shaking, the autoclave was cooled to room temperature; upon venting 2.5 g. of unchanged olefin was collected. The liquid product from the autoclave was stirred with 100 ml. of water and then made slightly alkaline with sodium bicarbonate. The water insoluble layer was separated, dried, and the solvent was removed by evaporation. The water layer was extracted three times with diethyl ether; the ether extract was dried and the ether removed by evaporation. The pale yellow oil residues were combined to provide 16 g. of a product that was vacuum distilled to give a colorless liquid, the constant boiling etherate of the nitro alcohol, $3CF_3CHOHCF_2NO_2 \cdot C_2H_5OC_2H_5$, b.p. 70° (100 mm.), $n^{29}D$ 1.335.

Anal. Calcd. for $C_{13}F_{15}H_{16}N_3O_{10}$: C, 23.7; H, 2.44; F, 43.2; N, 6.37; ethoxyl, 6.84. Found: C, 24.4; H, 2.78; F, 43.0; N, 6.35; ethoxyl, 6.92.

The infrared spectrum of this etherate showed strong bonded —OH in the 3-μ region, and a strong asymmetrical and symmetrical NO_2 stretching band at 6.25 and 7.33 μ, respectively.

The N-phenyl carbamate derivative of 2*H*-pentafluoro-1-nitro-2-propanol was prepared by treating the etherate of this nitro alcohol with an equimolar amount of freshly distilled phenyl isocyanate and a small amount of triethylamine as a catalyst. The reaction mixture was warmed for a few minutes on a steam bath and then cooled in ice to solidify the product. Recrystallization from petroleum ether gave $C_6H_5NHCO_2CH(CF_3)CF_2NO_2$, white needles, m.p. 88–89°.

Anal. Calcd. for $C_{10}F_5H_7N_2O_4$: C, 38.24; H, 2.25; N, 8.92. Found: C, 38.05; H, 2.27; N, 8.38.

The aqueous alkaline layer remaining after ether extraction of the nitro alcohol was acidified with dilute hydrochloric acid and extracted three times with diethyl ether. This ether extract was dried over magnesium sulfate and evaporated to give 15 g. of a base soluble oil consisting mainly of a hydrate of 3,3,3-trifluorolactic acid, $CF_3CHOHCOOH$, b.p. 57° (123 mm.)

Anal. Calcd. for $CF_3CHOHCOOH$: F, 39.6; neut. equiv., 144; calcd. for $CF_3CHOHCOOH \cdot H_2O$: F, 35.2; neut. equiv., 162. Found: F, 36.15; neut. equiv., 154.

Acknowledgment.—This work was supported in part by the United States Air Force. We wish to thank Mr. Gordon E. Webb for technical assistance and Miss Ruth Kossatz, Mr. Howard J. Francis, Jr., and co-workers for spectroscopic and analytical determinations.

The Reaction of 1,1-Difluoroethylene with Mixtures of Dinitrogen Tetroxide and Iodine. Difluoroiodonitroethanes and 1,1-Difiuoro-1-alkoxynitroethanes

Murray Hauptschein, Robert E. Oesterling, Milton Braid, Edward A. Tyczkowski, and David M. Gardner

Research and Development Department, Pennsalt Chemicals Corporation, Philadelphia 18, Pennsylvania

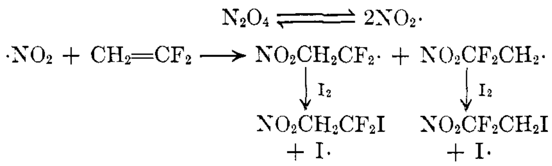
Received October 9, 1962

The reaction of 1,1-difluoroethylene with a mixture of dinitrogen tetroxide and iodine has been found to give the two novel isomeric adducts, 1,1-difluoro-1-iodo-2-nitroethane (predominantly) and 1,1-difluoro-2-iodo-1-nitroethane. The unusual facile reaction of the former isomer with alkanols to yield the novel fluoronitro ethers $ROCF_2CH_2NO_2$, where R = CH_3- or CH_3CH_2-, is described. 1,1,1-Trifluoro-2-nitroethane was produced in good yield by the reaction of anhydrous sodium fluoride in tetramethylene sulfone with 1,1-difluoro-1-iodo-2-nitroethane.

The reaction of olefins with mixtures of dinitrogen tetroxide and iodine has been reported to produce either β-iodoalkyl nitrates or β-nitroalkyl iodides, depending on the olefin used and on the reaction conditions.[1-3]

As part of our studies on the chemistry of the olefin 1,1-difluoroethylene,[4,5] we wished to investigate the synthesis and reactivity of the nitroiodides of 1,1-difluoroethylene. Of the theoretically possible adducts, $ICF_2CH_2NO_2$, $ICH_2CF_2NO_2$, ICH_2CF_2ONO (ICH_2COOH after hydrolysis), and ICF_2CH_2ONO (ICF_2CH_2OH after hydrolysis), the first three were obtained from the reaction of a mixture of dinitrogen tetroxide and excess iodine with 1,1-difluoroethylene using methylene chloride as the solvent.

The predominant nitroiodide isomer produced was 1,1-difluoro-1-iodo-2-nitroethane, whether the olefin was added to a mixture of dinitrogen tetroxide and iodine or whether dinitrogen tetroxide was added slowly to the other reactants. The latter procedure minimized the formation of iodonitrite (or iodonitrate), which after hydrolysis gave iodoacetic acid, *i.e.*, $ICH_2CF_2ONO \rightarrow [ICH_2CF_2OH] \rightarrow ICH_2COOH$. The mechanism of formation of the nitroiodides probably involves the trapping of an intermediate β-nitroalkyl radical with iodine.



$$\begin{tikzcd}
 & N_2O_4 \arrow[r, shift left, ""] & 2NO_2\cdot \arrow[l, shift left] & \\
\cdot NO_2 + CH_2{=}CF_2 \arrow[r] & NO_2CH_2CF_2\cdot \arrow[d, "I_2"] & + & NO_2CF_2CH_2\cdot \arrow[d, "I_2"] \\
 & NO_2CH_2CF_2I + I\cdot & & NO_2CF_2CH_2I + I\cdot
\end{tikzcd}$$

The nitro radical preferentially, but not exclusively, attacked the CH_2 group of 1,1-difluoroethylene to give predominantly $ICF_2CH_2NO_2$. This finding is similar to the attack of a perfluoralkyl radical, *e.g.*, $C_3F_7\cdot$ from C_3F_7I, on 1,1-difluoroethylene, which gave 95% of $C_3F_7CH_2CF_2I$ and only 5% of $C_3F_7CF_2CH_2I$.[6]

The main isomer $ICF_2CH_2NO_2$ was found to react readily with dry sodium fluoride in tetramethylene sulfone to give a good yield of 1,1,1-trifluoro-2-nitroethane, $CF_3CH_2NO_2$, demonstrating that the iodine atom was attached to the —CF_2 group. The infrared and ultraviolet spectra of both of these compounds were consistent with the presence of a —CH_2NO_2 group (see Experimental) and with a —CF_2I group for the former, *i.e.*, λ_{max} at 270 mμ in the ultraviolet.

The isomer 1,1-difluoro-1-iodo-2-nitroethane is unstable in basic aqueous solution, and has been found

---

(1) G. B. Bachman and T. J. Logan, *J. Org. Chem.*, **21**, 1467 (1956).

(2) T. E. Stevens and W. D. Emmons, *J. Am. Chem. Soc.*, **80**, 338 (1958).

(3) G. B. Bachman, T. J. Logan, K. R. Hill, and N. W. Standish, *J. Org. Chem.*, **25**, 1312 (1960).

(4) M. Hauptschein, A. H. Fainberg, and M. Braid, *ibid.*, **23**, 322 (1958).

(5) M. Hauptschein, M. Braid, and F. E. Lawlor, *J. Am. Chem. Soc.*, **80**, 846 (1958).

(6) (a) M. Hauptschein and R. E. Oesterling, *ibid.*, **82**, 2868 (1960); (b) We favor this explanation for the principal mode of formation of the isomer 1,1-difluoro-2-iodo-1-nitroethane over alternative interpretations involving ionic species (*e.g.*, NO_2^-, I^+) or iodine atom attack.

to undergo facile reactions with alkanols such as ethanol and methanol.

$$ROH + ICF_2CH_2NO_2 \longrightarrow ROCF_2CH_2NO_2 + HI$$

It is believed likely that the reaction proceeds through the *in situ* formation of the very reactive nitroölefin.

$$ICF_2CH_2NO_2 \xrightarrow{-HI} [CF_2{=}CHNO_2]$$

$$[CF_2{=}CHNO_2] + ROH \longrightarrow ROCF_2CH_2NO_2$$

Experimental

The Reaction of 1,1-Difluoroethylene with a Mixture of Dinitrogen Tetroxide and Iodine.—A stainless steel autoclave of 1400-ml. capacity was charged with 500 ml. of methylene chloride, 92 g. (1.0 mole) of dinitrogen tetroxide and 381 g. (1.5 moles) of iodine. The autoclave was connected to a cylinder of 1,1-difluoroethylene, and placed on a shaking apparatus. The olefin at a pressure of 250 p.s.i.g. was introduced into the autoclave at room temperature. Within 5–10 min. the pressure dropped to less than 100 p.s.i.g. The reactor was repressured with 1,1-difluoroethylene several times over a period of about 4 hr. until the pressure remained constant at 200 p.s.i.g. During this procedure, the reaction temperature remained at 25–30°; very little heat of reaction was observed. The autoclave was vented and the concents were filtered to remove unchanged iodine. The methylene chloride solution was washed with aqueous sodium bisulfite until all iodine color was removed, leaving a pale yellow solution. The solution was dried over anhydrous magnesium sulfate, and the methylene chloride was removed by distillation. The residue was distilled through a Vigreux column at 161 g. (68%)[7] of product having a boiling range of from 65 to 70° at 20 mm. was collected.

This product was shown by vapor–liquid chromatographic analysis to consist of the isomers 1,1-difluoro-1-iodo-2-nitroethane, $ICF_2CH_2NO_2$, and 1,1-difluoro-2-iodo-1-nitroethane, $ICH_2CF_2NO_2$, in about a 3:1 ratio.

Anal. Calcd. for $C_2F_2H_2INO_2$: C, 10.13; H, 0.85; N, 5.91. Found: C, 10.46; H, 0.87; N, 6.07.

Pure $ICH_2CF_2NO_2$, the first isomer component to be trapped by preparative chromatography, using a DC-200 column (10% substrate on Chromosorb) at 75°, boiled at about 50° (10 mm.). The mass spectrum showed a parent peak (*m/e*) of 237 (molecular weight), and peaks (*m/e*) for $C_2F_2H_2I$ (191), $C_2F_2H_2NO_2$ (110), and $C_2F_2H_2$ (64), corresponding to the loss of NO_2, I, or both NO_2 and I, respectively. The corresponding peaks for NO_2 (46) and for I (127) were also present, as well as many of the possible one carbon cleavage products and NO (30). The principal absorption bands (in microns) for the liquid in the infrared spectrum were at 3.27 m, 3.35 m, 3.40 m, 6.28 vvs, 7.09 s, 7.40 vs, 7.76 vs, 7.96 vs, 8.51 s, 8.88 vs, 9.36 vs, 10.15 vs, 11.82 vs, 13.47 vs, 14.55 s (s = strong, vs = very strong, vvs = very, very strong, m = medium). The peaks at 6.28 and 7.40 μ correspond to the asymmetric NO_2 and symmetric NO_2 stretching vibrations, respectively, of the $—CF_2NO_2$ group.[8] The ultraviolet spectrum of the isomer $ICH_2CF_2NO_2$ taken in isoöctane solution had a maximum absorption at 267 mμ, corresponding to the $—CH_2I$ group in that compound.

Pure $ICF_2CH_2NO_2$, the second isomer component to be trapped out by preparative chromatography, and also obtained by fractional distillation, boiled at 61° (11 mm.) and at 30° (1 mm.), $n^{26}D$ 1.4750.

Anal. Calcd. for $C_2F_2H_2INO_2$: C, 10.13; H, 0.85; N, 5.91. Found: C, 10.13; H, 0.87; N, 5.97.

The mass spectrum of 1,1-difluoro-1-iodo-2-nitroethane showed a parent peak (*m/e*) of 237, as well as the other peaks noted for the isomer 1,1-difluoro-2-iodo-1-nitroethane, although in quite different relative intensities, as expected for isomers. It is of interest to note that the relative intensity of the *m/e* peak at 110 representing loss of an iodine was much greater for $ICF_2CH_2NO_2$ than for the isomer $ICH_2CF_2NO_2$, whereas the reverse was true (to a lesser extent) for the *m/e* peak at 191 representing loss of a NO_2 group.

The infrared spectrum of $ICF_2CH_2NO_2$ (liquid) displayed the following principal absorption bands (in microns): 3.27 m, 3.36 m, 3.42 m, 6.37 vvs, 7.08 vs, 7.31 vs, 7.51 vs, 8.06 vs, 8.50 vs, 9.02 vs, 9.58 vs, 10.57 vs, 10.98 vs, 11.23 vs, 11.96 s, 13.17 s, 15+ s. The peaks at 6.37 and 7.31 μ correspond to the asymmetric NO_2 and symmetric NO_2 stretching vibrations, respectively of the $—CH_2NO_2$ group.

The ultraviolet spectrum of $ICF_2CH_2NO_2$ taken in isoöctane solution has an absorption maximum at 270 mμ, corresponding to the $—CF_2I$ group.[9,10]

Isolation of By-product Iodoacetic Acid.—The aqueous bisulfite wash from the previous experiment was not examined. From a prior run, however, carried out in a 300-ml. autoclave, charged with 100 ml. of methylene chloride, 51 g. of dinitrogen tetroxide, 1.55 g. of iodine, and 64 g. of 1,1-difluoroethylene, which yielded 34 g. of crude nitroiodide adduct, mostly $ICF_2CH_2NO_2$, the bisulfite aqueous layer was extracted with diethyl ether and dried with anhydrous magnesium sulfate. After removal of the ether by distillation there was obtained 15 g. of iodoacetic acid, m.p. 80–81°, the infrared spectrum of which was identical to an authentic sample. An additional 16 g. of iodoacetic acid was found in the residue after vacuum distillation of the nitroiodide. (Note that since no significant residue containing iodoacetic acid was found after distillation of the nitroiodide of the previous reaction, it is probable that relatively small quantities of iodoacetic acid were present in the aqueous wash of that reaction.)

Reaction of 1,1-Difluoroethylene with a Mixture of Dinitrogen Tetroxide and Iodine (Alternative Procedure).—A 300-ml. stainless steel autoclave was charged with 155 g. (0.61 mole) of iodine crystals, 75 ml. of methylene chloride, and 64 g. (1.0 mole) of 1,1-difluoroethylene. A stainless steel cylinder was charged with 51 g. (0.55 mole) of dinitrogen tetroxide and 25 ml. of methylene chloride. The methylene chloride solution of dinitrogen tetroxide was pumped slowly into the autoclave over a period of about 16 hr. while shaking at room temperature. After venting of the autoclave and removal of about 68 g. of solid iodine, the methylene chloride solution was washed with water and then with an aqueous solution of sodium bisulfite. The solution was dried over anhydrous magnesium sulfate. The methylene chloride was removed by distillation to give 97 g. of a red liquid. Fractional distillation and infrared analysis showed it to consist mostly of the isomer $ICF_2CH_2NO_2$ and minor amounts of the reverse addition product $ICH_2CF_2NO_2$. There was recovered from this run only 3 g. of iodoacetic acid.

Preparation of 1,1,1-Trifluoro-2-nitroethane from 1,1-Difluoro-1-iodo-2-nitroethane.—A mixture of 25 ml. of dry tetramethylene sulfone, 9.3 g. (0.04 mole) of $ICF_2CH_2NO_2$ and 3 g. of dry sodium fluoride (0.07 mole) was stirred at 100° for 1.5 hr. The reaction mixture was then diluted with 200 ml. of water and steam distilled giving a pale yellow oil which was separated and dried over anhydrous magnesium sulfate. A yield of 3.5 g. (68%) of crude $CF_3CH_2NO_2$ was obtained which on distillation gave the pure colorless liquid, 1,1,1-trifluoro-2-nitroethane, b.p. 96°.[11]

Anal. Calcd. for $C_2F_3H_2NO_2$: N, 10.86. Found: N, 10.99.

The infrared spectrum (liquid) showed the characteristic asymmetric NO_2 vibration of 6.34 μ and the symmetric NO_2 vibration at 7.33 μ. The ultraviolet spectrum of $CF_3CH_2NO_2$ taken in isoöctane had a maximum absorption of low intensity at 277 mμ.

The Reaction of 1,1-Difluoro-1-iodo-2-nitroethane with Ethanol.—To 28 g. (0.61 mole) of absolute ethanol at room temperature there was slowly added while stirring 23 g. (0.097 mole) of $ICF_2CH_2NO_2$. The temperature rose during the addition to about 40°. Stirring was continued for an additional 4 hr. and the reaction product then was isolated by distillation of all volatile components boiling lower than 50° at 0.1 mm. and then treatment of the distillate with water. The water-insoluble parts were dried and redistilled affording 9.5 g. of the fluorinated nitro ether, 1,1-difluoro-1-ethoxy-2-nitroethane, $CH_3CH_2OCF_2CH_2NO_2$, b.p. 61° (20 mm.).

Anal. Calcd. for $C_4F_2H_7NO_3$: C, 30.97; H, 4.55; N, 9.03. Found: C, 30.40; H, 4.28; N, 8.93.

The infrared spectrum of $C_2H_5OCF_2CH_2NO_2$ (liquid) displayed the following absorption bands (in microns): 3.27 m, 3.35

---

[7] Based on utilization of two nitro groups from each mole of dinitrogen tetroxide.

[8] The corresponding values for the asymmetric and symmetric NO_2 vibrations for the compounds $R_fCHOHCF_2NO_2$ were at 6.25–6.26 μ and at 7.39–7.42 μ, respectively. See M. Hauptschein and R. E. Oesterling, *J. Org. Chem.*, **28**, 1279 (1963).

[9] R. N. Haszeldine, *J. Chem. Soc.*, 1764 (1953).

[10] M. Hauptschein, M. Braid, and A. H. Fainberg, *J. Am. Chem. Soc.*, **83**, 2495 (1961).

[11] E. T. McBee, H. B. Hass, and I. M. Robinson, *ibid.*, **72**, 3579 (1950).

ms, 3.42 m, 6.36 vvs, 7.04 s, 7.26 vs, 7.40 vs, 7.81 vs, 8.07 vs, 8.35 s, 8.72 s sh, 9.16 s, 9.38 s, 9.67 vs, 10.37 m, 10.97 ms, 11.30 s, 12.07 ms, 13.04 ms, 14.47 s. The peak at 6.36 μ corresponded to the asymmetric NO_2 stretching vibration in compounds containing the $—CH_2NO_2$ group.

On treatment of the nitro ether with a sodium hydroxide solution, much fluoride ion was liberated, a behavior similar to that for ethers of the type $ROCF_2CH_2Cl$.[12]

The Reaction of 1,1-Difluoro-1-iodo-2-nitroethane with Methanol.—$ICF_2CH_2NO_2$ (10.3 g.) was refluxed with 50 ml. of methanol for 4 hr. after which the excess methanol, as well as some methyl iodide and hydrogen iodide formed in the reaction, were boiled off at atmospheric pressure. The residue was dissolved in methylene chloride, washed with aqueous sodium bisulfite to remove iodine, dried over anhydrous magnesium sulfate, and distilled. The pure ether, 1,1-difluoro-1-methoxy-2-nitroethane, b.p. 57° (22 mm.), was obtained in 95% yield.

Anal. Calcd. for $C_3F_2H_5NO_3$: C, 25.54; H, 3.57; F, 26.93; N, 9.93. Found: C, 25.51; H, 3.41; F, 26.44; N, 9.84.

The infrared spectrum of $CH_3OCF_2CH_2NO_2$ (liquid) displayed the following absorption bands (in microns): 3.22 m, 3.32 ms, 3.46 m, 6.38 vvs, 6.89 s, 7.03 s, 7.22 s, 7.40 vs, 7.77 vs, 8.05 vs, 8.73 s, 8.90 s, 9.33 s, 9.71 s, 10.00 s, 10.97 vs, 12.02 s, 12.22 ms, 13.00 s, 14.46 s. The peak at 6.38 μ corresponds to the asymmetric NO_2 stretching vibration in compounds containing the $—CH_2NO_2$ group.

Vapor–Liquid Partition Chromatography.—A Perkin–Elmer, Model 154, vapor fractometer was used.

Infrared Spectra.—A Perkin-Elmer Infracord, Model 137, was used. The individual spectrograms were calibrated immediately after they were run using a polystyrene film as a standard. The absorption wave lengths are believed accurate to ±0.02 μ.

Ultraviolet Spectra.—A Beckman ratio recording spectrophotometer, Model DK-2, was used. The wave length accuracy was checked by means of the mercury-in-quartz arc lamp.

Mass Spectra.—A Bendix Time-of-Flight spectrometer (Model 12) at an ionizing potential of 70 volts was used.

Acknowledgment.—This work was supported in part by the United States Air Force. We wish to thank Dr. Arnold Fainberg for chromatographic and infrared spectroscopic work, Dr. J. G. Smith, Jr., for the mass spectra determinations, and Mr. Howard Francis for elemental analyses and ultraviolet spectra.

---

[12] P. Tarrant and H. C. Brown, *J. Am. Chem. Soc.*, **73**, 1781 (1951).

The Synthesis of DL-*threo*- and -*erythro*-Amicetose 2,4-Dinitrophenylhydrazones[1]

CALVIN L. STEVENS, BARRINGTON CROSS,[2] AND T. TODA

Department of Chemistry of Wayne State University, Detroit 2, Michigan

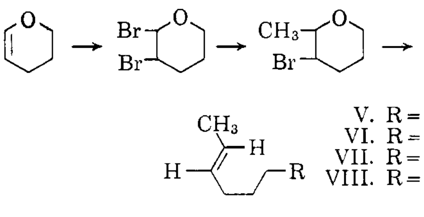
Received November 21, 1962

The DL-*erythro* (III) and -*threo* (IV) 2,4-dinitrophenylhydrazones of amicetose have been prepared from 1-nitro-4-hexene (VIII) which was synthesized from *trans*-4-hexen-1-ol (V). The structure proof of these isomers involved reaction with one mole of periodate. The natural isomer (I) was shown to be in the *erythro* series by an analysis of the rate of oxidation with periodate. Paper electrophoresis studies confirmed this result.

The antibiotic amicetin has been isolated from *Streptomyces plicatus*[3] and *Streptomyces vinaceus-drappus*.[4] Methanolysis of amicetin yielded, besides cytimidine,[5,6] a basic amino sugar, amosamine, and a neutral sugar amicetose isolated as its methyl glycoside in this laboratory.[7] Hydrolysis of the methyl glycoside of amicetose with 3 *N* hydrochloric acid gave free amicetose which was characterized as a crystalline 2,4-dinitrophenylhydrazone (I), m.p. 152–153°. The structure was established[7] by periodate cleavage of the 2,4-dinitrophenylhydrazone (I), which consumed only one mole of reagent in fifteen minutes with no further significant uptake in three hours. Acetaldehyde was isolated as its 2,4-dinitrophenylhydrazone in 51% yield as the volatile reaction product. The nonvolatile residue gave succindialdehyde bis-2,4-dinitrophenylhydrazone (II) in quantitative yield.

In this paper the synthesis of the DL-*erythro* and -*threo* isomers (III and IV) of amicetose 2,4-dinitrophenylhydrazone is reported and evidence presented that shows natural amicetose 2,4-dinitrophenylhydrazone to be in the *erythro* series.

4-Hexen-1-ol (V) was prepared from 3-bromo-2-methyltetrahydropyrane by the procedure of Brandon, Derfer, and Boord[8] in 55% over-all yield. The infrared absorption spectrum of (V) showed a strong absorption at 10.38 μ, characteristic of a *trans* double bond. The 3,5-dinitrobenzoate derivative (VI) was prepared from V in 41% yield and also showed a strong absorption at 10.38 μ. Addition of phosphorus tribromide to a cooled ethereal solution of *trans*-4-hexen-1-ol (V) gave a 53% yield of 1-bromo-4-hexene (VII). Treatment of VII with sodium nitrite in dimethylformamide[9] at −10° converted it to 1-nitro-4-hexene (VIII) in 65% yield.



V. R = –OH
VI. R = $C_6H_3(NO_2)_2$–COO–
VII. R = –Br
VIII. R = $–NO_2$

The reaction of 1-nitro-4-hexene (VIII) with silver acetate and iodine in acetic acid and water (1.5 moles)[10] gave the expected monoacetate of DL-1-nitro-4,5-

---

[1] This investigation was made possible by research grants CY 3772 and A 769 from the National Institutes of Health, Public Health Service.

[2] Wellcome Trust Travel Grant Recipient, 1960.

[3] T. H. Haskell, A. Ryder, R. P. Frohardt, S. A. Fusari, T. L. Jakubowski, and Q. R. Bartz, *J. Am. Chem. Soc.*, **80**, 743 (1958).

[4] J. W. Hinman, E. L. Caron, and C. DeBoer, *ibid* ., **75**, 5864 (1953).

[5] E. H. Flynn, J. W. Hinman, E. L. Caron, and D. O. Woolf, *ibid.*, **75**, 5867 (1953).

[6] T. H. Haskell, *ibid.*, **80**, 747 (1958).

[7] C. L. Stevens, K. Nagarajan, and T. H. Haskell, *J. Org. Chem.*, **27**, 2001 (1962).

[8] R. C. Brandon, J. M. Derfer, and C. E. Booard, *J. Am. Chem. Soc.*, **72**, 2120 (1950); L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1707 (1950), prepared V from the corresponding chlorotetrahydropyrane and showed the product to be mostly the *trans* isomer.

[9] N. Kornblum, H. O. Larsen, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, and G. E. Graham, *ibid.*, **78**, 1497 (1956).

[10] R. B. Woodward and F. V. Brutcher, *ibid.*, **80**, 209 (1958); S. Winstein and R. E. Buckles, *ibid.*, **64**, 2780, 2787 (1942).