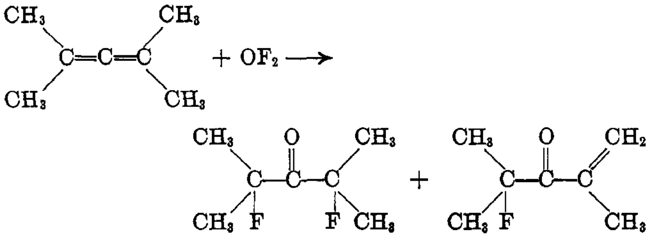


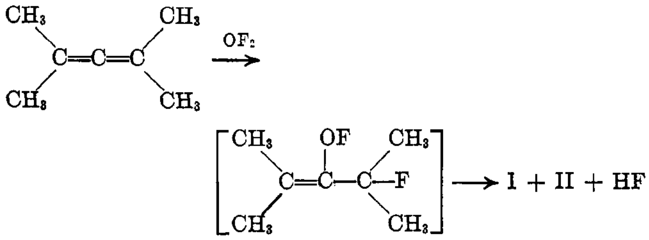
I II

precluded elemental analysis. The infrared spectrum of compound I contained a carbonyl group absorption at 1730 cm.$^{-1}$ representing a shift in the proper direction caused by the fluorine atoms on the α position.[3] The proton n.m.r. spectrum consisted of a doublet (J_{HF} = 20 c.p.s.) centered at δ 1.52. The proton–fluorine coupling is normal[4] for vicinal coupling. Geminal H–F^{19} coupling constants are usually in the order of 40–80 c.p.s.[4] The four methyl groups appear as a single doublet which is indicative of symmetrical substitution as well as the fact that the methyl protons are vicinal to a single fluorine atom. The F^{19} n.m.r. spectrum exhibited a septet structure centered at ϕ +148.3[5] (J_{FH} = 20 c.p.s.) which is typical of a fluorine atom coupling with six equivalent vicinal protons.

The α,β unsaturation of ketone II caused the carbonyl absorption to shift to 1681 cm.$^{-1}$ as expected[3] for this class of compound. The proton n.m.r. spectrum is consistent with the structure II in that the fluoroisopropyl group is a six-proton doublet (J_{FH} = 20 c.p.s.) centered at δ 1.52. The vinylogous protons (two) appear as the characteristic set of multiplets at δ 5.82 and 6.23. The remaining 3-proton broadened singlet at δ 1.90 is assigned to the vinylogous methyl group. The F^{19} n.m.r. spectrum consists of a septet (J_{FH} = 20 c.p.s.) centered at ϕ +144.6 which is again consistent with a single fluorine atom coupling with six equivalent vicinal protons.

The exact character of the attacking species cannot be inferred unequivocally from the existing data. It is very possible that an α-fluorovinyl hypofluorite (III), similar in nature to those postulated in acetylene–OF_2 additions, is first formed, which subsequently isomerizes with fluorine migration to the observed α,α'-difluoro ketone. The migration step includes the probable homolytic fission of the O–F bond followed by either C–F bond formation forming compound I or HF elimination leading to ketone II.

The addition of OF_2 to tetrafluoroallene has been recently reported.[6] The products are not revealing mechanistically, but a low yield of a three-carbon unsaturated hypofluorite of undefined structure was actually isolated. Hypofluorites containing, or in the presence of, C–H bonds have been shown by Thompson and Prager[7] to be of very limited stability and hence would not be expected to survive intact in the tetramethylallene case.



III

Experimental Section

Tetramethylallene (2.4 g., 25 mmoles) was dissolved in 20 ml. of CCl_3F and this mixture was slurried with 1.0 g. of NaF. The slurry was stirred vigorously and degassed at −78°; the OF_2 (25 mmoles) was slowly admitted to the reaction vessel with care to ensure that the pressure of OF_2 never exceeded 20 mm. When the uptake was complete, the volatile products were distilled under reduced pressure from the reactor. The solvent was separated and the residue (~2.1 g.) was rectified by vapor phase chromatography (GESF96 at 68°). Decomposition of both components started when the crude mixture was warmed to ambient temperature and continued throughout the purification procedure. Owing to the instability of the compounds, no estimate of the yield could be made.

Acknowledgment.—The author is grateful to Mr. Jack Brooks for technical assistance and to Mrs. Carolyn Haney for the n.m.r. spectra.

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[3] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

[4] J. A. Pople, *Mol. Phys.*, **1**, 216 (1958).

[5] Fluorine n.m.r. spectra are reported in ϕ values (parts per million from internal CCl_3F).

[6] R. Reed, Jr., K. Prabil, and L. Marantz, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[7] P. G. Thompson and J. H. Prager, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

Isomerization of Alkyl Tropilidenes. II. Rearrangement during Gas Chromatography

KENNETH CONROW AND LARRY L. REASOR[1]

Department of Chemistry, Kansas State University, Manhattan, Kansas 66504

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Two mechanisms have been shown to be responsible for the isomerization of samples of 7-methyltropilidene subjected to gas chromatography on certain columns: an acid-catalyzed mechanism and an intermolecular hydride-exchange mechanism. The most striking evidence for the latter mechanism is that a sample of 7-methyltropilidene injected on a tropylium fluoborate–nitromethylpimelonitrile column results in the elution of tropilidene exclusively.

Our interest in this isomerization during gas chromatography (g.c.) arose when, during a search for a column for g.c. analysis of the isomers of methyltropilidene,[2] very unusual behavior was noted when a picric acid–fluorene column[3] was used. Pure 7-methyltropilidene gave rise to a very broad peak, and rechromatography of the collected eluate on a suitable column revealed that isomerization of the 7 isomer to a mixture of the 1-, 2-, 3-, and 7-methyltropilidenes had occurred.

At least three different mechanisms can be postulated by which this isomerization might be explained: (1) thermally induced intramolecular hydride transfer in the tropilidene[4]; (2) protonation to form a cyclo-

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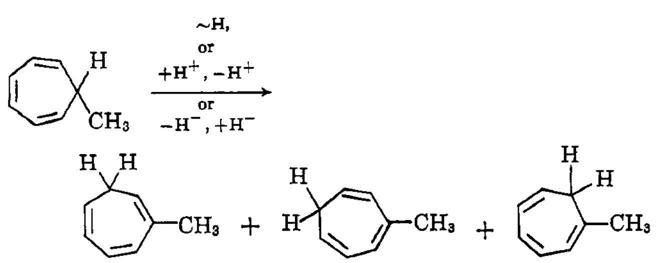
[1] Undergraduate Science Education Fellow of the National Science Foundation, 1962–1963.

[2] K. Conrow, *J. Am. Chem. Soc.*, **83**, 2343 (1961).

[3] A. I. M. Keulemans, A. Kwantes, and P. Zaal, *Anal. Chim. Acta*, **13**, 357 (1955).

[4] A. P. ter Borg, H. Kloosterziel, and N. van Meurs, *Proc. Chem. Soc.*, 359 (1962).



heptadienyl cation followed by loss of an allylic proton; or (3) oxidation of some tropilidene to the tropylium ion by the picric acid (or other oxidants), followed by intermolecular hydride exchange. It was shown earlier[2] that isomerization in acetonitrile solution at 25° is predominately due to intermolecular hydride exchange; thus, the third possibility was initially favored in this work.

Since intramolecular hydride transfer appears to be a purely thermal reaction, not subject to catalysis or inhibition, isomerization by this mechanism would be independent of the nature of the stationary liquid phase. In fact, certain columns, *e.g.*, γ-nitro-γ-methylpimelonitrile,[5] effect no isomerization under comparable conditions and are useful for analysis of the mixtures obtained. This fact eliminates intramolecular hydride exchange in the tropilidene as a possible mechanism for these isomerizations.

Our work was mostly concerned, then, with the investigation of the acid-catalyzed isomerization and the tropylium ion catalyzed isomerization. To this end, a number of g.c. columns were prepared to test specific predictions which can be based on the alternate hypotheses; the most meaningful of these are listed with the results obtained.

(1) A picric acid–dioctyl phthalate (35:65 by weight) column was prepared in the expectation that a change in the inert component would make no qualitative difference in the action of the picric acid. This expectation was completely fulfilled; the chromatograms showed the same broad and poorly defined peaks characteristic of the picric acid–fluorene column, and rechromatography of the collected eluates showed that extensive isomerization had occurred.

(2) A tricresyl phosphate–syrupy phosphoric acid (1:1 by weight) column was prepared to test the activity of a Brønsted acid which is not a π acid and is, presumably, less oxidizing than picric acid. The fact that extensive isomerization occurred indicates that the isomerization may occur *via* acid catalysis.

(3) A consequence of the hypothesis that isomerization occurred *via* oxidation and subsequent intermolecular hydride exchange is that there should be storage of tropilidenes on the column in the form of tropylium salts which could later be displaced by a new tropilidene when hydride exchange occurred. Although fresh picric acid columns would not give evidence for this phenomenon, columns which had been in use for some time did store a tropilidene which could be displaced by another tropilidene. For example, a 3-year-old column, after repeated injections of 7-methyltropilidene, gave about 2% of 1-methyltropilidene in the eluate when pure, unsubstituted tropilidene was injected.

(4) A γ-nitro-γ-methylpimelonitrile–tropylium fluoroborate (1:1 by weight) column was prepared to confirm the possibility of intermolecular hydride exchange under g.c. conditions. Injections of 7-methyltropilidene on this column gave an eluate which, on rechromatography, proved to be unsubstituted tropilidene exclusively. Clearly, then, when a column contains a large amount of tropylium salt, the intermolecular hydride exchange occurs sufficiently rapidly that the injected sample of methyltropilidene is completely absorbed and the eluate consists solely (within experimental limits) of tropilidene derived by chemical reaction.

(5) To test the remote possibility that π acids, as distinct from Brønsted acids, might catalyze the isomerization, a trinitrobenzene–γ-nitro-γ-methylpimelonitrile (mole/mole) column was made. No evidence of isomerization of injected 7-methyltropilidene to its position isomers was obtained.

Thus, there are two distinct mechanisms by which isomerization of alkyltropilidenes subjected to g.c. between 80 and 120° may occur. One mechanism, which requires a protonic acid and does not effect storage of a tropilidene on the column, is presumed to involve a cycloheptadienyl cation as intermediate. The other mechanism, which does effect storage of a tropilidene on the column and which arises only very slowly in a picric acid column, is presumed to be an intermolecular hydride exchange between tropilidene and tropylium ions on the column.

It is interesting to note the inversion of the relative importance of the two mechanisms under two different sets of conditions. In solution,[2] where concentrations of acid, tropilidene, and tropylium ion are of the same order of magnitude, the hydride-exchange mechanism predominates. In g.c., where the stationary phase predominates over tropilidene, the acid-catalyzed mechanism predominates in an acidic column. The hydride-exchange mechanism is so rapid that in the tropylium fluoroborate column the entire sample of an injected tropilidene undergoes hydride exchange, but no estimate of the relative rates of the two mechanisms on g.c. columns can be made with the available data.

Experimental Section

The vapor phase chromatography unit used in this work was a Wilkins Aerograph Model A-90-P, operating between 80 and 120°. Columns were prepared on 60–80-mesh firebrick with approximately 20% by weight of the stationary liquid phase. The coated support was sifted into 0.25-in. copper tubing, 2 m. in length, carefully packed with a vibrator, coiled, and fitted with Swagelock fittings. Fresh columns were baked out at least overnight at 100–120° in a slow helium stream before use.

7-Methyltropilidene was prepared as described earlier.[1] Pure samples of tropilidene were obtained by preparative g.c. of a commercial sample[6] on a dioctyl phthalate column. Tropylium fluoroborate was prepared in the usual way.[7] The preparation of γ-nitro-γ-methylpimelonitrile was similar to that of its congeners.[8]

Isomerization Experiments. Controls.—A sample of 7-methyltropilidene was passed through the nitromethylpimelonitrile column four successive times. The final injection proved to be unchanged 7-methyltropilidene of ≥98% purity. Similar results were obtained when the trinitrobenzene–nitromethylpimelonitrile column was used.

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(5) N. A. Nelson, J. H. Fassnacht, and J. U. Piper, *J. Am. Chem. Soc.*, **83**, 206 (1961).

(6) We thank the Shell Chemical Co. for generous samples of tropilidene.

(7) K. Conrow, *Org. Syn.*, **43**, 101 (1963).

(8) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **65**, 23 (1943).

Acid Isomerization.—The **picric acid columns** were used for four repeated injections of the same sample of 7-methyltropilidene. Portions of each successive eluate were retained for subsequent analysis on the nitromethylpimelonitrile column. Analysis showed that isomerization proceeded progressively and that changes were still observed during the last pass. The use of solvent (pentane) to facilitate handling of the small amounts of material collected made the peaks broad in the final analyses so that accurate quantitative isomer distributions could not be obtained, but the 7, 2, 3, and 1 isomers were about 63:8:9:19 from the picric acid–fluorene column. Isomerization went faster (final ratio after four injections about 36:11:8:45) on the picric acid–dioctyl phthalate column than on the picric acid–fluorene column, presumably because the retention time was much larger on the former so that the tropilidenes were exposed to picric acid for a longer period of time.

The **phosphoric acid column** gave results very similar to those obtained with the picric acid columns, except that the isomerization appeared still more rapid, and was more nearly complete at the end of four successive passes (ratio was about 6:13:24:57) of the same sample through the column. Once again, accurate analyses of the eluted materials were not obtained.

Hydride Exchanges.—The picric acid–fluorene column which had been prepared and used 3 years ago was again used. After the above isomerizations were studied and several injections of 7-methyltropilidene had been made, injection of 5 μl. of unsubstituted tropilidene and subsequent analysis of the collected eluate on the nitromethylpimelonitrile column gave evidence for the presence of about 1.6% of 1-methyltropilidene in the tropilidene sample which was collected.

The **tropylium fluoroborate–nitromethylpimelonitrile column** (which was prepared by coating the firebrick from an acetonitrile solution of the stationary phases and handling rapidly to minimize exposure to air) was used promptly after it was baked out with a helium stream overnight. The samples eluted from each of three 5-μl. injections of 7-methyltropilidene were analyzed on an SF-90 column and proved to be unsubstituted tropilidene with no discernible quantitity of methyltropilidenes present.

Low-Pressure Catalytic Hydrogenation of Some 1-(Tertiary amino)-2-methyl-2-nitropropanes

MORRIS FREIFELDER AND YEW HAY NG

Organic Chemistry Department,
Research Division, Abbott Laboratories,
North Chicago, Illinois

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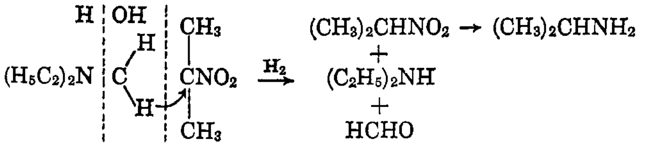
Hydrogenation of 1-(tertiary amino)-2-methyl-2-nitropropanes, $>NCH_2C(CH_3)_2NO_2$, was reported in good yield in cases where the tertiary amino nitrogen was in a cyclic system.[1] Under similar conditions (reduction in alcohol in the presence of Raney nickel at 30–50° and 33 atm.) 1-dimethylamino- and 1-dibutylamino-2-methyl-2-nitropropanes gave good yields of the corresponding diamines.[2] However, only a 20% yield of diamine II resulted from the attempted conversion of 1-diethylamino-2-methyl-2-nitropropane (I).[3]

A particular need in this laboratory for 1-diethylamino-2-methyl-2-propylamine (II) gave us an opportunity to evaluate the hydrogenation of I under low-pressure conditions. A number of failures resulted until it was found that I deteriorated on standing.[4] In a set of reductions over a 4-week period of a single lot of I in glacial acetic acid in the presence of rhodium-on-carbon catalyst, the amount of material corresponding to II, first obtained in 57.5% yield, decreased to 47% and then to 39%. In a second set with a fresh batch of I the yield went from 55 to 42% after 2 weeks standing and to 29% after I had been used after 4 weeks. To further complicate matters g.l.p.c. showed that the diamine obtained was a 2:1 mixture of II and its N-methyl derivative III.

A new series of experiments was inaugurated using freshly prepared I immediately after distillation. In one group, hydrogenations were run in glacial acetic acid in the presence of palladium on carbon, rhodium on carbon, and platinum oxide. The second group of reductions was run in absolute ethyl alcohol using the same catalysts as well as Raney nickel. The results, which are seen in Table I, show that many low-boiling components were obtained. It is further evident that considerable methylation took place, since in every experiment but one N',N'-diethyl-N^2-methyl-2-methylpropane-1,2-diamine (III) is noted.

Senkus has shown that, tertiary amino-2-alkyl-2-nitropropanes can be hydrolyzed by water. He has also reported that, in the hydrogenation of 1-diisopropylamino-2-methyl-2-nitropropane, diisopropylamine (reaction 2) and N-methyldiisopropylamine and isopropylamine (reaction 3) were among the products obtained.[5] Reaction 3 can be one of the pathways by which side reaction occurs in the reduction of I. It cannot, however, account for III. The following scheme could lead to III and indeed be the way to all the products found in addition to II and III. Water resulting from conversion of the nitro group causes rupture of I with the release of formaldehyde which by reductive alkylation gives the N-methylated products seen in Table I.



To determine whether II itself could lead to by-products, it was hydrogenated in the presence of rhodium catalyst in acetic acid and in the presence of Raney nickel in 95% ethyl alcohol. No uptake of hydrogen was observed nor was there any other component found by g.l.p.c.

The work was extended to cover a few other tertiary amino-2-methyl-2-nitropropanes. The 1-dimethylamino compound IV was converted to the diamine V in high yield during reduction in glacial acetic acid. The hydrogenation of IV to V could also be carried out in alcoholic solution in the presence of Raney nickel, but it was difficult to distil off solvent without loss of amine. When the corresponding 1-dibutylaminonitro compound VI was reduced, considerable cleavage occurred, giving about 25% of the diamine VII and

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[1] M. Senkus, U. S. Patent 2,426,375 (1947).

[2] H. G. Johnson, *J. Am. Chem. Soc.*, **68**, 12 (1946).

[3] G. H. Butler and F. N. McMillan, *ibid.*, **72**, 2978 (1950).

[4] Chromatography (g.l.p.c.) of I after standing several weeks showed a main peak (85%) plus 15% of a mixture of products. The vapors on opening the dark, stoppered bottle were strongly basic to test paper. Because of pressure of work in the chromatography laboratory when the material was reexamined, most of the low-boiling components had volatilized. It was possible to identify a small amount of what appeared to be N-methyldiethylamine, 0.34% of 2-nitropropane, and 0.3% of 2-methyl-2-nitro-1-propanol. The effect of air and moisture on the decomposition of I is to be studied in greater detail. Samples are to be aged in sealed moist ampoules so that low boils will not be lost and examined by g.l.p.c. after regular periods. The results will be reported at a later date.

[5] M. Senkus, *J. Am. Chem. Soc.*, **72**, 2069 (1950).