product was collected by filtration and washed with ether yielding 0.73 g. of β-hydroxy-β-methyl-δ-valerolactone, m.p. 26–28°. Recrystallization of the product gave material melting at 27–28°. The product is hygroscopic.

Anal. Calcd. for $C_6H_{10}O_3$ (130.14): C, 55.37; H, 7.75. Found: C, 55.94; H, 7.75; sapn. equiv., 131.

N,N′-Dibenzylethylenediammonium-bis-(3-hydroxy-3-methyl-5-(2-tetrahydropyranyloxy)-pentanoate.—Ethyl 3-hydroxy-3-methyl-5-(2-tetrahydropyranyloxy)-pentanoate (6.1 g.) was dissolved in 30 ml. of ethanol and 10 ml. of 3 *N* sodium hydroxide was added. The mixture was warmed on a steam-cone for 30 minutes.

The mixture was cooled, acidified to *p*H 4 and extracted with ether. The ether solution was washed with water, dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo* yielding 2.7 g. of oil.

The oil was dissolved in *ca.* 100 ml. of ether and 2.7 g. of N,N′-dibenzylethylenediamine in 20 ml. of ether was added. The salt precipitated and was collected by filtration yielding 3.3 g. of N,N′-dibenzylethylenediammonium-bis-(3-hydroxy-3-methyl-5-(2-tetrahydropyranyloxy)-pentanoate), m.p. 137–139°.

Anal. Calcd. for $C_{38}H_{60}N_2O_{10}$ (704.88): C, 64.74; H, 8.58; N, 3.98. Found: C, 64.69; H, 8.29; N, 4.46, 4.71.

N,N′-Dibenzylethylenediammonium-bis-(3,5-dihydroxy-3-methylpentanoate) from N,N′-Dibenzylethylenediammonium-bis-[3-hydroxy-3-methyl-5-(2-tetrahydropyranyloxy)-pentanoate].—N,N′-Dibenzylethylenediammonium-bis-[3-hydroxy-3-methyl-5-(2-tetrahydropyranyloxy)-pentanoate] (3.3 g.) was suspended in 10 ml. of water and 12 ml. of 1 *N* hydrochloric acid was added and warmed on the steam-cone for 10 minutes. The mixture was cooled and 10.8 ml. of 1 *N* sodium hydroxide was added. The mixture was filtered and the filtrate was lyophilized.

The residue was leached with 25 ml. of hot methanol. The methanol solution was cooled and diluted with ether yielding 450 mg. of N,N′-dibenzylethylenediammonium-bis-(3,5-dihydroxy-3-methylpentanoate), m.p. 122–123°. A mixture of this sample with an authentic specimen of the salt melted at 122–123°.

N,N′-Dibenzylethylenediammonium-bis-(5-benzyloxy-3-hydroxy-3-methylpentanoate).—A mixture of 40 g. (0.23 mole) of 4-benzyloxy-2-butanone and 37.5 g. (0.23 mole) of ethyl bromoacetate in 100 ml. of ether was added dropwise to 20 g. (0.32 mole) of clean, dry granular zinc. The reaction mixture was stirred at the reflux temperature for about two hours and was then added to a mixture of ice and 30 ml. of concentrated hydrochloric acid. The ether layer was separated and the aqueous phase was extracted with ether. The combined ether layers were washed with saturated sodium chloride solution, sodium bicarbonate solution and, again, with sodium chloride solution. The ether layer was concentrated yielding 40 g. of residual oil. A 30-g. portion of the product was distilled *in vacuo* to give *ca.* 15 g. of material boiling at <70° (0.4 mm.). The residue (14.7 g.) from this distillation was hydrolyzed on the steam-cone with 22 ml. of 1 *N* sodium hydroxide and 50 ml. of methanol. The solution was diluted with 50 ml. of water and concentrated at reduced pressure to a volume of *ca.* 50 ml. The solution was extracted with ether and the ether phase was discarded. The aqueous phase was acidified with concentrated hydrochloric acid and extracted with ether. The ether extract was washed with saturated sodium chloride solution, dried and concentrated, yielding 2.2 g. of 5-benzyloxy-3-hydroxy-3-methylpentanoic acid.

A 1.93-g. portion of the acid was dissolved in 5 ml. of methanol and treated with 0.97 g. of N,N′-dibenzylethylenediamine. When *ca.* 75 ml. of ether was added, 1.5 g. of the salt, m.p. 123–127°, crystallized. A 400-mg. portion of the salt was recrystallized from chloroform–ether, chloroform–petroleum ether and finally from methanol–ether yielding 200 mg. of N,N′-dibenzylethylenediammonium-bis-(5-benzyloxy-3-hydroxy-3-methylpentanoate), m.p. 131–133°.

Anal. Calcd. for $C_{42}H_{56}N_2O_8$ (716.89): C, 70.36; H, 7.87; N, 3.91. Found: C, 70.40; H, 7.60; N, 4.14.

5-Benzyloxy-3-hydroxy-3-methylpentanoic Acid.—Four hundred and eighty milligrams of N,N′-dibenzylethylenediammonium-bis-(5-benzyloxy-3-hydroxy-3-methylpentanoate) was suspended in 25 ml. of water and acidified with 2.5 *N* hydrochloric acid. The free acid was extracted into ether and then extracted into aqueous potassium bicarbonate. The bicarbonate solution was acidified and the product was extracted into ether. The ether extract was washed with water, dried and concentrated yielding 169 mg. of 5-benzyloxy-3-hydroxy-3-methylpentanoic acid, $n^{25}D$ 1.5130, neut. equiv. 243 (calcd. 238).

N,N′-Dibenzylethylenediammonium-bis-(5-benzoyloxy-3-hydroxy-3-methylpentanoate).—Ten grams of N,N′-dibenzylethylenediammonium-bis-(3,5-dihydroxy-3-methylpentanoate) was dissolved in 37 ml. of 1 *N* sodium hydroxide. The solution was extracted with ether and the ether extract was washed with 15 ml. of water. The combined aqueous phases were stirred and cooled while 6 g. of benzoyl chloride was added dropwise. Sodium hydroxide (1 *N*) was added dropwise during the addition of benzoyl chloride to keep the *p*H at *ca.* 9. After being stirred for one hour, the reaction mixture was washed with chloroform. The aqueous phase was acidified to *p*H 3 with hydrochloric acid and extracted with two 75-ml. portions of chloroform. The combined chloroform extracts were washed with water, dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo.*

The residue was leached with hot petroleum ether and then dissolved in 8 ml. of methanol. N,N′-Dibenzylethylenediamine (2.16 g.) was added, and the solution was diluted with *ca.* 80 ml. of ether. Two grams of N,N′-dibenzylethylenediammonium-bis-(5-benzoyloxy-3-hydroxy-3-methylpentanoate), m.p. 142–143°, crystallized from the solution.

Anal. Calcd. for $C_{42}H_{52}N_2O_{10}$ (744.86): C, 67.70; H, 7.04; N, 3.76. Found: C, 68.42, 68.31; H, 6.76, 6.93; N, 3.71.

Rahway, N. J.

[Contribution from the Department of Chemistry of the Massachusetts Institute of Technology]

Light-catalyzed Organic Reactions. VI.[1] The Isomerization of Some Dienones[2,3]

By G. Büchi and N. C. Yang

Received November 19, 1956

The isomerization of four dienones has been studied. β-Ionone yielded pyran X and spiroketone IX containing a cyclopropane ring. Irradiation of both pseudoionone and 6-methyl-3,5-heptadiene-2-one led to polymers. *trans–trans*-Crotonylideneacetone was converted to the $\Delta^{3,4}$-*cis* isomer. The changes observed are compared with the isomerization of tachysterol (III) and possible interpretations of the results are discussed.

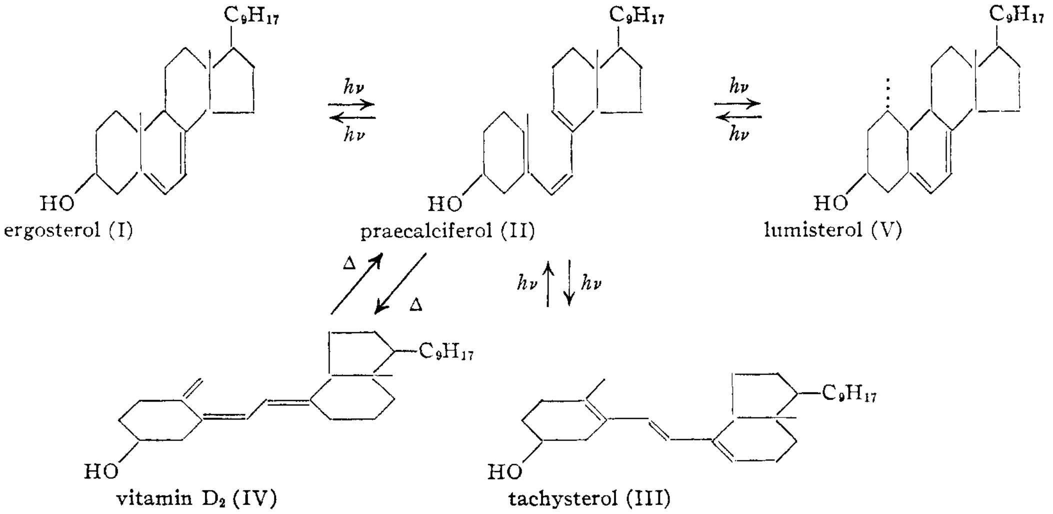
The conversion of ergosterol (I) to vitamin D_2 (IV) is unquestionably one of the most fascinating photochemical reactions known. The brilliant researches of Windaus and his School have led to the isolation and structure elucidation of lumisterol

---

(1) Part V, This Journal, **78**, 876 (1956).

(2) Part of a program of research supported by a grant from the Godfrey L. Cabot Fund, Publication No. 63, M. I. T. Solar Energy Conversion Project.

(3) A preliminary account of this work was reported in *Chemistry & Industry*, 357 (1955).



(V) and tachysterol (III), both of which are convertible to vitamin D_2 by further irradiation.[4] The isolation of an additional compound, praecalciferol,[5] present in the mixture obtained on irradiation of ergosterol, has shed some new light on the mechanism of vitamin formation. Velluz recently revealed experimental findings from which he deduced structure II for praecalciferol,[6] which would thus be the *cis* isomer of tachysterol (III). Of even greater interest is the ready conversion of praecalciferol (II) to vitamin D_2 (IV) by moderate heating in neutral solvents in the *absence* of light. The "enesyntheses" of Alder were quoted as analogies in an attempt to rationalize this remarkable change.

It thus appears that the first product formed in the photoisomerization is not V but II which in a subsequent dark reaction is converted to IV. The presence of both I and V in the mixture produced on irradiation of II points strongly to the reversibility of the initial photoreaction. The appearance also of III is easily rationalized by assuming reversible *cis* $\rightleftarrows$ *trans* photoisomerization of II and III, for which there is ample precedent in similar systems.

Similarities in the steric as well as electronic structures of tachysterol (III) and *trans*-β-ionone (VI) prompted us to investigate the photochemical isomerization of VI, as a potential synthetic route to γ-ionone[7] (VIII), which in turn should be convertible to a number of compounds with ambergris odor. In this paper we describe the photochemical isomerization of β-ionone and some related dienones.

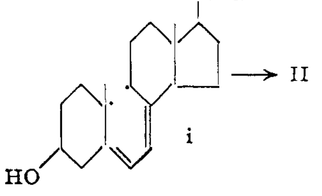
A solution of β-ionone (VI) in ethanol was irradiated with a low intensity mercury arc and the products separated by fractional distillation. Besides VI (12–22%) and polymers (30–50%), two new compounds, X (22–32%) and IX (2–4%), both isomeric with the starting material were isolated. In analogy to the photoisomerization of *trans*-α-ionone to *cis*-α-ionone[8] and the isomerization of III to II, we had anticipated *cis*-β-ionone (VII) in the low boiling fraction of the reaction product. This notion however was quickly dismissed after an inspection of both the ultraviolet (λ_{max} 286 mμ, log ε 3.68) and infrared spectra (*cf.* Fig. 1) of this fraction (X). The data indicated the presence of an enol ether rather than a ketone. Verification was obtained by catalytic reduction of X to a tetrahydro compound (XI) which was identical with a sample obtained by an unambiguous route.[9] Although the facts presented above show

---

[4] A recent review of the subject is presented by H. H. Inhoffen and K. Brückner in L. Zechmeister, "Progress in the Chemistry of Organic Natural Products," Vol. XI, Springer, Wien, 1954.

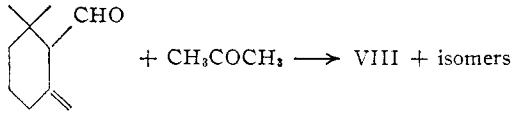
[5] L. Velluz and G. Amiard, *Compt. rend.*, **228**, 692 (1949); E. Havinga, A. L. Koevoet and A. Verloop, *Rec. trav. chim.*, **74**, 788, 1125, 1230 (1955).

[6] L. Velluz, G. Amiard and B. Goffinet, *Bull. soc. chim.*, 1341 (1955). The stereochemical argument presented rests entirely on rather subtle differences in the ultraviolet absorption spectra of II and III. However, it seems reasonable that a transition state (approximately i) should collapse to the *cis*-(II), rather than to the *trans* isomer III.



i

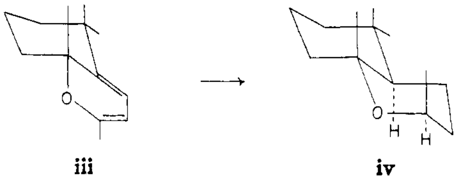
[7] To our knowledge pure γ-ionone has not been described in the literature; however, a mixture of isomeric ionones containing 15% of VIII has been obtained by condensation of ii with acetone (B. Willhalm, Ph.D. thesis, ETH Zurich, 1954).



ii

[8] G. Büchi and N. C. Yang, *Helv. Chim. Acta*, **38**, 1338 (1955).

[9] M. Stoll and P. Bolle, *ibid.*, **33**, 900 (1950); M. Stoll, P. Bolle and L. Ruzicka, *ibid.*, **33**, 1502 (1950). We would like to thank Dr. Max Stoll, Firmenich and Co., Geneva, for providing us with a sample of XI. The configuration of XI is unknown, but it seems safe to assume that catalytic reduction of iii leads to iv.



iii iv

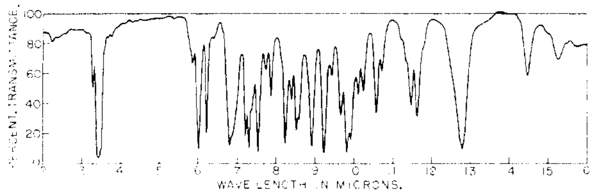
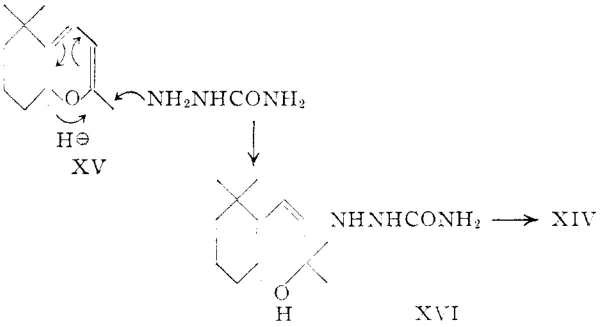
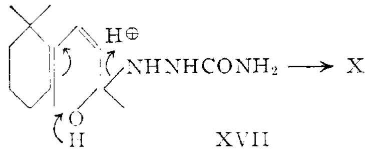


Fig. 1.

that X does not contain a carbonyl group, prolonged treatment with semicarbazide acetate in methanolic solution yielded a very unstable semicarbazone, λ_{max} 274 mμ, log ε 4.03, which we believe to be the derivative XIV of the unknown *cis*-*β*-ionone (VII). The formation of semicarbazones from enol ethers has been noticed with a similar enol ether,[10] and the appearance of the less stable *cis* derivative is reasonable if the reagent adds to the bicyclic ether (*cf.* XV → XVI). The semicarbazone of the *trans*-ketone would be the expected product of addition to the monocyclic ketone.[11]



Semicarbazone XIV was smoothly hydrolyzed by steam distillation in the presence of phthalic acid to the pyran X rather than VII. This finding suggests that the preferred elimination of semicarbazide in the intermediate XVI involves cyclization rather than direct 1,2-elimination (XVII arrows).



Isomerization of X with iodine, a reagent known to promote *cis* → *trans* isomerization in polyenes,[12] gave *trans*-*β*-ionone (VI) in 60% yield.

A second product formed in the photoisomerization of VI had λ_{max} 284; 214 mμ (log ε 2.1; 3.44). The ultraviolet absorption spectrum observed is similar to the one of 1-acetyl-2,2-dimethyl-3-(2-methyl-1-propenyl)-cyclopropane.[13] The infrared spectrum (Fig. 2) suggested the presence of CH_3CO- and $CH_2{=}C(R)_2$, and a positive iodoform test as well as the formation of formaldehyde on ozonization of IX confirmed this postulate. Ionene (XIII) was formed readily upon acid-catalyzed isomerization of IX, and this finding is interpretable with structures IX and XVIII, both of which contain the unchanged carbon skeleton of VI.

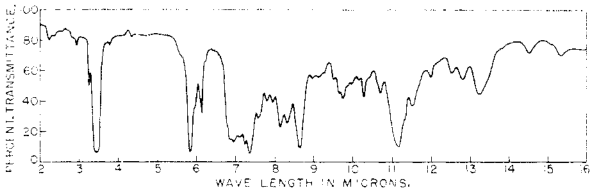
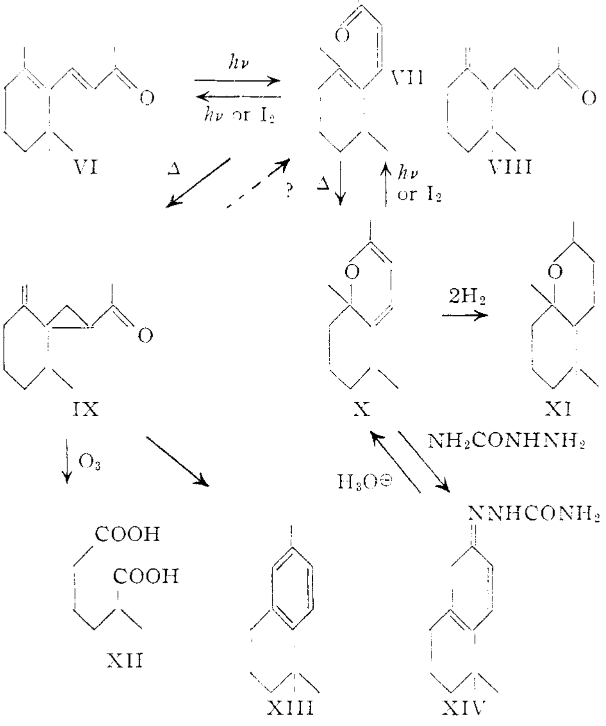
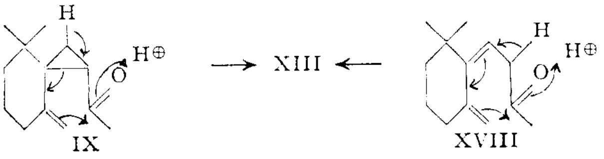


Fig. 2.



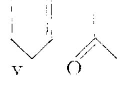


Some insight into the distribution of the functional groups in IX was gained through ozonization experiments which gave formaldehyde (12%) and 2,2-dimethyladipic acid (XII) (40%). The formation of XII from XVIII is self explanatory, but its formation from IX is puzzling because cyclopropanes are known to be stable to ozone. However, the breakdown of the cyclopropane ring does not necessarily have to occur during the ozonization and might well be caused by hydrogen peroxide

---

[10] M. Stoll, L. Ruzicka and C. F. Seidel, *Helv. Chim. Acta*, **33**, 1245 (1950); M. Stoll and M. Hinder, *ibid.*, **34**, 334 (1951).

[11] In an attempt to prepare the phenylsemicarbazone of v the only isolable derivative was that of the *trans*-ketone [*cf.* W. Surber, V. Theus, L. Colombi and H. Schinz, *ibid.*, **34**, 1299 (1956)].



v

[12] L. Zechmeister, *Experientia*, **10**, 9 (1954); W. Oroshnik and A. D. Mebane, This Journal, **76**, 5719 (1954), and other examples cited in these papers

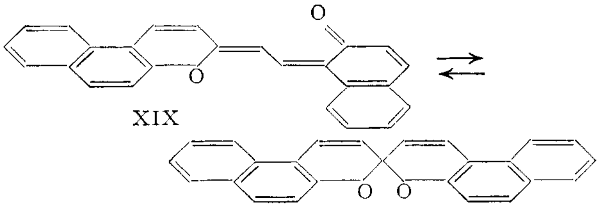
[13] R. H. Eastman and S. K. Freeman, *ibid.*, **77**, 6642 (1955), and earlier papers.

which was used to complete this oxidation.[14] Titration of IX with perbenzoic acid established the presence of only one double bond, and the photoisomer should therefore contain two carbocyclic rings. In sharp contrast to this result catalytic reduction of IX was only complete after the uptake of three moles of hydrogen. The alcohol thus formed was reoxidized with chromium trioxide and the ketone characterized by its semicarbazone. The derivative could not be obtained pure, but no melting point depression was observed on admixture of *cis*-tetrahydroionone semicarbazone.

We were thus forced to assume that our photoisomer contains either (a) two olefinic bonds, one of which is not oxidizable by perbenzoic acid, or (b) a vinylcyclopropane system reducible to the tetrahydro stage. Structure XVIII was excluded through consideration of the following facts: (i) basic conditions sufficiently drastic to cause isomerization of α- to β-ionone[15] did not bring about isomerization of the ketone to VI, and (ii) the ultraviolet absorption observed is scarcely attributable to the conjugated diene chromophore of XVIII because the less highly substituted 1,2-dimethylenecyclohexane has $\lambda_{\max}$ 220 mμ.[16] We therefore favor formula IX with which all of the described facts including the reduction[17] can be rationalized satisfactorily.

Discussion of Results

The first step in the conversion of β-ionone (VI) to IX and X is undoubtedly the reversible photoisomerization to *cis*-β-ionone (VII), a reaction for which analogies have been quoted already. We assume that the two products actually isolated are derived from the highly reactive *cis*-ketone VII by two distinct dark reactions (a) and (b). Thus (a), whenever the six atoms present in the chromophore of VII have approached planarity, cyclization can occur to give the bicyclic pyran X. As in the reversible dienone ⇄ pyran interconversion observed with thermochromic spiropyrans (*e.g.*, XIX ⇄ XX),[18] the equilibrium, at room temperature, is very much on the side of the pyran X. This seems reasonable if one compares the resonance energies of the planar pyran X with that of the *cis*-dienone VII which, in the ground state at least, is forced into a non-planar conformation by steric interference of methyl groups.

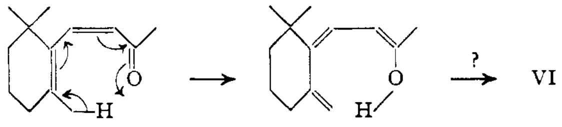

XIX

XX

Conversely, irradiation of X in alcoholic solution produces a mixture of VI, IX and X. A considerable amount of energy (ultraviolet light) is required to convert the pyran X back to the *cis*-ketone VII from which VI is formed by photoisomerization and IX probably by a dark reaction (see below). We have no direct evidence that the *cis*-ketone VII → pyran X conversion is indeed a thermal rather than a photochemical reaction, but since the appearance of our preliminary note,[3] Schinz[11] has reported the formation of pyrans by catalytic reduction of two acetylenic ketones in the absence of light. These findings thus support our postulate.

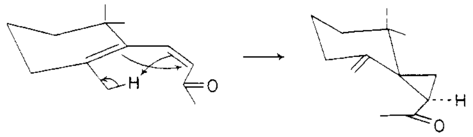
The formation of the *cis*-ketone VII from X is therefore analogous to the photosynthesis of praecalciferol (II) from ergosterol (I); the reverse reaction (X from VII), however, seems to occur very much more readily than the formation of ergosterol (I) and lumisterol (V) from praecalciferol (II).

The question (b) whether the *cis*-ketone VII undergoes an "enesynthesis" analogous to the praecalciferol (II) → vitamin D (IV) change cannot be answered because the product (XXI) from such a reaction might well convert to β-ionone (VI) rather than γ-ionone (VIII).



VII XXI

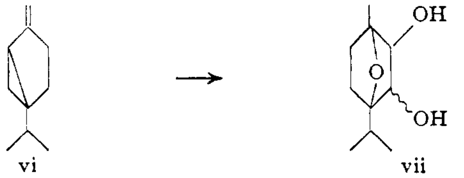
The unstable *cis*-ketone VII apparently can stabilize itself by another route (b) which results in the formation of the spiroketone IX.


XXII XXIII

The atomic model of the *cis*-ketone XXII shows that in the least strained conformation in which the side chain is approximately perpendicular to the plane of the cyclohexene ring, a methyl hydrogen is close in space to the first carbon atom of the side chain, and it is conceivable that bond formation between these atoms could occur (XXII arrows). Such a concerted reaction would lead to a definite configuration of IX shown in XXIII. The ready formation of ionene (XIII) (see above) is well in accord with this formulation because only in this diastereomer (XXIII) are the carbonyl carbon

---

[14] The oxidation of sabinene (vi) with hydrogen peroxide in acetic acid has been investigated by G. G. Henderson and A. Robertson [*J. Chem. Soc.*, 1849 (1923); *ibid.*, 2761 (1926)], who have found that two isomeric compounds $C_{10}H_{18}O_3$ were formed. The absence of a cyclopropane ring in the products seems certain, but structure vii advanced by the authors is by no means established.


vi vii

[15] H. Köster, *Chem. Ber.*, **77**, 553 (1944).

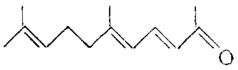
[16] W. J. Bailey and H. G. Golden, THIS JOURNAL, **75**, 4780 (1953).

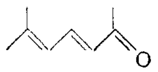
[17] Reductive fission of vinylcyclopropanes is known: *cf.* R. W. Kierstead, R. P. Linstead and B. C. L. Weedon, *J. Chem. Soc.*, 3610 (1952); 1799 (1953), and earlier references cited therein.

[18] For a discussion of this isomerization see C. F. Koelsch, *J. Org. Chem.*, **16**, 1362 (1951).

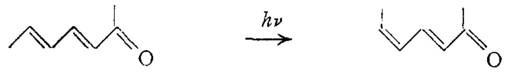
and the terminal methylene group in close spatial proximity. An analogous reaction has not been observed with praecalciferol (II), but whether such a mechanism is operative also in the photoisomerizations of pyrocalciferol and isopyrocalciferol[19] is now under investigation.

Our attempts to synthesize other pyrans by photoisomerization of dienones have been singularly unsuccessful. Irradiation of pseudoionone (XXIV) and 6-methyl-3,5-heptadiene-one-2 (XXV)


XXIV


XXV

has led to polymeric materials rather than the desired pyrans. We have been unable to determine whether the polymers have originated from the pyrans or the ketones. Photoisomerization of *trans–trans*-crotonylideneacetone (XXVI), λ_{max} 272 mμ, log ϵ 4.30, on the other hand has led to a new stereoisomer (XXVII), λ_{max} 279 mμ, log ϵ 3.99. We prefer the Δ-*cis*-5,6 structure for this isomer because (a) the ultraviolet absorption at longer wave lengths indicates that the newly introduced *cis* double bond is at the end of the chromophore[12] and (b) the $\Delta^{3,4}$-*cis* isomer would be expected to isomerize to the pyran.[11] The aliphatic nature of XXVII was established by hydrogenation to the known 2-heptanone.



XXVI XXVII

Acknowledgment.—The authors wish to acknowledge generous financial assistance from Eli Lilly and Co.

Experimental[20]

β-Ionone.—Commercially available β-ionone was purified either through its semicarbazone[21] or by recrystallization from petroleum ether at −75°,[22] n^{25}_{D} 1.5178–1.5180, λ_{max} 296 mμ, ϵ 10800.

Irradiation of β-Ionone (VI).—A solution of β-ionone (24 g.) in ethanol (600 ml.) was irradiated in a quartz apparatus[23] for 48 hr. at 35–40°. The ethanol was then removed by evaporation under reduced pressure and the residue distilled through a Hickman flask (b.p. 35–60° at 0.05 mm.). The distillates from 5 irradiations (81 g.) were combined and fractionated through a 40-inch spinning band column at 1 mm.: fraction 1, 68–72°, 31.5 g., n^{25}_{D} 1.4980; 2, 71–75°, 2.4 g.; 3, 75–85°, 4.8 g.; 4, 85–94°, 18 g., n^{25}_{D} 1.5060. Redistillation of fraction 1 through the same column yielded 24.5 g. (30% yield) of X, b.p. 70–71° at 1 mm., n^{25}_{D} 1.4992; ultraviolet spectrum in ethanol, λ_{max} 286 mμ, log ϵ 3.86. *Anal.* Calcd. for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.01; H, 10.25. Redistillation of fraction 3 (17.3 g. combined from six 72-hr. irradiations) through a 1-ft. spinning-band column gave 8.4 g. of IX, b.p. 81–82° at 1 mm., n^{25}_{D} 1.4860, λ_{max} 284 mμ, log ϵ 2.10; 214 mμ, log ϵ 3.44. *Anal.* Calcd. for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.06; H, 10.51.

The ketone IX was further characterized by a semicarbazone, m.p. 170–171°, recrystallized from ethanol. *Anal.* Calcd. for $C_{14}H_{23}ON_3$: C, 67.43; H, 9.30; N, 16.85. Found: C, 67.29; H, 9.23; N, 16.75.

Treatment with phenylsemicarbazide in methanol gave a derivative, m.p. 144–145°, recrystallized from ethanol. *Anal.* Calcd. for $C_{20}H_{27}ON_3$: C, 73.81; H, 8.36; N, 12.91. Found: C, 73.62; H, 8.52; N, 13.23.

Irradiation of X.—A solution of X (22 g.) in ethanol (650 ml.) was irradiated for 48 hr. at 35° and the organic material isolated as described above. The products (14 g.) were separated by fractionation through a 1-ft. spinning-band column at 1 mm.: fraction 1, b.p. 69–73°, 4.6 g.; 2, 73–75°, 1.2 g.; 3, 75–85°, 3.5 g.; 4, 85–92°, 4.4 g., n^{25}_{D} 1.5108. Fraction 1 was identified as unchanged X by its characteristic infrared spectrum. A semicarbazone prepared from 3 was identical with the corresponding derivative of the bicyclic ketone IX. Fraction 4 consisted mainly of β-ionone (VI) as indicated by its infrared spectrum and the formation of β-ionone semicarbazone, m.p. 147–148°.

Isomerization of X.—To a mixture of X (2 g.) in 40 ml. of benzene was added iodine (100 mg.) and the resulting solution kept at room temperature for 2 hr. After washing with aqueous sodium thiosulfate and evaporation of the solvent, an oil remained which was distilled, b.p. 63–66° (0.02 mm.), 1.2 g., n^{25}_{D} 1.5134, and identified as β-ionone by its infrared spectrum as well as by semicarbazone comparison.

Hydrogenation of X to XI.—A solution of X (1.92 g.) in glacial acetic acid (5 ml.) was stirred with Adams platinum catalyst (0.4 g.) under hydrogen at room temperature. The uptake of hydrogen ceased after 1.96 mole had been absorbed. After removal of the catalyst by filtration, the filtrate was diluted with water (40 ml.) and the product isolated by extraction with petroleum ether. The dried solution was passed over 50 g. of neutral alumina. Removal of the solvent from the eluate yielded a product which after distillation had b.p. 45–48° (0.05 mm.), 1.56 g., n^{25}_{D} 1.4714. *Anal.* Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.82; H, 12.06. The infrared spectrum of the product was indistinguishable from the spectrum of authentic epoxy-3,2[3]-tetrahydroionane (XI).

***cis*-β-Ionone Semicarbazone (XIV).**—The pyran X (4.0 g.) was allowed to react with excess semicarbazide–acetate in methanol solution in the absence of oxygen and sunlight. A crystalline precipitate formed slowly and was collected on a filter after 24 hr. After two rapid recrystallizations from aqueous methanol, the compound had m.p. 184–185° (vacuum capillary); λ_{max} 274 mμ, log ϵ 4.03. *Anal.* Calcd. for $C_{14}H_{23}ON_3$: C, 67.43; H, 9.30. Found: C, 67.38; H, 9.28. The infrared spectrum showed that a true semicarbazone was present (5.9, 6.25 μ).

Hydrolysis of *cis*-β-Ionone Semicarbazone (XIV).—The derivative (3.6 g.) was mixed with phthalic anhydride (3.6 g.) by grinding in a mortar and hydrolyzed by steam distillation. The organic material was extracted into petroleum ether and washed successively with aqueous sodium bicarbonate and water, concentrated to a liquid which on distillation gave the pyran X (0.7 g.), identified by b.p., n^{25}_{D} and infrared spectrum.

Air Oxidation of X.—On prolonged standing in the presence of air, X is converted to a crystalline colorless material which after recrystallization from benzene–petroleum ether had m.p. 130° dec. *Anal.* Calcd. for $C_{13}H_{22}O_3$: C, 69.00; H, 9.80. Found: C, 68.96, 69.01, 69.34; H, 9.46, 9.63, 9.55. No absorption in the ultraviolet region of the spectrum; principal infrared bands in KBr: 2.88, 3.05, 3.45, 7.20, 7.35, 8.2, 9.08, 9.25, 9.45, 9.64, 10.05, 10.55 and 11.65 μ.

Acid Isomerization of IX to XIII.—A solution of IX (240 mg.) in aqueous methanol (80%) containing sulfuric acid (400 mg.) was allowed to reflux for 90 min. The mixture was then poured into water (10 ml.) and extracted with ethyl ether. After washing, drying and evaporation, an oil was isolated which was purified successively by chromatography over alumina and vacuum distillation, b.p. 48–50° (0.05 mm.), n^{25}_{D} 1.5205 (*Anal.* Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.85; H, 10.10) and shown to be identical by b.p., n^{25}_{D} and infrared spectrum with ionene (XIII).

Oxidation of IX with Perbenzoic Acid.—The bicyclic ketone IX (0.4236 g.) was added to a solution of perbenzoic

---

(19) K. Dimroth, *Chem. Ber.*, **70**, 1631 (1937).

(20) Melting points and boiling points are uncorrected. Analyses by Mmes. N. Alvord and G. Kula and Dr. S. M. Nagy, M.I.T. Microanalytical Department. The infrared spectra were determined with a Baird double beam recording spectrophotometer. Ultraviolet spectra were measured with a Cary recording spectrophotometer.

(21) W. G. Young, S. J. Cristol, L. J. Andrews and S. L. Lindenbaum, This Journal, **66**, 855 (1944).

(22) T. G. Drustrup, U. S. Patent 2,638,483 (1951). We would like to thank Dr. Robert Kent, Chas. Pfizer and Co. for calling our attention to this reference.

(23) M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

acid in chloroform (5 ml., 1.17 *N*) and the mixture allowed to stand at 0–5°. Aliquot parts were removed for titration after 6, 8 and 24 hr. The following consumption of perbenzoic acid was observed: 1.02, 1.03 and 1.02 moles.

Hydrogenation of IX.—One gram of IX was hydrogenated in glacial acetic acid (5 ml.) over Adams platinum catalyst (from 0.5 g. of PtO_2) at atmospheric pressure. Hydrogen (368 ml., 3.0 mole equiv.) was absorbed within 12 hr. In two additional reductions, carried out under identical conditions, 2.86 and 2.95 moles of hydrogen was absorbed. Reoxidation of the secondary alcohol(s) thus formed with chromium trioxide in acetic acid solution gave a ketone which was characterized by its semicarbazone, m.p. 173–174°. Repeated recrystallization did not raise the melting point. No depression was observed on admixture of pure *cis*-tetrahydroionone semicarbazone, m.p. 179–180°.

Oxidation of IX with Ozone.—A large excess of ozone (2% in oxygen) was passed through a solution of IX (1 g.) in carbon tetrachloride at 0–5°. The escaping gases were passed through an absorption tube containing water (10 ml.) and after completion of the oxidation, dimedone (1.6 g.) in ethanol (20 ml.) was added to this water. The precipitate which had formed was filtered and on recrystallization yielded the dimedone derivative of formaldehyde, 180 mg., 12%, m.p. 188–190°. The actual reaction mixture was concentrated under reduced pressure and the remaining oil warmed to 85° for 4 hr. after a solution of aqueous hydrogen peroxide (10%) had been added. Aqueous sodium hydroxide was added and the small amount of neutral material extracted with ether. The water layer was then acidified with concd. hydrochloric acid and extracted exhaustively with ether. Purification of the residue obtained after evaporation of the solvent was achieved by chromatography on silica gel (Davison mesh size 28–200, 30 g.). A mixture of chloroform–ethyl acetate (7:3) was used to elute the material which was further purified by recrystallization from acetone–water. The acid (350 mg., 38% yield) had m.p. 86–87° (*Anal.* Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.28; H, 8.00), and was found to be identical by mixture melting point and infrared spectrum with authentic 2,2-dimethyladipic acid (XII).

Attempted Base-catalyzed Isomerization of IX.—A solution of IX in carefully dried ethanol containing 10% sodium ethoxide was allowed to stand for 24 hr. at room temperature. No change in the ultraviolet spectrum was observed.[24]

Irradiation of Crotonylideneacetone (XXVI).—A solution of crotonylideneacetone,[25] 20 g., b.p. 77–78° (24 mm.), $n^{25}\text{D}$ 1.5200, $\lambda_{\max}$ 272 mμ, log ϵ 4.30, was irradiated in ethanol (600 ml.) for 24 hr. The solvent was removed carefully by distillation through a Fenske column and the residue fractionated in a Hickman flask. The distillate was further purified by distillation through a 1-ft. spinning-band column. The first fraction, b.p. 62–77° (24 mm.), yielded 2.3 g. of a light yellow liquid which on redistillation through a semimicro fractionating column gave 700 mg. of XXVII, b.p. 62–64° (21 mm.), $n^{25}\text{D}$ 1.5040, $\lambda_{\max}$ 279 mμ, log ϵ 3.99; principal infrared bands: 3.48, 6.0, 6.15, 12.0, 13.5 and 14.6 μ. *Anal.* Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 75.78; H, 9.15. The semicarbazone, m.p. 118–140° dec., decomposed on attempted recrystallization from ethanol.

Hydrogenation of XXVII to 2-Heptanone.—A solution of XXVII (100 mg.) in absolute ethanol (5 ml.) was stirred with 2% palladium-on-calcium carbonate catalyst (100 mg.) under hydrogen at room temperature. The calculated amount of two mole equivs. of hydrogen (100%) was rapidly absorbed. After removal of the catalyst by filtration 2,4-dinitrophenylhydrazine reagent was added. The derivative (160 mg.) had m.p. 73–74° after two recrystallizations from methanol and was identical by mixture melting point determination with an authentic derivative of 2-heptanone.

CAMBRIDGE, MASSACHUSETTS

---

[24] We would like to thank Dr. Hans Rennhard for performing this experiment.

[25] H. Meerwein, *Ann.*, **358**, 85 (1908).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Perfluoroalkyl-substituted Dicarboxylic Acids and Derivatives[1,2]

BY E. T. MCBEE, C. W. ROBERTS[3] AND GORDON WILSON, JR.

RECEIVED JULY 2, 1956

The condensation of ethyl malonate with $C_3F_7CH{=}CHCO_2Et$ produced a tricarboxylic ester which was hydrolyzed and decarboxylated to $C_3F_7CH(CH_2CO_2H)_2$. The corresponding ester, glycol and acid chloride were synthesized from the acid. By the same synthetic route $C_7F_{15}CH(CH_2COCl)_2$ also was prepared. The addition of hydrogen sulfide to $C_3F_7CH{=}CHCO_2Et$ produced mainly $S[CH(C_3F_7)CH_2CO_2Et]_2$ with some $C_3F_7CH(SH)CH_2CO_2Et$. The acid, glycol and acid chloride of the sulfide were prepared.

Discussion

Recent interest in elastomers which are not affected by extremes in temperature and by organic solvents has led to investigations of fluorine-containing polyesters. This paper reports several dicarboxylic acids and derivatives containing perfluoroalkyl side chains which were prepared from 3-perfluoroalkylpropenoates and which are convertible to polymers by appropriate reactions.

In earlier investigations, 3-perfluoroalkylpropenoates were prepared by reaction of a perfluoroaldehyde with ethyl bromoacetate in the presence of zinc dust followed by dehydration of the resulting β-hydroxy ester.[4] Higher and more consistent over-all yields of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate and ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-2-decenoate have now been obtained by an alternate procedure in which the perfluoroaldehyde is first condensed with malonic acid in pyridine solution to give a β-hydroxy acid. This Knoevenagel reaction is somewhat surprising since perfluoroaldehydes are readily polymerized by organic bases and, in fact, when the pyridine solution of malonic acid is added to the aldehyde, polymerization occurs rapidly with the evolution of heat. However, as the reaction mixture is heated the polymer slowly dissolves and the condensation proceeds. The stability toward dehydration of β-hydroxy-β-perfluoroalkyl esters[4] and

---

[1] This investigation was performed on a subcontract with Hooker Electrochemical Co. and was supported in whole by the United States Air Force as part of Contract AF 33(616)-2421 monitored by Materials Laboratory, Directorate of Research, Wright Air Development Center. A paper covering this investigation was presented before the Division of Polymer Chemistry, 130th Meeting of the American Chemical Society, Atlantic City, N. J., 1956.

[2] From a thesis to be submitted by Gordon Wilson, Jr., to the Graduate School, Purdue University, in partial fulfillment for the degree of Doctor of Philosophy.

[3] Dow Chemical Co., Midland, Michigan.

[4] E. T. McBee, O. R. Pierce and D. D. Smith, THIS JOURNAL, **76**, 3722 (1954).