The Preparation of Allylic Alcohols from Citral a and Citral b. A Study of Their Dehydration Reactions[1]

P. B. VENUTO[2] AND A. R. DAY

Department of Chemistry, University of Pennsylvania, Philadelphia 4, Pennsylvania

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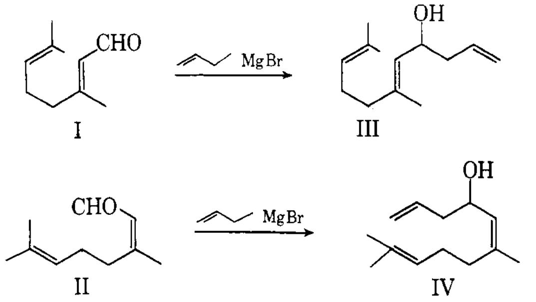
The citral isomers a and b have been separated and their configurations confirmed by nuclear magnetic resonance spectroscopy. From citral a (I) and b (II) the stereoisomeric alcohols, *trans*- and *cis*-6,10-dimethyl-1,5,9-undecatrien-4-ol (III and IV), have been prepared and their dehydration reactions investigated. Thermal and acid-catalyzed dehydrations were mainly associated with allylic rearrangements. Varying amounts of polymer and mixtures of four acyclic isomers ($C_{13}H_{20}$) were formed in most cases. Evidence for the structures and mechanism of formation of the dehydration products is presented.

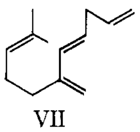
It was the purpose of this work to synthesize secondary allylic alcohols of known configuration from the citral[3] stereoisomers and allylmagnesium bromide and to characterize the products formed from their thermal and acid-catalyzed dehydrations.

The method of Naves[4] was used for the separation of the citral isomers from commercial citral. The physical properties and infrared spectra of the citral, so obtained, were in good agreement with those of Naves. Nuclear magnetic resonance furnished critical spectroscopic evidence for the configuration of the citral isomers. Most significant, in terms of stereochemistry, was the appearance of the signal for the β-methyl group of the α,β-unsaturated carbonyl system in citral b at τ 8.07 (doublet, J = 1.8 c.p.s.), instead of at τ 7.85 as in citral a. This is within 0.03 p.p.m. from its location in crotonic acid, where the carbonyl group is likewise *trans* to the methyl,[5] and a similar doublet is observed. These data are further in excellent agreement with the value of 0.2 p.p.m. listed by Jackman[6] for the differential shielding of protons of *trans* and *cis* methyl groups (δ_{tc}) by a β-aldehyde group.

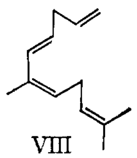


Treatment of citral a (I) and citral b (II) with allylmagnesium bromide gave 80–85% yields of allylic alcohols, *trans*- and *cis*-6,10-dimethyl-1,5,9-undecatrien-4-ol (III and IV). Alcohol III readily formed an acetate (V). There was no evidence for 1,4-addition to the α,β-unsaturated system of I or II, and catalytic hydrogenation of both III and IV gave the *same* saturated alcohol, 6,10-dimethylundecan 4-ol (VI). Aside from minor, nondefinitive infrared differences, the only spectroscopic evidence indicative of the *cis–trans* nature of III and IV lay in the n.m.r. spectra. The methyl resonance from the group —CCH_3=CHCHOH— in III occurred at 0.5 p.p.m. higher field (τ 8.39) than in its stereoisomer IV (τ 8.34). This data agrees well with values reported for stereochemically analogous systems in terpenoids[7] and conjugated dienes.[8] To provide chemical confirmation of these assignments, III and IV were treated with active manganese dioxide in petroleum ether (b.p. 35–60°). Instead of conversion to the corresponding α,β-unsaturated ketones, as expected, oxidative scission occurred at the weak 3,4-position, with regeneration of the parent aldehydes. Evidence for retention of original aldehyde stereochemistry in the derivative alcohols was thus provided.

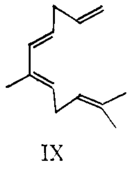
An initial direction for the study of III and IV was provided by their marked thermal instability. The *trans* alcohol (III) readily eliminated 1 mole of water when the pure liquid was heated at 150° and atmospheric pressure. A mixture of products was obtained, including four previously unreported $C_{13}H_{20}$ hydrocarbons, 6-methylene-10-methyl-1-*trans*-4,9-undecatriene (VII, 30%), 6,10-dimethyl-1-*trans*-4-*cis*-6,9-undecatetraene (VIII, 7%), 6,10-dimethyl-1-*trans*-4-*trans*-6,9-undecatetraene (IX, 16%), and 6,10-dimethyl-1-*trans*-3-*trans*-5,9-undecatetraene (X, 2%). A dimer, $C_{26}H_{40}$, was also isolated. Viscous, liquid polymers accounted for the remaining 41% of the products. The *cis* alcohol (IV) showed a similar product distribution when dehydrated thermally.



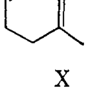
VII



VIII



IX



X

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[1] This work was presented in part at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962, and formed part of the Ph.D. Thesis of P. B. Venuto, University of Pennsylvania, 1962.

[2] Harrison Fellow, 1961–1962.

[3] For related work in this general field, see (a) M. Mousseron and M. Vedel, *Bull. soc. chim. France*, 1485 (1960); (b) M. Mousseron-Canet, M. Mousseron, and J. Boch, *ibid.*, 597 (1959); (c) M. Mousseron and M. Mousseron-Canet, *Compt. rend.*, **247**, 1937 (1958).

[4] Y. R. Naves, *Bull. soc. chim. France*, **19**, 521 (1952); Y. R. Naves and A. Odermatt, *ibid.*, 377 (1958).

[5] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalogue," Instrument Division of Varian Associates, Palo Alto, Calif., 1962, Spectrum No. 61.

[6] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p. 121.

[7] R. B. Bates and D. M. Gale, *J. Am. Chem. Soc.*, **82**, 5749 (1960).

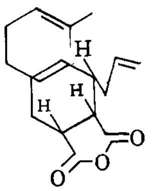
[8] H. O. House, D. D. Traficante, and R. A. Evans, *J. Org. Chem.*, **28**, 348 (1963).

The same four hydrocarbons, VII (39%), VIII (15%), IX (27%), and X (12%), were formed when alcohol III, in refluxing benzene, was treated with an appropriately mild acid catalyst (anhydrous oxalic acid). Only a small amount (6%) of polymer was formed in this case.

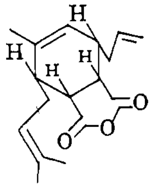
The $C_{13}H_{20}$ isomers were separated by fractional distillation and gas chromatography. Hydrogen numbers indicated the presence of four double bonds in *each* isomer, and the *same, single*, saturated hydrocarbon, identified as 6,10-dimethylundecane (XI),[9] was formed upon catalytic hydrogenation. Both formaldehyde and acetone were formed, in all cases, when the hydrocarbons were subjected to ozonolysis. The acyclic nature of VII–X was further demonstrated by the presence of isopropylidene group signals in their n.m.r. spectra near τ 8.4.[10] Signals at about τ 9.0,[11] arising from the *gem*-dimethyl groups that would almost certainly be present in any of the expected cyclization products of VII–X were notably absent.

Ultraviolet absorption at 228 mμ (ϵ 12,800) suggested that two double bonds were conjugated in tetraene VII. Infrared bands at 959 and 880 cm.$^{-1}$ were assigned to the out-of-plane deformation modes of a *trans* double bond and an asymmetric disubstituted ethylenic linkage, respectively. Further evidence for the disposition of double bonds in the molecular skeleton was provided by n.m.r. A doublet at τ 7.8 (J = 3 c.p.s.) arose from the four allylic methylene protons, and a triplet at τ 7.2 (J = 6 c.p.s.) from the two doubly allylic (=C—CH_2—C=) methylene protons. The consistency of the above spectroscopic assignments was confirmed by the vigorous reaction of isomer VII with maleic anhydride at room temperature to form an adduct (XII).

A substituted, conjugated diene system was also shown to be present in isomer IX, with ultraviolet absorption occurring at 236 mμ (ϵ 21,000). A *trans* double-bond absorption at 959 cm.$^{-1}$ in the infrared and an n.m.r. signal for methylene (-CH_2-) groups adjacent to two, but not one, double bonds, supported the structure indicated for IX. $C_{13}H_{20}$ isomer IX also reacted easily with maleic anhydride at room temperature to form an adduct (XIII). The facility of the reaction indicated not only the presence of a *trans*-4,5 double bond, but also demonstrated that the disposition of the large groups about the 6,7 (trisubstituted) double bond was *trans*. This observation is consistent with the fact that 1-substituted *cis*-1,3-butadienes do not easily undergo the Diels–Alder reaction at room temperature.[12] Further, translation of the rule of *endo* addition into the reactions of acyclic dienes requires that the adducts of *trans*-1- and 4-substituted dienes with simple dienophiles be completely *cis*-substituted cyclohexenes.[13] Hence, the all-*cis* structures are proposed for adducts XII and XIII.



XII



XIII

The structure proposed for isomer VIII is identical with that of isomer IX, except that, in VIII, the large groups about the 6,7 double bond are *cis*. Aside from absorption in the ultraviolet at a slightly longer wave length (238.5 mμ), the spectroscopic features of VIII were very similar to those of IX. The gas chromatographic retention time of VIII, however, was different from that of IX. A scale model of VIII demonstrates that steric repulsions, upon approaching the *s-cis* conformation, are very great. Since the planar cisoid form of a diene is the conformation required for the Diels–Alder reaction,[14] it would be predicted that these repulsions would induce an activation energy so high that VIII would not easily react with maleic anhydride. Such was indeed shown to be the case experimentally, for, when a mixture of VII, VIII, and IX was stirred with maleic anhydride at 25°, only VIII was recovered, the high-boiling adduct of VII and IX remaining in the pot. Unreacted VIII was also recovered after a 5-day reflux of this isomer with maleic anhydride in benzene.

The remaining $C_{13}H_{20}$ isomer (X) showed ultraviolet absorption at 272 mμ (ϵ 62,900), a wave length consistent with three double bonds in conjugation.[15] Infrared bands arising from the vinyl group and *trans* double bond in X were close to those reported for the corresponding vinyl group and *trans* double-bond vibrations in *trans*-1,3,5-hexatriene.[16] The shift of the peaks in X from the positions of the corresponding bands in VII, VIII, and IX is attributed to conjugation.

The most striking feature observed with alcohol III was the association of *allylic rearrangement* with its dehydration. Because of the reactive 5,6 double bond, the system has a more attractive path (π-electron shift) available than elimination of a proton at the 3-position. Thus X was formed in small amounts only, despite a conjugation effect[17] that might be expected to favor it.

It is quite probable that the dehydration over oxalic acid proceeded *via* ionic or polar intermediates. The similar isomer ratio and the fact that no differences in reaction rate or product distribution were observed when III was thermally dehydrated in the presence of a free-radical inhibitor under nitrogen suggest that an ionic[18] mechanism is involved here also. The intermediates may be visualized as allylic carbonium ion

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(9) Our paraffin XI showed identical physical and spectroscopic properties with those of a sample of 6,10-dimethylundecane recently prepared by Mr. J. B. Bendoraitis of Socony Mobil Oil Co., Paulsboro, N. J. This independent synthesis involved the condensation of *n*-pentylmagnesium bromide and 2-methylheptan-6-one, dehydration of the resulting alcohol to a mixture of olefins, and, finally, catalytic hydrogenation.

(10) M. Barber, J. Davis, L. Jackman, and B. Weedon, *J. Chem. Soc.*, 2870 (1960).

(11) F. Anet, *Can. J. Chem.*, **39**, 2262 (1961).

(12) K. Alder, *Ann.*, **571**, 157 (1951).

(13) J. Martin and R. Hill, *Chem. Rev.*, **61**, 537 (1961).

(14) D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.*, **83**, 2885 (1961).

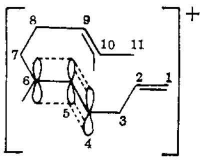
(15) Allocimene, which contains a similar conjugated system, absorbs at 277 mμ; see W. Oroshnik, G. Karmas, and A. Mebane, *ibid.*, **74**, 295 (1952).

(16) J. Hwa, P. de Benneville, and H. Sims, *ibid.*, **82**, 2537 (1960).

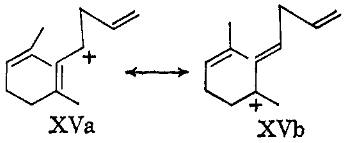
(17) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 436.

(18) This conclusion is consistent with recent studies of the pyrolytic decomposition of esters $R{-}CO{-}O{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H$, where it has been shown that the C–O bond breakage is heterolytic, and that the α-carbon atom develops some carbonium ion character in the transition state; see G. G. Smith, D. A. K. Jones, and D. F. Brown, *J. Org. Chem.*, **28**, 403 (1963).

XIV,[19] with considerable double-bond character in the 4,5-position, or resonance hybrid XV, with tertiary carbonium ion XVb predominating.



XIV



XVa XVb

The ratios of isomers VII–X may be explained on the basis of steric interactions. The large amount of 1-olefin (VII) formed is probably due to fewer (destabilizing) eclipsing effects from the bulky alkenyl groups in the transition state preceding it. The predominance of the *trans,trans* isomer (IX) over the *trans,cis* isomer (VIII) can be explained in a similar manner.[20]

Experimental[21]

Spectra.—Infrared spectra were run neat using a Perkin-Elmer 421 spectrophotometer unless otherwise specified. Ultraviolet spectra were run in ethanol solution on a Beckman DU spectrophotometer. Raman determinations were run on a Cary 81 spectrometer, using solutions (25% by weight) in carbon tetrachloride. Nuclear magnetic resonance spectra were recorded at a frequency of 60 Mc. on a Varian A-60 spectrometer; samples were run as solutions (10% by weight) in carbon tetrachloride, with a trace of tetramethylsilane added as an internal reference. Mass spectra were recorded at 70 e.v. on a Consolidated Electrodynamics Corporation Model 21-103 spectrometer with inlet temperature of 350°.

Citral a (I) and Citral b (II).—The fractional distillation method of Naves[4] was used except that the Todd distillation apparatus was used. Fractions having b.p. 77° (1.8 mm.), n^{20}_D 1.4898, d^{20}_4 0.8842, MR^{20} 49.73 (calcd. for $C_{10}H_{16}O$, 47.46), and giving a semicarbazone, m.p. 161–163° (lit.[4] m.p. 164°), were designated as citral a (I); infrared bands (cm.$^{-1}$) diagnostic of citral a (I): 1665 (vs, conjugated C=O), 1625 (s), 1603 (m), 1398 (w), 1190 (s), 1117 (s), 885 (w), and 860 (w); ultraviolet maximum at 236 mμ (ϵ 16,300).

N.m.r. spectrum of citral a (I) showed a doublet centered at τ 0.16 (J = 7.8 c.p.s., aldehyde proton), doublet at 4.2 (J = 8.4 c.p.s., olefinic proton in the group $\overset{|}{\text{—C}}\text{=CHCHO}$), unresolved multiplet at 5.0 (olefinic proton in the isopropylidene group), strong group of lines near 7.85 (four allylic $-CH_2-$ protons, with the signal from the β-methyl of the group $\mathrm{>C{=}C<}^{\quad\mathrm{H}}_{\mathrm{CH_3}\quad\mathrm{CHO}}$ superimposed), and doublet at 8.35 (J = 3 c.p.s., isopropylidene $-CH_3$).

Fractions giving b.p. 76.5° (2.3 mm.), n^{20}_D 1.4868–1.4869, d^{20}_4 0.8865, MR^{20} 49.37 (calcd. for $C_{10}H_{16}O$, 47.46), and yielding a semicarbazone, m.p. 173–174° (lit.[4] m.p. 171°), were designated as citral b (II); infrared bands (cm.$^{-1}$) diagnostic of citral b (II): 1665 (vs, conjugated C=O), 1621 (m), 1388 (s), 1178 (m), 1147 (s), 1088 (m) and 833 (s); ultraviolet maximum at 234 mμ (ϵ 12,700).

N.m.r. spectrum of citral b (II) was similar to that of stereoisomer I, except that the signal for the β-methyl group in the α,β-unsaturated carbonyl system appears at τ 8.07 (doublet, J = 1.8 c.p.s.), and the signals from the two allylic $-CH_2-$ groups are split up into a more complex pattern (τ 7.4–7.7). The doublet (J = 8.4 c.p.s.) arising from the aldehyde proton was shifted to a slightly higher field strength (τ 0.20).

***trans*-6,10-Dimethyl-1,5,9-undecatrien-4-ol** (III).—Citral a (I, 85 g., 0.56 mole) was treated with allyl bromide (108.6 g., 0.898 mole) and magnesium (16.2 g., 0.674 g.-atom) using the procedure of Knorr.[22] A saturated solution of ammonium chloride was used to decompose the adduct. The ether–benzene solution was washed with three 125-ml. portions of sodium bisulfite solution and two 125-ml. portions of water and then dried over anhydrous potassium carbonate. The crude alcohol was fractionally distilled *in vacuo*. The yield of III was 79%, b.p. 80–82° (0.1 mm.), n^{20}_D 1.4807, d^{20}_4 0.8766.

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.34; H, 11.42. Found: C, 80.12; H, 11.59.

Infrared spectrum (cm.$^{-1}$) of III showed vinyl peaks at 3078 (w, C–H), 1635 (m, C=C), 990 (s, =CH), 908 (s, =CH$_2$); other bands at 858, 838, and 810 (all w, $R_2C{=}CHR$ groups), 3350 (s, O–H), 1020 (s, C–O). Raman bands appeared at 1640 (w, C=CH$_2$) and 1672 (m, $R_2C{=}CHR$). Bands at 234 mμ (ϵ 240) and 274 mμ (sh, ϵ 55) were observed in the ultraviolet spectrum.[23] N.m.r. spectrum showed a finely split signal, τ 8.43–8.34 (superimposition of the three allylic $-CH_3$ groups), 7.8 (allylic $-CH_2-$ protons), singlet 6.91 not present in acetate of III (alcohol proton), multiplet centered at 5.7 (tertiary proton in group -CHOH-), 5.1 (vinyl = CH$_2$ protons), 4.9–3.9 (remaining olefinic protons). The expected ratio of olefinic to nonolefinic protons was observed.

***cis*-6,10-Dimethyl-1,5,9-undecatrien-4-ol** (VI).—Preparation and work-up were identical with those used for III, except that citral b (II) was used in place of citral a (I). An 84% yield was obtained, b.p. 80° (0.3 mm.), n^{20}_D 1.4810, d^{20}_4 0.8755.

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.34; H, 11.42. Found: C, 80.22; H, 11.50.

The infrared and Raman spectra were almost identical with those for III. Absorption in the ultraviolet occurred at 232 mμ (ϵ 280) and 274 mμ (sh, ϵ 58). The n.m.r. signals for the three allylic methyl groups appeared at τ 8.40–8.27, and were more finely split; otherwise, the spectrum was the same as that of III.

***trans*-6,10-Dimethyl-1,5,9-undecatrien-4-yl Acetate** (V).—Using a modified method of Mills,[24] this compound was prepared from alcohol III and acetyl chloride in benzene solution in the presence of a threefold excess of pyridine. The yield was 52%, b.p. 87–88° (0.5 mm.), n^{20}_D 1.4672, d^{20}_4 0.8882.

Anal. Calcd. for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24. Found: C, 76.12; H, 10.23.

Acetate V showed ester C=O stretch at 1733 cm.$^{-1}$ in the infrared. In the n.m.r. spectrum the ester showed a singlet at τ 8.74 (three acetate methyl protons) and a multiplet centered at 6.0 (proton on carbon bearing the acyl group); the peak at τ 6.91 (O–H) observed in alcohols III and IV was absent.

6,10-Dimethylundecan-4-ol (VI).—*trans* alcohol III (1.94 g., 0.01 mole) in 95% ethanol (50 ml.) was subjected to catalytic hydrogenation at 53–55 p.s.i. in a Parr catalytic apparatus. Platinum oxide (0.5 g.) was the catalyst. A single product (VI) was observed. The *same* product was obtained when *cis* alcohol (IV) was hydrogenated under identical conditions. After purification by preparative-scale gas chromatography (silicone gum rubber column), VI was identified as 6,10-dimethylundecan-4-ol b.p. (micro) 249°, n^{20}_D 1.44012.

Anal. Calcd. for $C_{13}H_{28}O$: C, 77.93; H, 14.09. Found: C, 78.34; H, 14.07.

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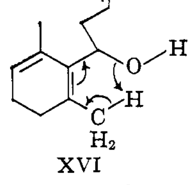
[19] A pseudo-cyclic six-membered transition state (XVI) in the pyrolysis reaction would explain the large amount of 1-olefin (VII) formed, but not the direct formation of the other isomers. Since it has been shown experi-



XVI

mentally that VII does not rearrange to VIII–X under the conditions of the pyrolysis, a different transition state must be involved.

[20] For an excellent discussion of such steric effects, see H. C. Brown and M. Nakagawa, *J. Am. Chem. Soc.*, **77**, 3614 (1955).

[21] All melting points are uncorrected. Molecular weights were determined with a Mechrolab vapor pressure osmometer, Model 301. Gas chromatographic analyses were carried out with a Burrell Kromo-Tog, Model K-1, using a column containing 20% Carbowax 20M on Chromosorb at a temperature of 172°. For micropreparative scale runs, an F & M Model 720 dual column chromatograph fitted with 0.5-in.-o.d. columns was used.

[22] A. Knorr (to I. G. Farbenindustrie), German Patent 544,388 (1932).

[23] Similar ultraviolet bands have been reported for the isoprenoids; farnesol and geraniol, by Y. Naves and P. Ardizio [*Helv. Chim. Acta*, **31**, 1240 (1948)].

[24] J. A. Mills, *J. Chem. Soc.*, 2332 (1951).

Key infrared bands (cm.$^{-1}$) for VI were 3335 (s, –OH), 1458 (s, $-CH_2-$), doublet 1375 and 1370 (m) and 1360 (m, *gem*-dimethyl), 1135 and 1114 (m, C–O) and 726 (w, $-(CH_2)_3-$); n.m.r. spectrum: intense doublet at τ 9.11 and 9.01 ($-CH_3$), multiplet centered at 8.67 ($-CH_2-$ saturated), overlapping weaker multiplet with signals at 8.58 and 8.53 and tailing off toward 8.1 ($-C\mathit{H}_2-\overset{|}{\underset{|}{C}}-OH$ and $CH_3R_1R_2C\mathit{H}$), singlet at 6.85 (O–H), flat multiplet centered at 6.23 ($R_1R_2C(OH)\mathit{H}$); all integrated areas were consistent with the proposed structure. Mass spectrum showed a base peak, $m/e = 55$ (100%), which appeared in the low-mass region; molecular ion peaks (M^+) for both alcohol VI ($m/e = 200$, 0.03%) and the monoolefin ($m/e = 182$, 2.06%) from dehydration of VI in the mass spectrometer inlet were observed; peaks at m/e = 73 (68.6%, C_4H_9O) and m/e = 157 (20.2%, $C_{10}H_{21}O$) clearly designate C-4 as the site of the hydroxyl group.

Attempted Preparation of *trans*- and *cis*-6,10-Dimethyl-1,5,9-undecatrien-4-one.—To a solution of alcohol III (36 g., 0.19 mole) in 1.75 l. of petroleum ether (30–60°) was added 359 g. of active manganese dioxide[25] and the mixture was stirred for 1 hr. After removing the solid, the solvent was stripped under reduced pressure to give 33.6 g. of yellow oil which was fractionally distilled to give 23 g. of alcohol III and 2 g. of an aldehyde identified by infrared and ultraviolet spectra as citral a (I). The melting point and spectra of the semicarbazone derived from this citral fraction were identical with those for citral a semicarbazone.[4]

Similarly, when the *cis* alcohol (IV) was treated as above with active manganese dioxide, most of the alcohol was recovered unchanged and a small amount of aldehyde was obtained. No other carbonyl compounds, including the hoped-for *cis*-6,10-dimethyl-1,5,9-undecatrien-4-one, were present. Infrared and ultraviolet spectra of this fraction, as well as the melting point and spectra of the semicarbazone derived from it, showed this fraction to be citral b (II).

Thermal Dehydration of *trans*-6,10-Dimethyl-1,5,9-undecatrien-4-ol (III).—Alcohol III (67.3 g., 0.347 mole) was heated (neat) at 150–155° for 6 hr. at atmospheric pressure. Within this time, 5 g. of water collected in a Dean-Stark tube. The oily residue was taken up in ether and dried over anhydrous sodium sulfate; the ether was removed *in vacuo*. A yellow oil remained, the infrared spectrum of which showed no O–H stretch. Distillation at 0.3–0.5 mm. showed the presence of 56.6% low-boiling hydrocarbons and 43.2% of higher-boiling species. Gas chromatographic analysis of the low-boiling fraction showed the presence of four products: VII (53.5%), VIII (13.2%), IX (28.1%), and X (3.1%). These showed retention times of 5.8, 6.9, 8.9, and 10.3 min., respectively. Samples for infrared and ultraviolet spectroscopic analysis were obtained by trapping the effluent gases from the chromatograph.

When the dehydration was repeated under nitrogen in the presence of a free-radical inhibitor (1% of 2,6-di-*t*-butyl-*p*-cresol), the same reaction products, and in similar distribution, were formed.

***trans*-6-Methylene-10-methyl-1,4,9-undecatriene (VII).**—The fraction, b.p. 83–85° (3.6 mm.), $n^{20}D$ 1.4882, d^{20}_4 0.8277, was assigned structure VII; hydrogen number calcd. 4, found 3.75; MR^{20} 61.40 (calcd. 60.36); mol. wt. calcd. 176, found 167.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.40; H, 11.34.

Isomer VII absorbed at 228 mμ (ϵ 12,800) and 271 mμ (ϵ 3500) in the ultraviolet. The infrared spectrum (cm.$^{-1}$) showed vinyl peaks, and bands at 1660 (w), 1600 (m, conjugated C=C), 1099 (m), 959 (s, *trans*-CH=CH), 880 (s, $R_2C=CH_2$), and 818 (m, $R_2C=CHR$); key Raman bands (cm.$^{-1}$) at 1643 and 1622 (s, C=C—C=C), and 1660 ($R_2C=CHR$). The n.m.r. spectrum showed a doublet at τ 8.39 (J = 4.2 c.p.s., isopropylidene $-CH_3$), a doublet at 7.8 (J = 3 c.p.s., allylic $-CH_2-$), a triplet centered at 7.2 (J = 6 c.p.s., doubly allylic $-CH_2-$), a singlet at 5.17 (superimposed vinyl and methylene $C=CH_2$ protons), and signals at 4.9–3.8 from the other olefinic protons.

It is important to observe that the isomer VII, on prolonged heating under the conditions of the original thermal dehydration, did not isomerize to VIII–X, but polymerized instead.

Reaction of VII with Maleic Anhydride.—Compound VII (3.52 g., 0.02 mole) and maleic anhydride (2 g., 0.02 mole) were stirred together. A yellow color appeared and heat was evolved. The mixture was then heated on a steam bath for 2 hr. Fractional distillation gave a 65% yield of yellow, viscous adduct XII, b.p. 149–152° (0.3 mm.), $n^{20}D$ 1.5081.

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.63; H, 8.34.

Important infrared bands (cm.$^{-1}$) for XII were 3078 (w, vinyl =C—H), 1840 (s) and 1774 (vs, anhydride C=O in five-membered ring), 1635 (m, vinyl C=C), 1240 (s) and 1195 (s, C–O–C).

The adduct is believed to be *cis*-1,2,3,6-tetrahydro-3-allyl-5-(4-methyl-3-pentenyl)phthalic anhydride (XII).

Ozonolysis of VII.—Ozone was passed into a solution of VII (1.76 g., 0.01 mole) in 70 ml. of ethyl acetate at −70°. After absorption of ozone had ceased, water (50 g.) and zinc dust (20 g.) were added and the mixture refluxed while passing a slow stream of nitrogen through the flask. The effluent gases were passed through a solution of dimedon in 50% ethanol.[26] The dimedon derivative of formaldehyde melted at 190–191°, yield 20%.

Anal. Calcd. for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 70.07; H, 8.34.

Ozonolysis of VII by the method of Bailey[27] gave a 20% yield of iodoform. A mixture melting point with an authentic sample of iodoform showed no depression. This confirms the presence of the isopropylidene grouping in VII.

6,10-Dimethyl-1-*trans*-4-*trans*-6,9-undecatetraene (IX). The fraction, b.p. 91–92° (3.1 mm.), $n^{20}D$ 1.5084, d^{20}_4 0.8239, was assigned structure IX; hydrogen number calcd. 4.0, found 3.8; MR^{20} 63.46 (calcd. 60.36); mol. wt. calcd. 176, found 170.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.48; H, 11.57.

Ultraviolet absorption for IX occurred at 236 mμ (ϵ 21,200) and 272 mμ (ϵ 5500). The infrared spectrum (cm.$^{-1}$) showed vinyl peaks, bands at 959 (s, *trans* CH=CH), and a series of weak bands at 860–788 (probably associated with groups $R_2C=CHR$). No band at 1600 cm.$^{-1}$ was observed. Strong Raman bands at 1646 and 1625 cm.$^{-1}$ were assigned to the two double bonds in conjugation. The n.m.r. spectrum showed a doublet at τ 8.34 (J = 3.6 c.p.s., three allylic $-CH_3$ groups), a triplet at 7.2 (J = 7.2 c.p.s., doubly allylic $-CH_2-$ protons), with the other signals (5.15–3.86) representing the olefinic protons.

Reaction of IX with Maleic Anhydride.—The procedure and work-up were identical with those used for VII. A 76% yield of the adduct (XIII) was obtained as a yellow oil, b.p. 161° (0.5 mm.), $n^{20}D$ 1.5130.

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.40; H, 8.17.

The adduct (XIII) showed important infrared bands (cm.$^{-1}$) at 3077 (w, vinyl=C–H), 1839 (s) and 1770 (vs, anhydride C=O), 1633 (m, vinyl C=C), 1231 (s) and 1190 (vs, C–O–C). Additional bands, not observed in the spectrum of adduct XII, were found at 1300 (w), 1250 (s), 1007 (vs), 955–908 (broad, s), and 790 (m).

The adduct XIII is believed to be *cis*-1,2,3,6-tetrahydro-3-allyl-5-methyl-6-(3-methyl-2-butenyl)phthalic anhydride.

Ozonolysis of IX.—The procedures used for VII were employed. Both formaldehyde (21%) and acetone (20%) were obtained.

6,10-Dimethyl-1-*trans*-4-*cis*-6,9-undecatetraene (VIII).—Distillation fractions boiling between those of VII and IX were enriched in VIII, b.p. 86–90° (3.2 mm.). Pure samples for spectroscopic analysis were obtained by collecting the effluent gas from the chromatograph. A sample containing 87% of VIII had a hydrogen number of 3.68; MR^{20} 61.75 (calcd. 60.36); mol. wt. calcd. 176, found 166.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.52; H, 11.59.

The infrared spectrum of VIII (CCl_4) was almost identical with that of IX. The major ultraviolet band occurred at 238.5 mμ. The n.m.r. spectrum was indistinguishable from that of IX.

Competitive Reactions of $C_{13}H_{20}$ Isomers with Maleic Anhydride.—A mixture of VII (24%), VIII (31%), IX (37%), and X (8%) (as shown by gas chromatography) was stirred with 1 equiv. of maleic anhydride. When heat was no longer evolved, the excess maleic anhydride was removed by sublimation. Subsequent distillation gave a fraction boiling at 55–57° (0.5 mm.). Gas chromatography showed that this fraction contained 83% of VIII. Unreacted VIII was also recovered even after a 5-day reflux in benzene with excess maleic anhydride. Ozonolysis of

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[25] E. F. Pratt and J. Van de Castle, *J. Org. Chem.*, **26**, 2973 (1961).

[26] E. Horning and M. Horning, *ibid.*, **11**, 95 (1946).

[27] P. Bailey, S. Bath, W. Thomsen, H. Nelson, and E. Kawas, *ibid.*, **21**, 297 (1956).

this fraction gave about the same yields of formaldehyde and acetone as were obtained from VII and IX.

Dimer, $C_{26}H_{40}$.—A higher boiling fraction from the pyrolysis of III proved to be a dimer; b.p. 168–173° (0.65 mm.); n^{20}_{D} 1.5201; d^{20}_{4} 0.9008; mol. wt. calcd. 352, found 329; yield 3.5%.

Anal. Calcd. for $C_{26}H_{40}$: C, 88.56; H, 11.44. Found: C, 88.42; H, 11.36.

While an ultraviolet band at 241 mμ (ε 14,360) was consistent with the presence of one highly substituted acyclic conjugated system, other spectroscopic and chemical data provided little definitive information as to the structure of the dimer.

Thermal Dehydration of *cis*-6,10-Dimethyl-1,5,9-undecatrien-4-ol (IV).—The apparatus, procedure, and work-up were identical with those used for pyrolysis of III, except that the heating period was 3 hr. instead of 6 hr. Fractional distillation showed that 68% of the products were monomers. Through distillation and gas chromatography, the same four $C_{13}H_{20}$ isomers were found: VI (59%), VIII (11.7%), IX (26.3%), and X (2%). These compounds were identified by the methods described above.

Dehydration of *trans*-6,10-Dimethyl-1,5,9-undecatrien-4-ol (III) with Anhydrous Oxalic Acid.—A solution of III (8 g., 0.04 mole) in 80 ml. of benzene was refluxed over 3.6 g. (0.04 mole) of anhydrous oxalic acid for 1.5 hr. After removal of the oxalic acid, the yellow solution was washed with three 10-ml. portions of water and dried over anhydrous sodium sufate. Distillation and gas chromatography showed that 94% of the products consisted of a mixture of $C_{13}H_{20}$ isomers. These were identified as VII (41.3%), VIII (16.3%), IX (29%), and X (13%) by the methods described earlier.

6,10-Dimethyl-1-*trans*-3-*trans*-5,9-undecatetraene (X).—Owing to the relatively large amount of X formed in the oxalic acid dehydration, it was possible to collect pure samples from the effluent gas of the chromatograph for spectroscopic studies.

Important infrared bands (in CCl_4, cm.$^{-1}$) in X occurred at 3087 (w, vinyl =C–H), 1665 (w, $R_2C{=}CHR$), 1632 (w), 1615 (m) and 1573 (w, C=C–C=C–C=C), 997 (s, vinyl =CH), 941 (s, *trans*-CH=CH), and 890 (s, vinyl =CH_2). Major ultraviolet bands occurred at 263 mμ (ε 53,000), 272 mμ (ε 62,900), and 281 mμ (ε 53,600).

6,10-Dimethylundecane (XI).—Each of the $C_{13}H_{20}$ isomers (VII–X) was separated by preparative-scale gas chromatography and individually subjected to catalytic hydrogenation as described under VI. The *same, single* product was obtained in each case, and was identified as 6,10-dimethylundecane (XI). After purification by vacuum distillation at 4.0–4.5 mm. and preparative-scale gas chromatography (Carbowax 4000 column), XI gave b.p. (micro) 219.0°, n^{20}_{D} 1.42435.

Anal. Calcd. for $C_{13}H_{28}$: C, 84.69; H, 15.31. Found: C, 84.52; H, 14.96.

Key infrared bands (cm.$^{-1}$) for paraffin XI were 1460 (s, —CH_2–), doublet 1377 and 1370 (s) and 1360 (s) (*gem*-dimethyl), and doublet 715 and 725 (w, –$(CH_2)_4$–). In the n.m.r. spectrum, the twelve CH_3– protons showed signals at τ 9.18, 9.12, and 9.08; the remaining sixteen protons appeared as an intense doublet centered at τ 8.76 (J = 1.2 c.p.s., –CH_2– in *acyclic* hydrocarbon) and a tail sloping toward 8.2 (H–C<) protons). The entire mass-spectroscopic fragmentation pattern of XI clearly defined its skeletal arrangement.[28] The expected intensity maximum in the low-mass region was observed, with a base peak of m/e = 57 (100%). A molecular ion peak (M^+) appeared at m/e = 184 (1.04%). A *relatively* large peak at m/e = 169 (M-15, 1.30%) attested to the easy loss of a methyl group. The position of the internal 6-methyl group was confirmed by the appearance of intense fragments at m/e = 113 (8.71%, $C_8H_{17}^+$) and m/e = 99 (4.89%, $C_7H_{15}^+$).

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[28] See K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 72, and references therein.

Reaction of Cyclohexene with a "Thermal Dichlorocarbene" from Chloroform

FREDERICK E. KUNG AND WILLIAM E. BISSINGER

Chemical Division, Pittsburgh Plate Glass Company, Barberton, Ohio

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The pyrolysis of chloroform in the presence of cyclohexene has produced the new compound, 3-dichloromethylcyclohexene, and its structural isomers. Dichloronorcarane and its pyrolysis product, toluene, were also formed. The formation of dichloronorcarane and toluene gives evidence that dichlorocarbene was formed by the pyrolysis of chloroform. The formation of 3-dichloromethylcyclohexene is explained by an insertion reaction of dichlorocarbene with cyclohexene. The major insertion product was identified by comprehensive structural studies.

Besides addition to the double bond of an olefin, Doering[1,2] showed that direct insertion reactions occurred with a highly activated methylene derived from the photolysis of diazomethane. Doering proved that a stepwise process involving free intermediates which can equilibrate and give mixed products was not the method of reaction. Instead, a concerted mechanism for the direct insertion was clearly illustrated.

Unlike methylene, the reaction of dichlorocarbene with olefin has only recently been found to give an insertion reaction. Usually dichlorocarbene[3] has been generated at room temperature or below, by the attack of a base on a haloform, or from an alkoxide on hexachloroacetone or trichloroacetate esters, or from a metal alkyl on a tetrahalomethane. A process involving slightly elevated temperatures is the "thermal" decomposition of salts of trichloroacetic acid at about 100°. Fields[4] suggested that the dichlorocarbene formed by this method has a higher energy level and undergoes reactions not observed with dichlorocarbene produced at low temperatures. Evidence is presented that a dichlorocarbene produced from such a sodium trichloroacetate decomposition reacts with cumene at the benzylic carbon–hydrogen bond to give a 33% yield of insertion product, whereas yields were only 0.5–5% with a low-temperature dichlorocarbene process.

Parham[5] emphasized the importance of the structure of the olefin upon the course of the reaction with his observation that dichlorocarbene underwent, solely, insertion reactions with 2H-1-benzothiopyran and the expected addition to the double bond was not found. On the other hand, no insertion reaction occurred with the isomeric 4H-1-benzothiopyran, and only addi-

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[2] W. von E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959).

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[5] W. E. Parham and R. Koncos, *ibid.*, **83**, 4034 (1961).