[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IMPERIAL COLLEGE OF SCIENCE, LONDON, AND THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Synthesis of the Violet Leaf Perfume, 2(*trans*),6(*cis*)-Nonadienal[1a]

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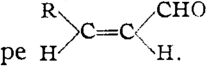
A novel synthesis of 2,6-nonadienal (I) through acetylenic intermediates is described, which, in contrast to previous routes to I, gives satisfactory yields throughout. The product is shown to have the 2(*trans*),6(*cis*) configuration, and to be identical with the perfume material obtained from violet leaf oil. The synthesis is extended to the preparation of 2(*cis*), 6(*cis*)-nonadien-1-ol, converted to I on oxidation.

2,6-Nonadienal (I) and the corresponding alcohol (II) have been shown to be important components of violet leaf oil[2] and to be chiefly responsible for its characteristic odor. A synthesis of a 2,6-nonadienal from 3-hexen-1-ol *via* 2,6-nonadien-1-ol was devised by Ruzicka and Schinz,[3] and the aldehyde obtained by these workers must have been the *trans,trans* isomer. This assignment of configuration follows from its identity with the *trans,trans* compound prepared by Hunsdiecker (*vide infra*), rather than from its method of formation, as the synthetic 3-hexen-1-ol from which it was prepared has recently been shown not to be the pure *trans* compound.[4,5] The synthetic nonadienal was later shown by the Swiss workers to differ from the natural compound,[6] and the synthesis was repeated, as far as 2,6-nonadien-1-ol (II), the naturally occurring 3-hexen-1-ol ("leaf alcohol") being used as starting material. The latter is known to be the *cis* isomer,[4,5,7] and the synthetic II therefore had the 2(*trans*),6(*cis*) configuration.[6,8] It was considered to be identical with the naturally occurring alcohol, although the evidence for identity presented was not conclusive. The same reaction sequence from *cis*-3-hexen-1-ol was also carried out by Takei and his co-workers,[9] and the 2(*trans*), 6(*cis*)-alcohol so obtained was oxidized to the corresponding aldehyde. Unfortunately no direct comparison with the natural nonadienal seems to have been made. Finally, in 1947, Hunsdiecker[10] not only developed an entirely new route to 2,6-nonadien-1-ol and thence 2,6-nonadienal (which from the method of formation must have had the *trans,trans* configuration), but also repeated the syntheses of Ruzicka and Schinz,[3,6] and prepared the 2(*trans*),6(*trans*) and 2(*trans*),6(*cis*) aldehydes from the impure *trans* and pure *cis*-3-hexen-1-ols, respectively. Careful mixed melting point determinations of the semicarbazones indicated that none of the synthetic preparations were identical with the natural aldehyde, although the derivative of the 2(*trans*),6(*cis*) isomer only showed a 2° depression on admixture with the natural semicarbazone. On the other hand, the derivatives of the two synthetic *trans,trans* isomers did not cause a depression in melting point on admixture. It thus appeared, when the work described in this paper was initiated, that the naturally occurring form of 2,6-nonadienal had not been synthesized.

A compound such as I, containing two double bonds, could of course in principal exist in any one of four configurations: *cis,cis*, 2(*cis*),6(*trans*), 2(*trans*),6(*cis*), and *trans,trans*. The possibility existed that the natural aldehyde might be one of the isomers represented by the first two of these alternatives (not previously synthesized), although very little seems to be known about the stability of *cis*-α,β-unsaturated aldehydes of the type  $\mathrm{(R)(H)C{=}C(CHO)(H)}$. For this reason a synthesis of I was devised, which employed acetylenic intermediates, and which (by catalytic semihydrogenation at some stage) would give the *cis*-α,β-unsaturated aldehyde if the latter had any degree of stability. The key intermediate in this synthesis is 1,5-octadiyne (III), an attempted preparation of which had previously proved abortive.[5] On the other hand, employment of the general method involving the differential alkylation of a terminal diacetylene[11] has now proved successful. Dipropargyl (1,5-hexadiyne) (IV) was prepared by the coupling of allyl bromide to give diallyl, followed by addition of bromine and dehydrobromination with sodamide in liquid ammonia.[12] When IV was allowed to react first with 1.1 moles of sodamide in liquid ammonia, and then with ethyl iodide, the required monoalkylation product III was obtained in 61% yield (allowing for recovered starting material). A little of the dialkylation product, 3,7-decadiyne, could also be isolated. The diacetylene III was converted to the Grignard complex, which with ethyl orthoformate gave 2,6-nonadiynal diethyl acetal (V) (81% yield). Hydrolysis of the acetal grouping of V was effected by steam distillation in the presence of dilute sulfuric acid, and 2,6-nonadiynal (VI) was obtained as a faintly unpleasant smelling liquid. Partial hydrogenation of VI in the presence of a palladium–calcium carbonate catalyst led to a mixture of products, from which no pure compounds were isolated.

On the other hand, direct hydrogenation of the

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(1) (a) This paper is Part IV in the Series "Studies of Compounds Related to Natural Perfumes." For Part III, see *J. Chem. Soc.*, 3361 (1950). (b) Syntex, S. A., Laguna Mayran 413, Mexico, D. F., Mexico.

(2) H. Walbaum and A. Rosenthal, *J. prakt. Chem.*, [2] **124**, 55 (1930); E. Späth and F. Kesztler, *Ber.*, **67**, 1496 (1934); L. Ruzicka and H. Schinz, *Helv. Chim. Acta*, **17**, 1592 (1934); *ibid.*, **18**, 381 (1935).

(3) L. Ruzicka and H. Schinz, *ibid.*, **17**, 1602 (1934).

(4) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 873 (1950).

(5) F. Sondheimer, *ibid.*, 877 (1950).

(6) L. Ruzicka, H. Schinz and B. P. Susz, *Helv. Chim. Acta*, **27**, 1561 (1944).

(7) M. Stoll and A. Rouvé, *ibid.*, **21**, 1542 (1938).

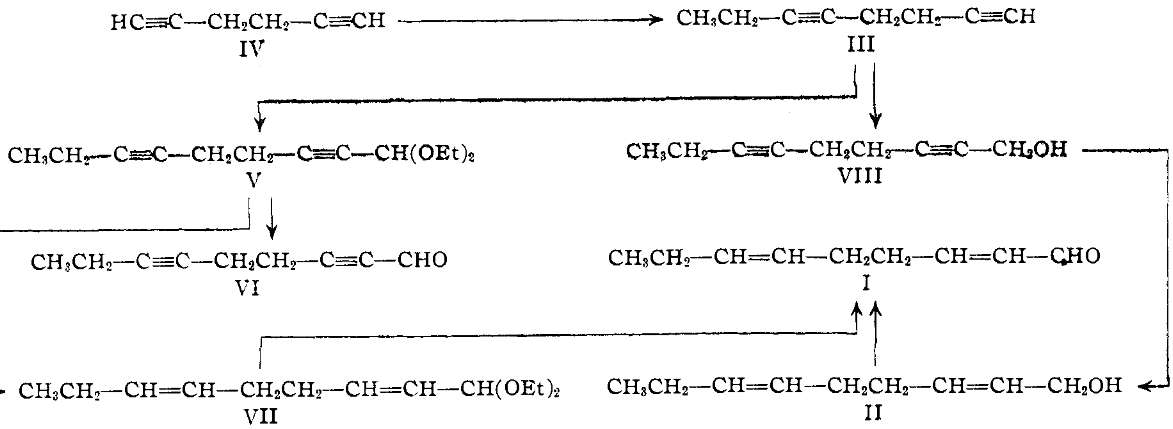
(8) *Cf.* B. Grédy, *Bull. soc. chim.*, [5] **3**, 1101 (1936), for assignment of the *trans* configuration to the Δ^2 double bond.

(9) S. Takei, M. Ôno, Y. Kuroiwa, T. Takahata and T. Sima, *Bull. Agr. Chem. Soc.* (*Japan*), **14**, 64 (1938); *Chem. Zentr.*, **109, II**, 3696 (1938).

(10) H. Hunsdiecker, *Chem. Ber.*, **80**, 137 (1947).

(11) R. A. Raphael and F. Sondheimer, *J. Chem. Soc.*, 115 (1950).

(12) R. A. Raphael and F. Sondheimer, *ibid.*, 120 (1950).



acetylenic acetal V with a palladium-calcium carbonate catalyst proceeded smoothly, and when the reaction was stopped after the uptake of 2 moles of hydrogen, 2(*cis*),6(*cis*)-nonadienal diethyl acetal (VII)[13] was obtained in 81% yield. Whereas the diacetylenic acetal V had a slight but unpleasant smell, the diethylenic acetal VII had a very powerful pleasant cucumber-like odor, very similar to that of natural nonadienal itself. The acetal VII was readily hydrolyzed by steam distillation in the presence of dilute sulfuric acid, and the 2,6-nonadienal (I) so obtained was characterized by the formation of a number of crystalline derivatives. The physical properties of the synthetic compounds are set out in Table I, and are compared with those of the natural nonadienal, and also with those of the 2(*trans*),6(*cis*)-nonadienal[9,10] obtained from *cis*-3-hexen-1-ol.

TABLE I

	Synthetic I, this paper	Synthetic I from *cis*-3-hexen-1-ol	Natural I
B.p., °C.	88 (10 mm.)[a]	......	88–90 (12 mm.)[6,b] 89–90 (12 mm.)[14]
n_D (temp. in parentheses)	1.4710 (21°)[a]	......	1.4700 (24°)[6,14]
Semicarbazone (m.p., °C.)	156–157	157.5[9] 157–158[10]	157–158[14,c]
2,4-Dinitrophenylhydrazone (m.p., °C.)	112–113	113[9]	111–112[c]
p-Nitrophenylhydrazone (m.p., °C.)	97.5–98.5	......	95–97[6]

[a] These values are for a sample regenerated from the semicarbazone. [b] The value 88–90° (72 mm.) given in footnote 6 is obviously a misprint. [c] Determined by the author.

It can be seen that the physical properties of both synthetic series are very similar to those of the natural series. The melting points of the semicarbazone and 2,4-dinitrophenylhydrazone of our synthetic aldehyde were undepressed on admixture with samples prepared from the natural nonadienal. Final proof that our synthetic aldehyde was identical with the natural was provided by comparison of infrared spectra (Fig. 1). The spectrum of the synthetic nonadienal (A) is identical with the spectrum of the natural material (B). Again the spectra of the corresponding semicarbazones (C and D) are superimposable.

It now became of interest to determine whether during the hydrolysis of VII to I, inversion to the 2(*trans*)-aldehyde had taken place. For this reason, tetrolaldehyde diethyl acetal ($CH_3—C\equiv C—CH(OEt)_2$)[15] was partially hydrogenated in the

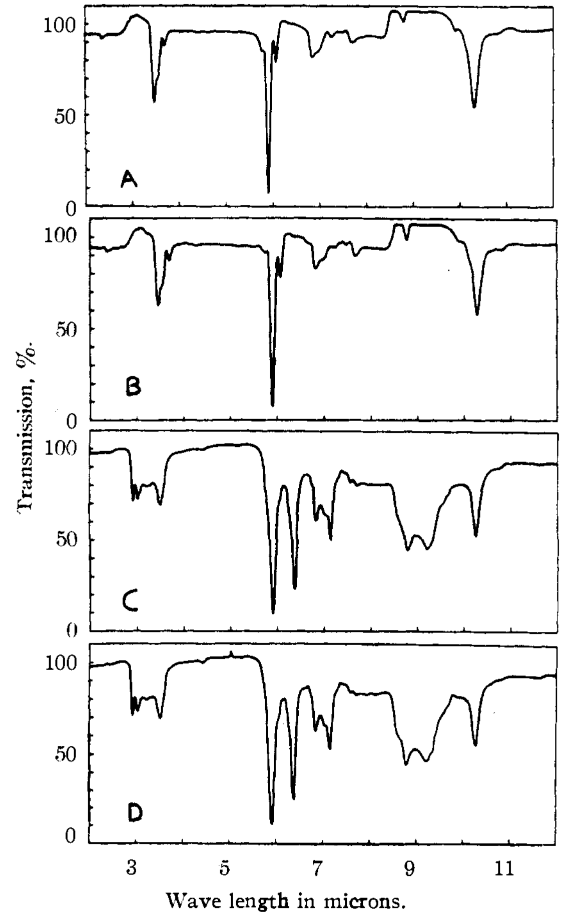


Fig. 1.—Infrared spectra: curve A, synthetic nonadienal; curve B, natural nonadienal; curve C, synthetic nonadienal semicarbazone; curve D, natural nonadienal semicarbazone.

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(13) For references regarding the formation of *cis*-ethylenes by the catalytic semihydrogenation of acetylenes, see footnote 11. A product of this type is probably contaminated with small amounts of *trans* ethylenic material (*cf.* footnote 5) as well as with substances formed by over-reduction and non-reduction of the acetylenic linkages. These impurities cannot be removed by simple fractional distillation and their presence is neglected in the nomenclature employed.

(14) L. Ruzicka and H. Schinz, *Helv. Chim. Acta*, **17**, 1592 (1934).

(15) J. C. Lunt and F. Sondheimer, *J. Chem. Soc.*, 3361 (1950).

presence of a palladium–calcium carbonate catalyst. The product, presumably *cis*-crotonaldehyde diethyl acetal, was hydrolyzed with acid and the crude aldehyde was converted to crystalline derivatives. These proved to be identical with samples prepared from normal *trans*-crotonaldehyde. When the aldehyde was oxidized with silver oxide, the acid obtained was identical with *trans*-crotonic acid.[16] It thus became evident that on acid hydrolysis of a compound possessing the *cis*-—CH=CH—CH(OEt)$_2$ grouping, the *trans*-aldehyde is obtained. Consequently, the synthetic 2,6-nonadienal, and therefore also the natural aldehyde derived from violet leaf oil, must possess the 2(*trans*),6(*cis*) configuration. This conclusion is confirmed by the infrared spectra of the aldehydes (A and B) and of their semicarbazones (C and D), all of which show a strong band at 10.3 μ typical of a *trans* double bond,[17] but is at variance with the findings of Hunsdiecker.[10] Fortunately a sample of 2(*trans*),6(*cis*)-nonadienal semicarbazone (prepared from *cis*-3-hexen-1-ol by the method of Ruzicka and Schinz[3,6]) was obtained through the courtesy of Dr. H. Schinz. Contrary to the report of Hunsdiecker,[10] this did not depress the melting point of natural nonadienal semicarbazone on admixture. Its infrared spectrum was also identical both with that of the natural material and with that of the synthetic nonadienal semicarbazone reported in this paper. There is therefore no doubt that the aldehyde occurring in violet leaf oil is 2(*trans*),6(*cis*)-nonadienal. It was found that thorough grinding of nonadienal semicarbazone lowered its melting point by *ca.* 2–3°, and this may perhaps explain the melting point depression observed by Hunsdiecker.

The synthesis described above was also applied to the preparation of 2(*cis*),6(*cis*)-nonadien-1-ol. Reaction of the Grignard complex of III with gaseous formaldehyde gave 2,6-nonadiyn-1-ol (VIII) in 72% yield as a somewhat unpleasant smelling liquid. It was hydrogenated in the presence of a palladium–calcium carbonate catalyst, and the reaction was stopped after the uptake of two moles of gas. The 2(*cis*),6(*cis*)-nonadien-1-ol[13] thus obtained (75% yield) had the powerful fresh odor associated with the naturally occurring alcohol, although no direct comparison was made with the latter (which presumably has the 2(*trans*),6(*cis*) configuration[6]). Oxidation of the synthetic alcohol with chromium trioxide[3,6,9,10] gave 2(*trans*),6(*cis*)-nonadienal, which yielded derivatives identical with those of the aldehyde prepared by the first method.

Experimental[18]

1,5-Octadiyne (III).—A suspension of sodamide in liquid ammonia (350 cc.) was prepared from sodium (7.90 g.), the ferric nitrate catalyst described by Vaughn, Vogt and Nieuwland[19] being used to catalyze the transformation. Dipropargyl[12] (24.4 g.) in dry ether (50 cc.) was added during 15 minutes to the cooled (alcohol–carbon dioxide) and stirred suspension, which was then stirred for another 1.5 hours. Ethyl iodide (58.0 g.) in dry ether (100 cc.) was added during 30 minutes, and the cooled mixture was stirred for six hours more. The ammonia was evaporated on the steam-bath, ether and water were added to the residue, the aqueous layer was washed with ether, and the combined ethereal extracts were washed successively with dilute sulfuric acid, sodium bicarbonate solution and water. The dried ($MgSO_4$) extract was evaporated through a short Vigreux column, and the residue was distilled through the same column. Unchanged dipropargyl (5.6 g.) was obtained first. The next fraction (b.p. 120–170° (762 mm.)) on redistillation yielded pure 1,5-octadiyne (15.5 g., 61% yield, 47% conversion), b.p. 45–47° (21 mm.), n^{15}D 1.4580.

Anal. Calcd. for C_8H_{10}: C, 90.51; H, 9.49. Found: C, 90.24; H, 9.25.

In addition a higher boiling fraction (5.1 g.), b.p. 188–192° (762 mm.), 78–81° (21 mm.), n^{17}D 1.4660, was obtained. This was probably the dialkylation product, 3,7-decadiyne, but it was not further investigated.

2,6-Nonadiynal Diethyl Acetal (V).—A solution of ethylmagnesium bromide in dry ether (120 cc.) was prepared from magnesium (4.3 g.) and ethyl bromide (*ca.* 25 g.) in the usual way. 1,5-Octadiyne (15.3 g.) in ether (60 cc.) was added during five minutes, and the stirred solution was heated under reflux in a nitrogen atmosphere for two hours. Ethyl orthoformate (45 g.) was added in a thin stream, and heating in nitrogen was continued for a further six hours. The ether was distilled off, and the residue was heated on the steam-bath for 1 hour. Ether and saturated ammonium chloride solution were added, and the organic layer, after being washed with more ammonium chloride solution and water, was dried ($MgSO_4$) and evaporated. Distillation of the residue gave 2,6-nonadiynal diethyl acetal (24.2 g., 81% yield) as a mobile liquid, b.p. 104–105° (0.3 mm.), n^{18}D 1.4605.

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.95; H, 9.68. Found: C, 75.54; H, 9.66.

2,6-Nonadiynal (VI).—The diacetylenic acetal (9.0 g.) was added to 2 *N* sulfuric acid (100 cc.) and the mixture was rapidly distilled in steam until the distillate no longer gave a precipitate with aqueous 2,4-dinitrophenylhydrazine reagent. The aqueous distillate (*ca.* 300 cc.), which had been kept under a nitrogen atmosphere during the distillation, was extracted with ether, the organic layer was washed with water, dried, and evaporated. Distillation of the residue through a short Vigreux column yielded 2,6-nonadiynal (4.7 g., 81% yield), b.p. 111–112° (18 mm.), 58–59° (0.3 mm.), n^{19}D 1.4899.

Anal. Calcd. for $C_9H_{10}O$: C, 80.57; H, 7.51. Found: C, 80.29; H, 7.77.

The semicarbazone crystallized from aqueous methanol as colorless plates, m.p. 169–170°.

Anal. Calcd. for $C_{10}H_{13}ON_3$: N, 21.98. Found: N, 21.92.

The 2,4-dinitrophenylhydrazone crystallized from aqueous methanol as bright yellow needles, m.p. 74–75°.

Anal. Calcd. for $C_{15}H_{14}O_4N_4$: N, 17.83. Found: N, 17.85.

When an ethereal solution of the acetal was shaken for two hours with tartaric acid, no appreciable hydrolysis occurred.

2(*cis*),6(*cis*)-Nonadienal Diethyl Acetal (VII).—The diacetylenic acetal (10.3 g.) in ethyl acetate (50 cc.) and a palladium–calcium carbonate catalyst (1 g., 3% Pd) were shaken in hydrogen until two moles of gas (2362 cc. at 14° (750 mm.)) had been absorbed. The catalyst was filtered off, and the solvent was evaporated. Distillation of the residue gave 2(*cis*),6(*cis*)-nonadienal diethyl acetal (8.5 g., 81%) as a colorless mobile liquid, b.p. 67–70° (0.2 mm.), n^{18}D 1.4439.

Anal. Calcd. for $C_{13}H_{24}O_2$: C, 73.55; H, 11.40. Found: C, 73.62; H, 11.11.

2(*trans*),6(*cis*)-Nonadienal (I).—A mixture of the diethylenic acetal (4.5 g.) and 2 *N* sulfuric acid (75 cc.) was distilled in steam in the same way as described above for the diacetylenic compound. The aldehyde (1.8 g., 79% yield, 61% conversion) was obtained as a colorless mobile liquid

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(16) The details of these experiments have now been published in connection with another synthesis [R. A. Raphael and F. Sondheimer, *ibid.*, 2693 (1951)].

(17) R. S. Rasmussen, R. R. Brattain and P. S. Zucco, *J. Chem. Phys.*, **15**, 135 (1947).

(18) Melting points and boiling points are uncorrected.

(19) T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, THIS JOURNAL, **56**, 2120 (1934).

with a very powerful fresh cucumber-like odor (identical with that of the natural material), b.p. 94–95.5° (18 mm.), n^{17}D 1.4699. In addition, unchanged acetal (1.0 g., 22%) was recovered.

The 2,4-dinitrophenylhydrazone was prepared from the acetal as well as from the aldehyde. In either case it crystallized from methanol as orange plates, m.p. 112–113°.

Anal. Calcd. for $C_{15}H_{18}O_4N_4$: N, 17.61. Found: N, 17.80.

The 2,4-dinitrophenylhydrazone was also prepared from a sample of the natural aldehyde. It had m.p. 111–112° and was undepressed on admixture with the synthetic specimen.

The *p*-nitrophenylhydrazone crystallized from ligroin (b.p. 60–90°) as regular orange plates, m.p. 97.5–98.5°.

Anal. Calcd. for $C_{15}H_{19}O_2N_3$: N, 15.38. Found: N, 15.37.

The semicarbazone crystallized from aqueous methanol as sparkling plates, m.p. 156–157°. A sample prepared from the natural material had m.p. 157–158°, and no depression was observed on admixture.

The synthetic semicarbazone (0.5 g.), 2 *N* sulfuric acid (20 cc.) and petroleum ether were stirred and heated under reflux in a nitrogen atmosphere. After 3.5 hours, two clear layers were obtained. The aqueous layer was extracted with ether, the combined organic extracts were washed with water, dried and evaporated. Distillation of the residue furnished the pure aldehyde, b.p. 88° (10 mm.), n^{21}D 1.4710.

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.00; H, 10.45.

The hydrolysis of the acetal could also be carried out by shaking an ethereal solution of the latter with saturated aqueous tartaric acid for 14 hours, but inferior yields of aldehyde were obtained by this method.

2,6-Nonadiyn-1-ol (VIII).—A solution of ethylmagnesium bromide in dry ether (80 cc.) was prepared from magnesium (1.95 g.) and ethyl bromide (12 g.) in the usual way. 1,5-Octadiyne (6.85 g.) in ether (30 cc.) was added during ten minutes, and the stirred solution was heated under reflux in a nitrogen atmosphere for 2.5 hours. Excess formaldehyde generated by the method of Gilman and Catlin,[20] was passed into the stirred Grignard reaction mixture by means of a slow current of nitrogen. The ether boiled gently, although no external heat was applied. The mixture was then heated under reflux for 30 minutes. It was poured into dilute sulfuric acid and ice, and the organic layer was washed with sodium bicarbonate solution and water. The dried extract was evaporated, and the residue was distilled through a Vigreux column. 2,6-Nonadiyn-1-ol (6.3 g., 72%) was obtained as a mobile liquid, b.p. 83–85° (0.3 mm.), n^{24}D 1.4842.

Anal. Calcd. for $C_9H_{12}O$: C, 79.38; H, 8.89. Found: C, 79.01; H, 8.74.

2(*cis*),6(*cis*)-Nonadien-1-ol.—The diacetylenic alcohol (1.60 g.) in ethyl acetate (10 cc.) was shaken in hydrogen in the presence of a palladium–calcium carbonate catalyst (0.2 g., 3% Pd) until two moles of gas (583 cc. at 21° (740 mm.)) had been absorbed. The residue, after removal of the catalyst and solvent, was distilled. 2(*cis*),6(*cis*)-Nonadien-1-ol (1.23 g., 75%) was obtained as a colorless liquid, b.p. 108–110° (24 mm.), n^{23}D 1.4580.

Anal. Calcd. for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.75; H, 11.85.

2(*trans*),6(*cis*)-Nonadienal (I) by Oxidation of 2(*cis*),6-(*cis*)-Nonadien-1-ol.—The alcohol (0.5 g.) was oxidized with chromium trioxide in dilute sulfuric acid by the procedure described by Hunsdiecker[10] for the *trans,trans* isomer. The crude undistilled aldehyde was converted to the 2,4-dinitrophenylhydrazone (m.p. 112–113°) and semicarbazone (m.p. 155–156°) in the usual way; neither of these melting points was depressed on admixture with the corresponding derivatives prepared by the acetal route.

Infrared Absorption Spectra.—The infrared spectra were determined in chloroform solution with a Baird Infrared Recording Spectrophotometer, Model B.

Acknowledgments.—The author wishes to express his thanks to Dr. H. Schinz (Eidg. Technische Hochschule, Zürich) for the gift of samples of natural nonadienal and its derivatives, and to Dr. J. C. Lunt (Imperial College of Science, London) for carrying out the partial hydrogenation of tetrolaldehyde diethyl acetal.

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[20] H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I John Wiley and Sons, Inc., New York, N. Y., 1941, p. 188.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

Saponins and Sapogenins. XXX. The Isomeric Norechinocystenediones and Some Related Compounds[1a]

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The isomerization of the norechinocystenediones has been reinvestigated and additional examples of isomerization have been found. An explanation of the isomerizations is given.

When methyl echinocystate is oxidized with dichromic acid, a diketo methyl ester is formed which saponifies readily with loss of carbon dioxide. The product forms a dioxime and was called norechinocystenedione.[2,3] If echinocystic acid is oxidized in the same way as the methyl ester, carbon dioxide is lost directly, and a product isomeric with norechinocystenedione is obtained which was called isonorechinocystenedione.[3] This compound forms only a monoxime and is isomerized by alcoholic potassium hydroxide to norechinocystenedione. The absorption spectrum of the isonordione in ethyl ether failed to show the presence of a carbonyl group and, as a working hypothesis, it was suggested that the isonordine might be a cyclic hemiacetal of the monoenol form of a diketone.[2b] No evidence could be found for this structure, but during attempts to form a thioacetal by heating with butyl mercaptan in the presence of hydrogen chloride, a new isomeric diketone was obtained which is an α,β-unsaturated ketone.[4]

Since these results could not be explained readily, the work has been repeated and extended. Previous work has been confirmed except that all of our present preparations of the isonordione show simple

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[1] (a) This paper is based on a portion of the Ph.D. dissertation of F. A. Alves, Instituto para a Alta Cultura Fellow; (b) Laboratorio Quimico, Universidade de Coimbra, Portugal.

[2] W. R. White and C. R. Noller, THIS JOURNAL, **61**, 983 (1939).

[3] R. N. Jones, D. Todd and C. R. Noller, *ibid.*, **61**, 2421 (1939).

[4] J. F. Carson, D. B. Cosulich and C. R. Noller, *ibid.*, **66**, 1265 (1944).