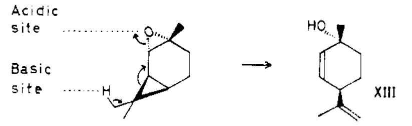
[a] Figures in parentheses show calcination temperatures. [b] With 0.5 mL of the epoxide in 2.5 mL of toluene. [c] 75 min. [d] 30 °C, 1 h. [e] 100 °C, 2 h. [f] Registry no.: 35071-29-5; XI, 65293-08-5; XII, 1195-32-0; XIII, 7212-40-0; XIV, 1686-20-0; *cis*-XV, 4017-76-9; *trans*-XV, 4017-77-0; XVI, 65293-09-6; XVII, 1197-01-9.

cis-2,8(9)-*p*-menthadien-1-ol (XIII), α-phellandren-8-ol (XIV), *cis*- and *trans*-1,8(9)-*p*-menthadien-3-ol (XV), α-phellandren-8-ol (XVI), *p*-cymen-8-ol (XVII), and unidentified materials.

Table II shows the catalytic activity and selectivity for the isomerization of 2-carene oxide at 80 °C in 10 min. The reactivity was exceedingly high in comparison with that of 3-carene oxide. However, since $FeSO_4$ and TiO_2 heat-treated at 900 °C or CaO, which has basic character,[21] were almost inactive, it appears that the reaction does not take place without a catalyst at 80 °C. The epoxide used was a mixture of 2- and 3-carene oxides (4:1), but the yields of the products formed from 3-carene oxide are excluded from the table. However, the conversion of 3-carene oxide was quite low except in the case of SiO_2–Al_2O_3, as is expected from the results in Table I.

All products resulted from opening of the cyclopropyl ring, in contrast with the observations on 3-carene oxide, though 2-carene oxide yields allylic alcohols corresponding to IX and X with retention of the cyclopropane ring on exposure to lithium diethylamide.[12] It is also remarkable that the cleavage of the C(3)–O bond is much more favorable for 3-carene oxide, while the C(2)–O bond is cleaved in 2-carene oxide.

Large amounts of III and XIII were produced. Cymene (III) is considered to be formed from XIII by acid-catalyzed dehydration through a stable tertiary carbonium ion. In accord with this, SiO_2–Al_2O_3 produced complete dehydration of XIII on its very strongly acidic sites,[17,18] as did the protonic acid, HCl/SiO_2. However, it is also possible that SiO_2–Al_2O_3 causes dehydration of the oxide to form cymene without forming XIII first.

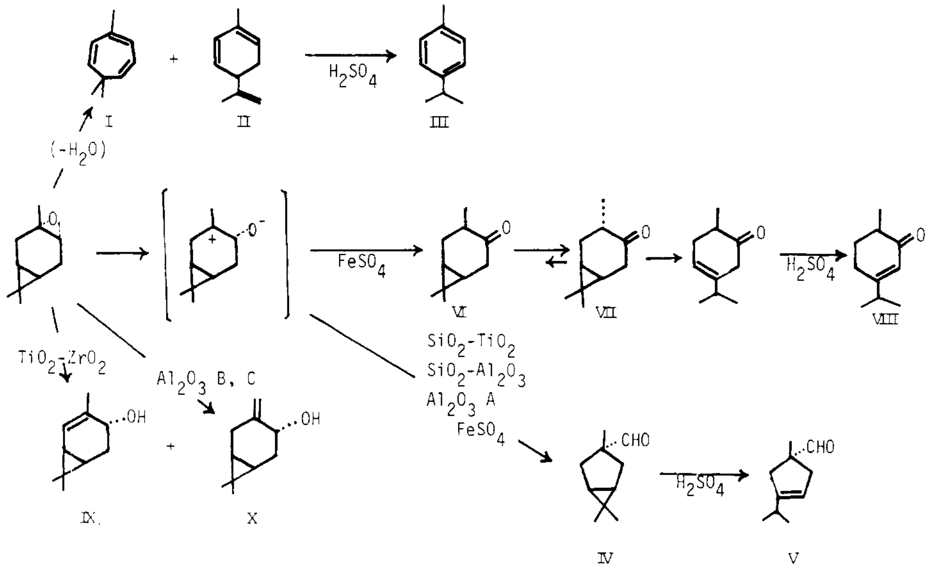


The formation of XIII can be interpreted by taking into account the great stability of a cyclopropyl carbinyl cation.[22] Hence, cleavage of the β bond of oxygen, adsorbed on an acid site of the catalyst, is much more favorable, and is followed by opening of the cyclopropane ring.[23]

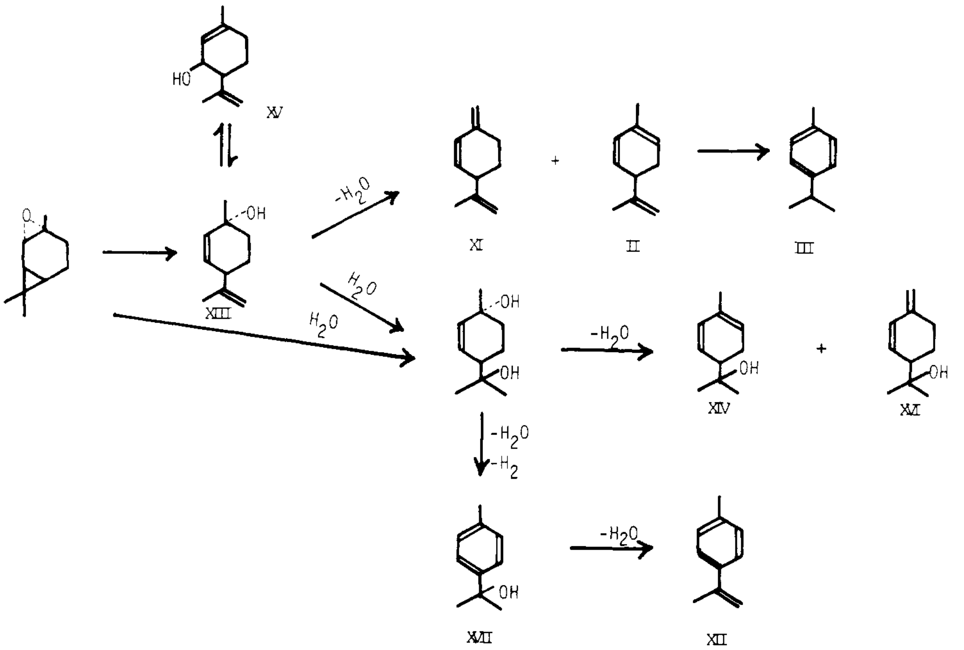
Abstraction of a hydrogen from C-9 by the basic site facilitates opening of the 3-ring by the push effect of the anion. This helps explain the high selectivity of TiO_2–ZrO_2 (75%), which is a remarkable catalyst for bifunctional catalytic action[16,20] for formation of XIII and gave 100% of XIII even at 30 °C.

The formation of allylic alcohols with a hydroxyl group in the 3 or 8 position of the cymene structure was observed. XV

Scheme I



Scheme II



consists of cis and trans forms and is certainly formed by isomerization of compound XIII. Compounds XIV and XVI were presumably formed by hydration of 2-carene oxide or XIII (H_2O being produced by cymene formation) and subsequent dehydration. XII and XVII are presumably formed via a dehydrogenation step on the basis of mechanistic considerations. A dehydrogenated product, carvone, was found in the isomerization of *d*-limonene oxide over TiO_2–ZrO_2 at 108 °C for 75 min.[15] This is similar to the present observations; that is, a considerable amount of XII and XVII was given by TiO_2–ZrO_2 under the severe conditions, at 100 °C for 2 h. Dehydrogenation is considered to take place on the basic sites of the TiO_2–ZrO_2 surface, but it is not clear of what stage dehydrogenation occurs. The reaction scheme for 2-carene epoxide is summarized in Scheme II.

Experimental Section

3-Carene oxide and 2-carene oxide (containing 20% 3-carene oxide) were supplied by the Organic Chemicals Group, SCM Corp., the latter material being purified to better than 96% by preparative gas–liquid chromatography (2-m column, 20% PEG). Toluene was purified by distillation over sodium metal.

Standard Reaction Procedure. The reaction was carried out at 80 °C in the presence of toluene as solvent. A mixture of 0.5 mL of the epoxide, 2.5 mL of toluene, and about 0.3 g of catalyst, ground to below 100 mesh, was stirred magnetically. In the case of 2-carene oxide, the mixture consisted of equal amounts of the reagents. At appropriate time intervals, a small amount of the sample was withdrawn with a 1-mL syringe, separated from catalyst by using a centrifuge, and analyzed by GLC (TCD detector) using a 3-m column of 20% polyethylene glycol 20M on Celite 545 SK (150 °C, He 1.0 kg/cm^2). Yields were based on epoxide and calculated by measurement of GLC peak areas (uncorrected).

Catalysts. SiO_2–Al_2O_3 [N361(L)(Al_2O_3; 15 wt %) from Nikki Chemical Co.] was calcined at 500 °C. SiO_2–TiO_2 (molar ratio 1:1) was prepared by coprecipitation of the mixed solution of ethyl orthosilicate and titanium tetrachloride with aqueous ammonia. The precipitate was aged over a water bath for 1 h, washed with distilled water until no chloride ion was detected, dried at 100 °C for 20 h, and calcined at 500 °C. H_2SO_4/SiO_2 was prepared as follows: 10 g of granular silica gel was immersed in 12 mL of 1 N H_2SO_4, evaporated, dried, and then calcined at 150 °C. HCl/SiO_2 was prepared by the same method. $FeSO_4$, $Fe_2(SO_4)_3$, and $NiSO_4$ were prepared by calcining their guaranteed hydrates. TiO_2 and TiO_2–ZrO_2 (molar ratio 1:1) were prepared by thermal decomposition, at 500 °C, of H_4TiO_4 and H_4TiO_4–$Zr(OH)_4$, respectively. These hydrogels were precipitated by heating a mixed aqueous solution of titanium tetrachloride, zirconium oxychloride, and excess urea on a boiling water bath, followed by washing thoroughly with distilled water until no chloride ions were detected in the filtrate and drying in air at 110 °C. Al_2O_3 A and B were Albes C and Albes FF, respectively, supplied from Showa Tansan Kaisha, Ltd., and Al_2O_3 C was KAT 6 of Nishio Chemical Co. All the aluminas were heat-treated at 500 °C before use. CaO was prepared by calcining its hydrates in air at 550 °C. All the catalysts were calcined in Pyrex glass tubes (quartz tubes for 900 °C) in air for 3 h and stored in sealed ampules until use.

Identification of Products. All reference materials for comparison of spectra were obtained from the Organic Chemicals Group, Division of SCM Corp., Jacksonville, Fla.

GLC component I (RRT = 0.37, the compound of RRT = 1 being the starting epoxide) was identified as 3,7,7-trimethyltropilidene.[24,25] An authentic sample was isolated from the reaction of 3-carene oxide with aluminum isopropoxide;[11,26] its spectral data were in agreement with the proposed structure.

Peaks IV and V (RRT = 0.81 and 1.15) had almost identical mass spectra, but there was one striking difference as can be seen by comparison of the mass spectra.

Catalyst	Peak	Mass spectra (8 most intense peaks) *m/e*
H_2SO_4/SiO_2	V	137, 81, 41, 152 (M^+), 109, 67, 43, 79
SiO_2–Al_2O_3	IV	109, 41, 81, 67, 43, 137, 39, 91

Compound IV had a base peak of 109, whereas compound V had a base peak of 137. 3-Carene oxide was reacted with 10% by weight of Davison (W. R. Grace Co.) silica-alumina catalyst at 60 °C, whereupon the temperature rose to 140 °C before the reaction mixture was cooled to room temperature. A pure compound having a retention time similar to that of IV was distilled from this reaction mixture (70 °C (10 mmHg); lit.[9] 70–72 °C (9 mmHg)). The IR, NMR, and mass spectra showed it to be 3,6,6-trimethylbicyclo[3.1.0]hexane-3-carboxaldehyde[9] [IR 1725 cm^{-1} aldehyde, 1035, 835 cm^{-1} cyclopropane; NMR δ 9.38 (s, 1, CHO), 1.02 (s, 11, $-CH_3$ and methine bridgehead protons), 2.4–2.0 and 1.5–1.07 ppm (m, 4, $>CH_2$); MS 109, 41, 81, 67, 137, 43, 123, 152 (M^+)]. Compound V is considered to be 1-methyl-1-formyl-3-isopropyl-3-cyclopentene. The base peak of 137 is explained by ready loss of one of two allylic methyl groups.

Compounds VI and VII (RRT = 1.51 and 1.68) were identified as 4-isocaranone and 4-caranone, respectively. Authentic samples were obtained as a mixture by reaction of 3-carene oxide with silica-alumina catalyst. The mixture showed a ketone band at 1704 cm^{-1} and a parent ion peak at *m/e* 152 in the IR and mass spectra, respectively. The two compounds were purified by preparative GLC; the NMR spectrum of the higher boiling isomer showed methyl signals at δ 0.91(s), 1.04(s), and 1.16 ppm(s); lit.[11] for isocaranone δ 0.86(s), 1.05(s), and 0.92(d) and 1.2 ppm(d). There was good NMR spectral agreement between the higher boiling compound and caranone (VII), but the purified lower boiling compound did not produce a good NMR spectrum consistent with the structure of isocaranone; MS VI, 81, 67, 41, 69, 109, 108, 82; VII, 81, 67, 41, 82, 152, 55, 95.

Compounds IX and X (RRT = 2.50 and 2.97) were identified as *trans*-2-caren-4-ol and *trans*-3(10)-caren-4-ol, respectively. An authentic sample of X was obtained by isomerization of 3-carene oxide over aluminum isopropoxide (AIP).[8]

Peak XIII (RRT = 2.13) was identified as *cis*-2,8,(9)-*p*-menthadien-1-ol by comparison of retention time and mass spectrum with those of an authentic sample prepared by isomerization of 2-carene oxide with metatitanic acid[13]: MS 134, 119, 91, 109, 79, 43, 41, 152 (M^+); reference 91, 119, 134, 41, 79, 77, 43, 152 (M^+).

Peaks XIV and XVI (RRT = 2.58 and 3.13) had nearly identical mass spectra. The base peak in the mass spectrum at *m/e* 59 (Me_2COH^+) suggested loss of the dimethylcarbinol ion. A fragment of *m/e* 94 ($C_7H_{10}^+$) together with the 59 fragment suggested structures of α- and β-phellandren-8-ol for the pair of isomers, XIV, and XVI, respectively. The IR and NMR spectra of the isolated compound XIV were consistent with those of an authentic sample [IR 3400, 1170, 1130 cm^{-1} tertiary alcohol; NMR δ 1.18 (s, 6, $>C(CH_3)_2$), 1.70 (s, 3, vinylic CH_3), 2.1–2.3 (m, 3, $>CH_2$ and $>CH$), 2.56 (s, 1, OH), 5.3–5.6 (broad, 1) and 5.79 ppm (d, 2) for vinylic protons]. The structure of XVI was only inferred because its mass spectrum was almost identical with that of compound XIV [MS XIV, 59, 79, 94, 91, 93, 119, 77, 134 ($M^+ - 18$); XVI, 59, 79, 94, 91, 43, 77, 119, 134 ($M^+ - 18$)].

GLC peaks II, III, VIII, XI, XII, XV, and XVII (RRT = 0.42, 0.55, 2.77, 0.46, 0.96, 3.03, and 4.13) were identified as 1,5,8(9)-*p*-menthatriene, *p*-cymene, carvenone, 1(7),2,8(9)-*p*-menthatriene, α,*p*-dimethylstyrene, a mixture of *cis*- and *trans*-1,8(9)-*p*-menthadien-3-ol and *p*-cymen-8-ol, respectively, by comparison of GLC retention times and mass spectra with reference materials.

References and Notes

(1) Epoxide Rearrangement 11. Part 10: see ref 16.
(2) I. C. Nigam and L. Levi, *Can. J. Chem.*, **46**, 1944 (1968).
(3) R. L. Settine, G. L. Parks, and G. L. K. Hunter, *J. Org. Chem.*, **29**, 616 (1964).
(4) E. E. Royals and L. L. Harrell, Jr., *J. Am. Chem. Soc.*, **77**, 3405 (1955).
(5) J. M. Coxon, E. Dansted, M. P. Hartshorn, and K. E. Richards, *Tetrahedron*, **25**, 3307 (1969).
(6) J. P. Montheard and Y. Chretien-Bessiere, *Bull. Soc. Chim. Fr.*, 336 (1968).
(7) M. P. Hartshorn, D. N. Kirk, and A. F. A. Wallis, *J. Chem. Soc.*, 5494 (1964).
(8) E. I. Eschinasi, *Isr. J. Chem.*, **6**, 713 (1968).
(9) R. L. Settine and C. McDaniel, *J. Org. Chem.*, **32**, 2910 (1967).
(10) Z. G. Isaeva and G. A. Bakaleinik, *Dokl. Akad. Nauk SSSR*, **176**, 1310 (1967); *Chem. Abstr.*, **68**, 95988*u* (1968).
(11) V. S. Joshi, N. P. Damodaran, and S. Dev, *Tetrahedron*, **24**, 5817 (1968); **27**, 459, 475 (1971).
(12) *Chem. Abstr.*, **76**, 14728*z* (1972).
(13) J. O. Bledsoe, Jr., J. M. Derfer, and W. E. Johnson, Jr., U.S. Patent, 3 814 733 (1974).
(14) K. Arata, S. Akutagawa, and K. Tanabe, *J. Catal.*, **41**, 173 (1976).
(15) K. Arata, H. Takahashi, and K. Tanabe, *Rocz. Chem.*, **50**, 2101 (1976).
(16) K. Arata, S. Akutagawa, and K. Tanabe, to be published.
(17) H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).
(18) K. Tanabe, "Solid Acids and Bases", Academic Press, New York, N.Y., 1970, p 58.
(19) However, the direct rearrangement of 3-carene oxide to carvenone is reported to occur in the presence of boron trifluoride etherate; see P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4926 (1966).
(20) K. Arata and K. Tanabe, to be published.
(21) T. Iizuka, H. Hattori, Y. Ohno, J. Soma, and K. Tanabe, *J. Catal.*, **22**, 130 (1971).
(22) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", McGraw-Hill, New York, N.Y., 1968, p 128.
(23) This type opening of 2-carene oxide by acids was also reported by Ohloff and Giersch, *Helv. Chim. Acta*, **51**, 1328 (1968).
(24) E. J. Corey, H. J. Burke, and W. A. Remers, *J. Am. Chem. Soc.*, **78**, 180 (1956).
(25) J. R. B. Campbell, A. M. Islam, and R. A. Raphael, *J. Chem. Soc.*, 4096 (1956).
(26) J. A. Berson and M. R. Willeott, *J. Am. Chem. Soc.*, **88**, 2494 (1966).
(27) J. G. Grasselli, "Atlas of Spectral Data and Physical Constants for Organic Compounds", CRC Press, 1973.

Intramolecular 1,3-Dipolar Cycloaddition Reactions of Alkenyl-Substituted Nitrile Imines[1]

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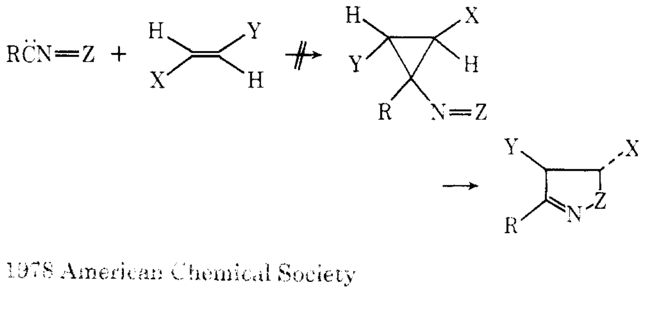
A series of nitrile imines bearing alkenyl substituents on the nitrogen atom of the 1,3 dipole were generated in situ by the photolysis of 2-alkenyl-5-phenyl-substituted tetrazoles or by the base treatment of 1-chlorohydrazones. Intramolecular 1,3-dipolar cycloaddition leading to substituted pyrazoles was the exclusive reaction observed. When the nitrile imine was generated in the presence of an active dipolarophile, bimolecular 1,3-dipolar cycloaddition occurred. Under these conditions, the intramolecular cycloaddition reaction is entirely suppressed. The mode of internal cycloaddition of the allyl-substituted nitrile imine is very different from that previously encountered in the closely related nitrile ylide system. With that system, intramolecular 1,1 cycloaddition was the predominant mode of reaction. Insight into the differences in chemical behavior of the two nitrilium betaines was obtained from molecular orbital calculations. These calculations show that the introduction of a nitrogen atom in the 1,3 dipole results in a significant flattening of the molecule. As the dipole becomes less bent it is less likely to undergo the 1,1-cycloaddition reaction.

The thermally induced addition of 1,3 dipoles to multiple bonds is an extremely versatile and important reaction.[2-4] Numerous possibilities for variation are available by changing the structure of both the dipolarophile and dipole. Some of the more interesting members of the 1,3-dipole family are the nitrilium betaines.[2] This class of 1,3 dipoles always contains nitrogen as the middle atom since only this element can supply an unshared electron pair while in the trivalent neutral state. Among the possible geometric forms of a nitrilium betaine, a carbene structure can be envisaged which makes conceivable a 1,1 cycloaddition of this 1,3 dipole. The possibility that the 1,3-dipolar cycloaddition reaction of a nitrilium betaine with a dipolarophile actually proceeds via a 1,1 cycloaddition followed by ring expansion has been discounted by Huisgen and co-workers.[5] These workers were able to show that three-membered rings are not primary products in the cy-

$$[R\overset{-}{C}=\overset{+}{N}=Z \leftrightarrow R\overset{-}{C}\equiv\overset{+}{N}Z \leftrightarrow R\overset{+}{C}=N\overset{-}{Z} \leftrightarrow R\ddot{C}N=Z]$$

$$Z = C, N, O$$



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