Formation of the Sodium and Lithium Salts of 18f. The procedures used were identical with those employed to make the salts of **3f**.

Decomposition of the Salt of 18f. The flask containing the salt was connected through a short-path distillation head to a trap. A high vacuum was applied to the often vain hope of removing all the THF. The trap was then cooled to −78° and the flask warmed quickly to 70° and then more slowly to 90–100° at which point decomposition began. The products were removed from the trap and analyzed and collected by gas chromatography on column A operated at 100°. Two new hydrocarbons, *cis*-bicyclo[5.2.0]nona-2,4,8-triene (**20**) and bicyclo[3.2.2]nonatriene (**21**) were isolated, in addition to the known bicyclo[4.2.1]nonatriene; precise mass measurement (**20**) calcd for C_9H_{10}: 118.07862; found: 118.078247; precise mass measurement (**21**) found: 118.078456.

Hydrogenation of *cis*-Bicyclo[5.2.0]nona-2,4,8-triene (20). A solution of 5.3 mg of **20** in 3 ml of MeOH was hydrogenated at atmospheric pressure and room temperature over platinum oxide. After 70% of the theoretical uptake absorption of hydrogen ceased. The single product was isolated by gas chromatography on column C operated at 90°.

Hydrogenation of *cis*-Bicyclo[5.2.0]non-8-ene (22). The sodium salt of bicyclo[5.1.0]nonan-8-carboxaldehyde tosylhydrazone (prepared by the method of Kirmse and Pook[9]) was decomposed to give **22** identical with that prepared by these authors.[9] A solution of 14.1 mg of **22** in 1.5 ml of MeOH was hydrogenated at atmospheric pressure and room temperature to give, after collection from gas chromatography column C operated at 95°, *cis*-bicyclo[5.2.0]-nonane identical with that from the hydrogenation of **20** and with that produced by Allinger, *et al.*[39]

Hydrogenation of Bicyclo[3.2.2]nonatriene (21). A solution of 4.2 mg of **21** in 2.5 ml of MeOH was hydrogenated at atmospheric pressure and room temperature over platinum oxide. After absorption of 92% of the theoretical amount of hydrogen, uptake ceased. Isolation by gas chromatography on column C operated at 90° gave bicyclo[3.2.2]nonane (mp 157–158° lit.[64] 159°).

Hydrogenation of Bicyclo[3.2.2]non-6-en-2-one (23). Bicyclo-[3.2.2]nonan-2-one Semicarbazone. A solution of 46.1 mg of **23** in 6 ml of MeOH was hydrogenated at atmospheric pressure and room temperature over platinum oxide. After 114% of the theoretical amount of hydrogen had been absorbed uptake ceased. The filtered solution was used directly for the formation of the semicarbazone (mp 187–190° dec).

Bicyclo[3.2.2]nonane. A mixture of 25 mg of bicyclo[3.2.2]-nonan-2-one semicarbazone and 45 mg of $NaOCH_3$ in 0.5 ml of EtOH was sealed under nitrogen in a Pyrex bomb and heated at 195° for 12 hr. The bomb was cooled, opened, and 2 ml of H_2O added. The solution was extracted with 10×0.2 ml of pentane. Gas chromatography of the dried pentane solution gave bicyclo-[3.2.2]nonane identical with that produced above.

Pyrolysis of Bicyclo[5.2.0]nona-2,4,8-triene (20). A flowing system, consisting of an 18-cm Pyrex tube heated over 5 in. of its length to 360° and fitted with a nitrogen inlet and a trap at the exit, was used to pyrolyze 7.2 mg of **20.** Nitrogen flowing at the rate of 60 ml/min was allowed to pass over the liquid **20** thus slowly passing it through the hot tube and into the trap. Analysis by gas chromatography on column A operated at 100° showed only *cis*-8,9-dihydroindene.

Pyrolysis of Bicyclo[4.2.1]nonatriene (19). In the above flowing system 10 mg of **19** was pyrolyzed in exactly the same fashion. Infrared analysis of the single product showed it to be recovered **19.**

Photolysis of Bicyclo[4.2.2]deca-2,4,7,9-tetraene (8). A solution of 6.5 mg of **8** in 0.3 ml of pentane was irradiated through Pyrex at room temperature with a Hanovia 450-W medium-pressure mercury arc. After 23 min, analysis and collection of the products gave 4 mg of recovered **8** and 1.2 mg of **1.**

Photolysis of Bullvalene (1). A solution of 330 mg of **1** in 75 ml of ether was irradiated through a Vycor shield with a 450-W Hanovia medium-pressure mercury arc. Analysis on gas-chromatography column A at 100° revealed five products: Nenitzescu's hydrocarbon (**32**), tricyclo[5.3.0.0^{4,8}]deca-3,7,9-triene (**33**), tetracyclo[4.4.0.0^{2,8}0^{5,7}]deca-3,9-diene (**34**), the pentacyclic hydrocarbon **35**, and bicyclo[4.2.2]deca-2,4,7,9-tetraene (**8**). Of these **34** and **35** are new; precise mass measurement (**34**) calcd for $C_{10}H_{10}$: 130.078247. Found: 130.078296.

Anal. (**35**) Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.02; H, 7.81

Pyrolysis of Tricyclo[5.3.0.0^{4,8}]deca-3,7,9-triene (33). In the flowing system described previously 10 mg of **33** were pyrolyzed at 280°. Analysis and collection on gas-chromatographic column C operated at 110° gave *cis*-9,10-dihydronaphthalene (**6**, 50%) and starting material (50%).

Pyrolysis of Tetracyclo[4.4.0.0^{2,8}0^{5,7}]deca-3,9-diene (34). A solution of 20 mg of **34** in CCl_4 was heated at 130° for 20 min. Analysis by nmr revealed conversion to a mixture of 50% *cis*-9,10-dihydronaphthalene, 35% starting material, and 15% naphthalene.

---

(64) K. Alder, S. Hartung, and G. Hausmann, *Chem. Ber.*, **89**, 1972 (1956).

The Claisen Rearrangement of 3,4-Dihydro-2H-pyranylethylenes. A New Method for the Synthesis of Cyclohexenes[1]

G. Büchi and J. E. Powell, Jr.[2]

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

Received September 9, 1969

Abstract: The Claisen rearrangement of 3,4-dihydro-2H-pyranylethylenes provides a useful method for the preparation of substituted cyclohexenes. It complements the method of Diels and Alder by allowing the structurally specific synthesis of cyclohexenes often not available by the latter method. The ease of rearrangement is critically dependent upon the geometry of bulky substituents attached to the terminal carbon atom of the aliphatic double bond. The thermolysis of *trans*-olefins proceeds rapidly and efficiently but the rearrangement of *cis*-olefins is only of limited preparative value.

Of the various methods available for the synthesis of cyclohexenes, that associated with the names of Diels and Alder is perhaps the most versatile.[3] Condensation of dienes with dienophiles is characterized by high stereospecificity,[4] but the structural specificity is less pronounced and the combination of unsym-

---

(1) A preliminary communication appeared in *J. Amer. Chem. Soc.*, **89**, 4559 (1967).

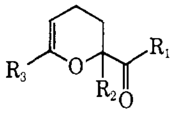
(2) National Institutes of Health Predoctoral Fellow, 1967–1969.

(3) A. S. Onishenko, "Diene Synthesis," Daniel Davey and Co., Inc., New York, N. Y., 1964 (translated from Russian).

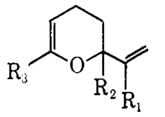
(4) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

metrically substituted components often leads to mixtures of isomeric adducts.[5] Addition of α,β-unsaturated carbonyl compounds to dienes results in the formation of γ,δ-unsaturated adducts which in principle should be available also by Claisen rearrangement of appropriate allyl vinyl ethers.

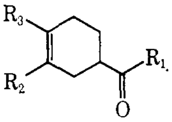
In this paper we describe a structurally selective method for the preparation of certain cyclohexenes by thermal reorganization of 3,4-dihydro-2H-pyranylethylenes. The first substance studied experimentally was the olefin **2**, readily available from acrolein dimer (**1**) by modified Wittig condensation.[6] Pyrolysis in hexane solution in a flow system afforded the known aldehyde **3**.[3] Rearrangement of the diene **5**, prepared from the dimer of methyl vinyl ketone (**4**) under the same conditions or in a sealed tube without added solvent, gave the ketone **6**[7] uncontaminated by its isomer **7**. The thermal rearrangement of the vinyl ether **5** to the ketone **6** is of interest for two reasons. First, it demonstrates how the new method can serve in the exclusive preparation of a substance which is the minor structural component of a Diels–Alder reaction. It should be recalled that condensation of methyl vinyl ketone with isoprene gives a mixture of adducts containing 29% of **6** and 71% of its isomer **7**.[8] Second, this finding demonstrates that the overall change is not the result of a reverse Diels–Alder reaction to isoprene and methyl vinyl ketone followed by recombination of these cleavage products.



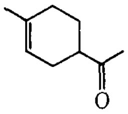
1, $R_1 = R_2 = R_3 = H$
4, $R_1 = R_3 = CH_3$; $R_2 = H$
8, $R_1 = R_3 = H$; $R_2 = CH_3$



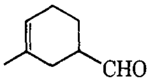
2, $R_1 = R_2 = R_3 = H$
5, $R_1 = R_3 = CH_3$; $R_2 = H$
9, $R_1 = R_3 = H$; $R_2 = CH_3$



3, $R_1 = R_2 = R_3 = H$
6, $R_1 = R_2 = CH_3$; $R_3 = H$
10, $R_1 = R_2 = H$; $R_3 = CH_3$



7



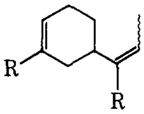
11

To study the effect of a nuclear substituent on the Claisen rearrangement the diene **9** was prepared. The *t*-butylimine of acrolein dimer (**1**) was transformed to the aldehyde **8**[9] by consecutive treatments with ethylmagnesium bromide, methyl iodide, and aqueous acetic acid.[10] A Wittig olefin synthesis again served in the transformation of the aldehyde **8** to the olefin **9**. Pyrolysis of the latter afforded the aldehyde **10**. In contrast, combination of isoprene with acrolein produces a mixture of adducts containing 85% of the 1,4-disubstituted cyclohexene **10** and 15% of its isomer **11**.[11]

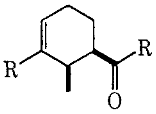
From the successful isomerization of the diene **5** to the ketone **6** we already knew that a substituent on the nonterminal carbon atom of the allylic double bond in dihydropyranylethylenes did not interfere with the Claisen rearrangement. What would be the effect of a terminal substituent? Wittig condensation of ethylidenetriphenylphosphorane with acrolein dimer gave a mixture of olefins which in agreement with other work[12] contained mostly the *cis*-isomer **12**. Heating it furnished, in addition to polymeric material, less than 8% of an equilibrium mixture of the *cis*-aldehyde **13** and the *trans*-epimer **14**. This finding indicates that dihydropyranylethylenes with *cis*-oriented alkyl substituents on the aliphatic double bond probably do not undergo the Claisen rearrangement. The small amounts of rearranged products observed may well have originated from a minor portion of *trans*-olefin present in the starting material.

In view of this situation it became of interest to study the thermal rearrangement of the *cis*-olefin **12** in the presence of olefin isomerization catalysts. Addition of diphenyl disulfide[13] increased the yield of rearrangement products **13** and **14** to 22% but also triggered the production of a by-product identified as octa-4,6-dienal.

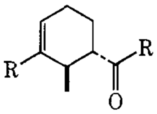
Pyrolysis of a mixture of stereoisomeric olefins **15** produced the epimeric ketones **16** and **17**. The configurations of the two epimers were assigned as follows. Exposure of either ketone to potassium *t*-butoxide in *t*-butyl alcohol led to an equilibrium mixture containing 70% of what is assumed to be the more stable *trans*-epimer **17** and 30% of the *cis*-epimer **16**.



12, R = H
15, $R = CH_3$



13, R = H
16, $R = CH_3$



14, R = H
17, $R = CH_3$

The effect of electron-withdrawing groups conjugated with the allylic double bond was studied next. Condensation[14] of methyl dimethylphosphonoacetate with acrolein dimer (**1**) gave a mixture of α,β-unsaturated esters containing 82% of *trans*-**18** and 18% of *cis*-isomer **19**. Combination of the same ylid with the dimer of methyl vinyl ketone (**4**) resulted in a 2:1 mixture of the *trans*-ester **23** and its stereoisomer **24**.[15] Thermolysis of the *trans*-ester **18** gave a mixture of products containing the *cis*-aldehyde **20** and the α,β-unsaturated ester **22**. Similarly isomerization of the *trans*-ester **23** was rapid at 230° and afforded a mixture of rearranged products consisting of *cis*-**25** and *trans*-**26** epimers. As anticipated, the rearrangement of the two *cis*-esters **19** and **24** required more drastic conditions. Thermolysis of the *cis*-olefin **19** gave a low yield of a mixture of the three rearrangement products **20**, **21**, and **22**. Similarly, heating the *cis*-olefin **24**

---

(5) J. Sauer, *Angew. Chem.*, **79**, 76 (1967), and references cited therein.

(6) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

(7) For the transformation of this ketone to *m*-menthanes see G. Ohloff and W. Giersch, *Helv. Chim. Acta*, **51**, 1328 (1968).

(8) E. F. Lutz and G. M. Bailey, *J. Amer. Chem. Soc.*, **86**, 3899 (1964).

(9) Previously prepared in low yield by condensation of acrolein with methacrolein: R. R. Whetstone, U. S. Patent No. 2,479,283 (1949); *Chem. Abstr.*, **44**, 667h (1950).

(10) G. Stork and S. R. Dowd, *J. Amer. Chem. Soc.*, **85**, 2179 (1963).

(11) (a) K. Alder and W. Vogt, *Ann.*, **564**, 109 (1949); (b) I. N. Nazarov, G. P. Kugatowa, and S. A. Laumenskas, *Zh. Obshch. Khim.*, **27**, 2450 (1957).

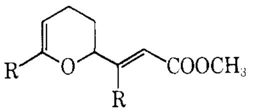
(12) L. D. Bergelson, L. I. Barsukov, and M. M. Shemyakin, *Tetrahedron*, **23**, 2709 (1967), and earlier references cited.

(13) C. Moussebois and J. Dale, *J. Chem. Soc., C*, 260 (1966); C. Walling and W. Helmreich, *J. Amer. Chem. Soc.*, **81**, 1144 (1959).

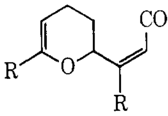
(14) W. S. Wadsworth and W. D. Emmons, *ibid.*, **83**, 1733 (1961); L. Horner, H. Hoffmann, W. Klink, H. Ertel, and V. G. Toscano, *Ber.*, **95**, 581 (1962).

(15) A. Maercker, *Org. Reactions*, **14**, 270 (1965), and H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **26**, 4278 (1961).

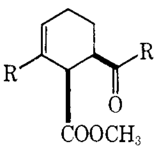
afforded a mixture of the epimeric ketones **26** and **25**. We have followed the rearrangement of the two *cis*-olefins **19** and **24** by gas chromatographic analysis. The first products formed were the two *trans*-epimers **21** and **26** which only subsequently isomerized partly to the corresponding *cis*-epimers **20** and **25**. These experiments demonstrate that the two *cis*-olefins **19** and **24** containing a terminal substituent with trigonal geometry do indeed undergo the Claisen rearrangement. The rates however are low and isomerization is accompanied by much polymerization. As predicted an 83:17 mixture of *trans*- and *cis*-α,β-unsaturated esters **27** rearranged smoothly to an aldehyde to which we have assigned the *cis*-geometry **28** because it is thermodynamically less stable than its epimer **29**.



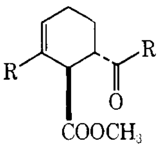
18, R = H
23, R = CH_3



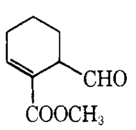
19, R = H
24, R = CH_3



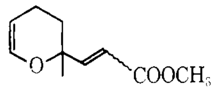
20, R = H
25, R = CH_3



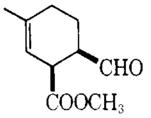
21, R = H
26, R = CH_3



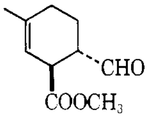
22



27

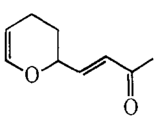


28

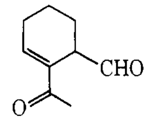


29

Also, the α,β-unsaturated ketone **30**, prepared from the aldehyde **1** and the acetonylphosphonate **32**,[16] was thermally labile. The major product formed was not the β,γ-unsaturated ketone but its more stable conjugated isomer **31**. Finally we investigated the Claisen rearrangement of the triene **33** and the tetraene **35**. The former, obtained as a mixture of *cis–trans* isomers by condensation of methacrolein dimer with allylidenetriphenylphosphorane, on thermolysis afforded a mixture of stereoisomeric aldehydes **34** which we were not able to separate by vapor phase chromatography. The tetraene **35**, prepared from the ketone **30** and 4-methyl-3-pentenyltriphenylphosphonium bromide, on heating rearranged to the aldehyde **36** which is of some interest as a potential intermediate in the synthesis of the antibiotic fumagillin (**37**).[17]



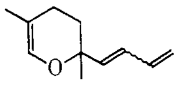
30



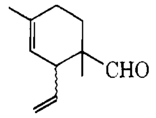
31

$CH_3COCH_2PO(OC_2H_5)_2$

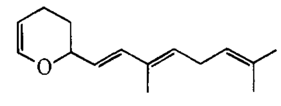
32



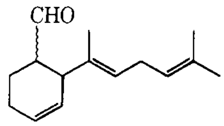
33



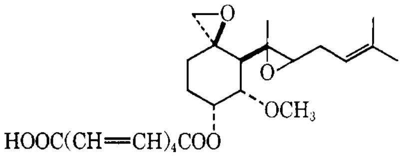
34



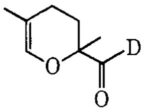
35



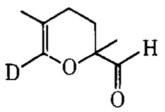
36



37

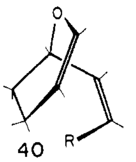


38

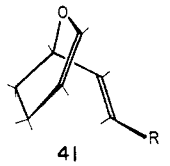


39

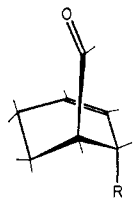
Studies on the mechanism of the aliphatic Claisen rearrangement have shown that a chair-like transition state is favored over a boat-like transition state[18] and a theory explaining this phenomenon has been presented.[19] However, molecular models clearly show that the Claisen rearrangement of the dihydropyranylethylenes discussed in this paper must proceed through a boat-like transition state. Such a transition state conformation has previously been invoked to rationalize the thermal interconversion of the two aldehydes **38** and **39**,[20] and it was in fact this finding which led us to study the rearrangement of the corresponding olefins. In agreement with our findings rearrangement of a *trans*-olefin **41** by a boat-like transition state in a stereospecific manner[21] leads to a 1,2-*cis*-disubstituted cyclohexene **43** while the corresponding *cis*-olefin **40** affords the *trans*-epimer **42**. The three-dimensional representation of the reactant **40** clearly shows how a *cis*-oriented substituent R retards the rate of rearrangement by sterically interfering with two vicinal hydrogen atoms of the dihydropyran ring.



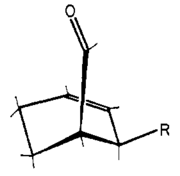
40



41



42



43

---

(16) Prepared by condensation of diethyl methylphosphonate with ethyl acetate as suggested by E. J. Corey and G. T. Kwiatkowski, *J. Amer. Chem. Soc.*, **88**, 5654 (1966). See also H. Takahashi, K. Fujiwara, and M. Ohta, *Bull. Chem. Soc. Jap.*, **35**, 1498 (1962).

(17) N. J. McCorkindale and J. G. Sime, *Proc. Chem. Soc.*, 331 (1961); D. S. Tarbell and J. R. Turner, *Proc. Natl. Acad. Sci. U. S.*, **48**, 733 (1962).

(18) P. Vittorelli, T. Winkler, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **51**, 1457 (1968); A. W. Burgstahler and I. C. Norden, *J. Amer. Chem. Soc.*, **83**, 198 (1961).

(19) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 4389 (1965); R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(20) R. P. Lutz and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 2198 (1961).

(21) R. K. Hill and A. G. Edwards, *Tetrahedron Lett.*, 3239 (1964).

Experimental Section

Flow-system pyrolyses were performed in the following manner. The material was introduced through a pressure-equalizing dropping funnel into a Pyrex tube packed with 17.5 cm of Pyrex helices and heated over this distance by an electric furnace. Nitrogen was used as a carrier gas at a flow rate of 30 bubbles/min in conjunction with a material drop rate of 20 drops/min. The temperature recorded is that measured by a thermocouple taped to the exterior, middle portion of the pyrolysis tube. The pyrolyzed material was collected in a flask cooled in an ice–salt water bath. Both the tube and the packing were washed with concentrated ammonium hydroxide solution before use.

Sealed tube thermolyses were performed in base-washed, heavy-walled Pyrex tubes heated in an electric bomb furnace. The temperature was measured by a thermocouple taped to the tube's exterior. Reaction times of the thermolyses do not include the period required to reach the recorded temperature.

Melting points were determined on a hot-stage microscope and are uncorrected, as are boiling points. Routinely, reactions and product mixtures were monitored by vapor phase chromatography (vpc) on a Varian-Aerograph A-700 instrument. Infrared (ir) spectra were measured on Perkin-Elmer 237 and 237-B spectrophotometers. Ultraviolet (uv) spectra were recorded on a Cary Model 14 instrument. Nuclear magnetic resonance (nmr) spectra were obtained with a Varian A-60 spectrometer, and peak positions are given in parts per million downfield from tetramethylsilane as an internal standard. The abbreviations s, d, t, q, and m refer to singlet, doublet, triplet, quartet, and multiplet; the coupling constant (J) is measured in hertz.

Acrolein Dimer (1). The acrolein dimer used was either redistilled commercial material (City Chemical Corp. of Union Carbide Corp.[22]) or material synthesized from acrolein as described.[23] The pure material possessed the following properties: bp 49–51° (19 mm) (lit.[23] bp 50–51° (17 mm)); semicarbazone mp 120–121° (lit.[24] mp 123°); nmr (CCl_4) δ 9.55 (1 H, s), 6.43 (1 H, d of t, J = 6.5, 1), 4.71 (1, H, m), 4.20 (1 H, m), and 1.98 (4 H, m).

2-Vinyl-3,4-dihydro-2H-pyran (2). The modified Wittig procedure[6] was employed. Sodium hydride (4.53 g; 0.10 mol of a 53% mineral oil dispersion) was placed into a 500-ml, three-necked flask. This material was washed by decantation with three 50-ml portions of pentane. The flask was then fitted with two rubber septums and a reflux condenser topped with a two-way stopcock attached to nitrogen and the water aspirator. The remaining pentane was removed by successively evacuating and filling the flask with nitrogen. Next, while under vacuum, dry dimethyl sulfoxide (50 ml, DMSO) was added by syringe to the sodium hydride powder. The mixture was heated at 75° and stirred magnetically until the hydrogen evolution ceased (~1 hr). Then, under a nitrogen atmosphere, a solution of 35.7 g (0.10 mol) of dry triphenylmethylphosphonium bromide in 100 ml of warm DMSO was added with stirring and ice–water cooling to the dimethylsulfinyl carbanion solution. The resultant greenish red solution was stirred for 15 min at room temperature before 11.2 g (0.10 mol) of freshly distilled acrolein dimer (1) was added by syringe. After an immediate color change, stirring was continued for 1 hr at room temperature.

The reaction solution was diluted with cold water (300 ml), and the solids which formed were removed by suction filtration and washed with pentane. The aqueous phase of the filtrate was extracted with pentane (3 × 100 ml) and the combined organic layers were washed with 1:1 DMSO–H_2O (100 ml), dried, and concentrated *in vacuo* to give 8.44 g of a colorless liquid. Short-path distillation gave 3.49 g (32%)[25] of olefin **2**: bp 59–60.5° (25 mm); nmr (CCl_4) δ 6.28 (1 H, d of t, J = 6.5, 1.0), 5.84 (1 H, d of d of d, J = 18, 10, 5), 5.40–4.85 (2 H, m), 4.56 (1 H, m), 4.22 (1 H, m), and 2.30 – 1.30 (4 H, m).

Anal. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.40; H, 9.40.

3-Cyclohexene-1-carboxaldehyde (3). A solution of 1.247 g (11.33 mmol) of 2-vinyl-3,4-dihydro-2H-pyran (**2**) in hexane (20 ml) was pyrolyzed at 410°. Evaporation of the solution *in vacuo* gave 905 mg of yellow liquid which was distilled to provide 861 mg (68%) of cyclohexene **3** as a colorless liquid: bp 79–80° (16 mm) (lit.[26] bp 58–58.5° (20 mm)); semicarbazone mp 154–155° (lit.[26] mp 153.5–154.5°); nmr (CCl_4) δ 9.47 (1 H, s), 5.58 (2 H, s), and 2.75–1.12 (7 H, m).

2-Acetyl-6-methyl-3,4-dihydro-2H-pyran (Methyl Vinyl Ketone Dimer) (4). As described in the literature[27] methyl vinyl ketone (267 g, 3.8 mol) was dimerized in an autoclave at 145° for 22 hr to give after vacuum distillation 148.5 g (56%) of **4** as a colorless liquid: bp 66–73° (13 mm) (lit.[27] bp 68–69° (13 mm)); nmr (CCl_4) δ 4.46 (1 H, m), 4.13 (1 H, m), 2.13 (3 H, s), and 1.88 and 1.76 (7 H, m with two prominent peaks).

2-(2-Propenyl)-6-methyl-3,4-dihydro-2H-pyran (5). This material was prepared as described for **2** and obtained in 77% yield as a colorless liquid homogeneous on vpc:[28a] bp 66.5–69.5° (17 mm); nmr (CCl_4) δ 4.86 (1 H, broadened s), 4.72 (1 H, broadened s), 4.30 (1 H, broadened s), 4.06 (1 H, m), and 2.42–1.40 (10 H, m with prominent broadened singlet at 1.68 (6 H)).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.99; H, 10.51.

1-Acetyl-3-methyl-3-cyclohexene (6). (a) Flow-System Pyrolysis. A solution of olefin **5** in hexane was pyrolyzed at 425°. Concentration *in vacuo* followed by distillation gave 75% of ketone **6**, a colorless liquid homogeneous on vpc:[28a] bp 80–83° (9.5 mm); semicarbazone (89%) mp 170–172.5° (lit.[11a] mp 172–175°); ir (CCl_4) 1715 cm^{-1}; nmr (CCl_4) δ 5.26 (1 H, broadened s), 2.78–1.18 (13 H, m with strong peaks at 2.06 and 1.62, each approximately 3 H).

(b) Sealed Tube Thermolysis. A sealed glass tube containing **5** was heated for 25 min at 240°. Distillation of the reaction product gave 73% of a colorless liquid, bp 71–75° (7 mm), shown to be 89% **6**, 2% **5**, and 9% unknown component by vpc.[28a]

(c) Comparison of Ketones 6 and 7. The comparison compound **7** was prepared from isoprene and methyl vinyl ketone in the presence of stannic chloride as described in the literature.[8] This procedure has been shown to yield a mixture of 93% **7** and 7% **6**. The "*para*"-isomer **7** and the "*meta*"-isomer **6** were indistinguishable by ir, tlc, and vpc.[29] However, these two substances were differentiated by field-expanded nmr studies. At a field width of 500 Hz, **7**, **6**, and a 50:50 mixture of the two gave superimposable nmr spectra. Yet, when the region encompassing the CH_3CO signal at δ 2.06 was expanded to a field width of 50 Hz, two peaks of roughly equal intensity separated by 0.75 Hz appeared in the sample composed of the 50:50 mixture. The two samples containing **7** from Diels–Alder condensation and pure **6** from rearrangement of **5** showed only singlets under this instrument setting. Thus **6** appears to be essentially pure and free of the isomer **7**. Furthermore, the semicarbazone prepared from **7** [(92%), mp 153–154° (lit. mp 149°,[11a] 150–151°,[30a] 147–149°[30b])] when mixed with the semicarbazone of **6** (mp 170–172.5°) had a depressed melting point of 144–153°.

***t*-Butylimine of Acrolein Dimer (1).** A solution of 89.6 g (0.8 mol) of acrolein dimer (**1**) in 90 ml of absolute ethanol was added dropwise to a solution of 70.5 g (0.96 mol) of *t*-butylamine in 90 ml of absolute ethanol. The addition, which required about 1 hr, was performed under a nitrogen atmosphere and with water-bath cooling to maintain a reaction temperature of 25°. The solution was stirred further for 1 hr at 25°. Concentration *in vacuo* left 130.6 g of liquid. Because of serious frothing the crude reaction product was flash distilled in a Büchi rotatory evaporator to give 114.0 g (86%) of pale yellow liquid of >99% purity by vpc.[28c] Vacuum distillation of a small sample gave the pure imine: bp 63.5–65° (7 mm); ir (CCl_4) 1670, 1650 cm^{-1}; nmr (CCl_4) δ 7.55 (1 H, d, J = 3.4), 6.32 (1 H, d of t, J = 6, 1.5), 4.60 (1 H, m), 4.28 (1 H, m), 1.92 (4 H, m), and 1.10 (9 H, s).

---

[22] We gratefully acknowledge a generous gift of acrolein dimer from Union Carbide Corporation.

[23] V. V. Fedorova, G. P. Pavlov, and I. D. Sinovich, *Neftekhimiya*, **3** (2), 259 (1963); *Chem. Abstr.*, **59**, 7361h (1963).

[24] S. M. Sherlin, A. Y. Berlin, T. A. Serebrinnikova, and F. E. Rabinovick, *J. Gen. Chem. USSR*, **8**, 22 (1938); *Chem. Abstr.*, **32**, 5398^2 (1938).

[25] No efforts were made to improve this yield.

[26] O. Diels and K. Alder, *Ann.*, **460**, 121 (1928).

[27] K. Alder, H. Offermanns, and E. Ruder, *Chem. Ber.*, **74**, 905 (1941).

[28] The vpc columns employed were: (a) 30% Carbowax 20 M on Chromosorb P, 10 ft; (b) 10% Carbowax 20 M on Chromosorb W, 12 ft; (c) 5% SE-30 on Chromosorb P, 9 ft; (d) 25% Carbowax 20 M on Gas Chrom P, 8 ft; (e) 10% Carbowax 20 M on Anakrom ABS, 4 ft; (f) 10% Carbowax 20 M on Chromosorb P, 12 ft.

[29] Isomers **6** and **7** have been separated on a 200-ft capillary vpc column.[8]

[30] (a) A. A. Petrov and N. P. Sapov, *Zh. Obshch. Khim.*, **22**, 591 (1952); *Chem. Abstr.*, **47**, 2735h (1953); (b) A. Manjarrez, J. Rios, and A. Guzman, *Tetrahedron*, **20**, 333 (1964).

Methylation of Acrolein Dimer *t*-Butylimine.[10] To 10 ml of dry tetrahydrofuran (THF) was added 8.40 ml (0.0252 mol) of ethylmagnesium bromide as a 3 *M* solution in diethyl ether. Then with stirring a solution of 4.18 g (0.025 mol) of acrolein dimer *t*-butylimine in 15 ml of dry THF was added. An exothermic reaction ensued and the reaction mixture was heated until the evolution of gas ceased ($\sim$20 min). After cooling in an ice–water bath 3.90 g (0.027 mol) of methyl iodide was added dropwise. The reaction mixture was allowed to stand at room temperature for 20 hr under nitrogen and then diluted with an equal volume of water and extracted with ether. The combined extracts were washed with water and saturated salt solution, dried ($MgSO_4$), and concentrated *in vacuo* to give 4.51 g of an orange liquid. Distillation gave 2.98 g (70%) of pure alkylated imine as a single component on vpc:[28c] bp 63–66° (7 mm); ir (CCl_4) 1670, 1650 cm^{-1}; nmr (CCl_4) δ 7.54 (1 H, s), 6.32 (1 H, d of t, J = 6.5, 1), 4.62 (1 H, m), 1.85 (4 H, m), 1.24 (3 H, s), and 1.14 (9 H, s).

2-Methyl-3,4-dihydro-2H-pyran-2-carboxaldehyde (8). To a cold solution of 6.00 g (0.10 mol) of glacial acetic acid in 150 ml of water was added, with stirring and ice–water bath cooling, 18.1 g (0.10 mol) of methylated acrolein dimer *t*-butylimine. Stirring was continued under nitrogen at 5° for 15 min, and then the reaction mixture was saturated with sodium chloride and extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution, water, and saturated salt solution, dried ($MgSO_4$), and concentrated *in vacuo* to give 10.6 g of pale yellow liquid which showed only one component on vpc.[28c] Combination with identical material (total 44.6 g) and distillation gave 39.6 g (75%) of pure aldehyde **8** as a colorless liquid: bp 59.5–60° (23 mm); semicarbazone mp 145.5–147° (lit.[9] bp 84.4–85.5° (90 mm), semicarbazone mp 144.5°); ir (CCl_4) 1740 cm^{-1}; nmr (CCl_4) δ 9.60 (1 H, unsymmetrical d[31]), 6.48 (1 H, d of t, J = 6, 1.5), 4.72 (1 H, m), 1.88 (4 H, m), and 1.24 (3 H, s).

Anal. Calcd for $C_7H_{10}O$: C, 66.64; H, 7.99. Found: C, 66.75; H, 8.15.

2-Methyl-2-vinyl-3,4-dihydro-2H-pyran (9). Prepared as described for **2** this substance was obtained in 20% yield[26] as a yellow liquid 98% pure by vpc:[28a] bp 44–45.5° (18 mm); nmr (CCl_4) δ 6.25 (1 H, d of t, J = 6.5, 1.5), 5.78 (1 H, d of d, J = 17.5, 10.0), 5.30–4.85 (2 H, AB portion of ABC pattern), 4.53 (1 H, d of t, J = 6.5, 4.0), 2.10–1.55 (4 H, m), and 1.25 (3 H, s).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.08; H, 9.77.

1-Methyl-1-cyclohexene-4-carboxaldehyde (10). Pyrolysis of **9** in hexane at 400° gave 71% of aldehyde **10** as a colorless liquid, >99% pure by vpc:[28a] bp 72–72.5° (8 mm); semicarbazone (87%) mp 162–163.5° (white plates from EtOH with correct analysis, see below) (lit. bp 73–75° (20 mm),[11b] semicarbazone mp 141–141.5°,[11b] 144°[11a]); ir (CCl_4) 1730 cm^{-1}; nmr (CCl_4) δ 9.74 (1 H, d, J = 0.7), 5.36 (1 H, m), 2.55–1.50 (10 H, m with prominent peaks at 2.20, 1.86, and 1.64 ($\sim$3 H)).

Anal. (semicarbazone) Calcd for $C_9H_{15}N_3O$: C, 59.64; H, 8.34; N, 23.19. Found: C, 59.79; H, 8.60; N, 23.26.

***cis*-2-(1-Propenyl)-3,4-dihydro-2H-pyran (12).** This product, prepared in the same manner as **2**, was a colorless liquid pure by vpc:[28a] bp 57–59° (16 mm); nmr (CCl_4) δ 6.16 (1 H, d of t, J = 6.5, 1.5), 5.68–5.10 (2 H, m), 4.68–4.18 (2 H, m), 2.50–1.35 (7 H, multiplet with strong doublet centered at 1.65, J = 5).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.40; H, 9.78.

***cis*- and *trans*-2-Methyl-3-cyclohexene-1-carboxaldehyde (13 and 14). (a) Flow-System Pyrolysis.** A solution of olefin **12** in hexane when pyrolyzed at 430° in a flow system gave 12% of a colorless liquid, bp 46–47° (4 mm), composed of 17% of **12**, 19% of **14**, and 64% of **13**. Isomer **13**, obtained in 94% purity (6% of **14**) by preparative vpc,[28a] possessed the following characteristics: ir (CCl_4) 1730 cm^{-1}; nmr (CCl_4) δ 9.60 (1 H, d, J = 1.0), 5.55 (2 H, m), 2.92–1.40 (6 H, m), 0.98 (3 H, d, J = 6.5); n^{19}D 1.4780 (lit.[32] n^{20}D 1.4722); semicarbazone mp 181.5–183° (lit.[32] mp 190–191°).

Anal. Calcd for $C_9H_{15}NO_3$: C, 59.64; H, 8.34; N, 23.19. Found: C, 59.77; H, 8.65; N, 23.43.

Isomer **14**, obtained 100% pure by preparative vpc,[28a] had ir (CCl_4) 1730 cm^{-1}; nmr (CCl_4) δ 9.50 (1 H, d, J = 1.5), 5.46 (2 H, m), 2.65–1.35 (6 H, m), 1.05 (3 H, d, J = 6.5); n^{19}D 1.4700 (lit.[33] n^{20}D 1.4562); semicarbazone mp 139–140° (lit.[33] mp 138–139°).

Each of the isomers **13** and **14** when treated separately with potassium *t*-butoxide in *t*-butyl alcohol at 25° gave an equilibrium mixture of 86% of **14** and 14% of **13**.

(b) Sealed Tube Thermolysis. A sealed tube pyrolysis of **12** at 230° for 18.5 hr gave 8% of a colorless liquid, vpc analysis[28a] of which showed a mixture of 84% of **14** and 16% of **13**.

Thermolysis of *cis*-2-(1-Propenyl)-3,4-dihydro-2H-pyran (12) with Diphenyl Disulfide. A sealed-glass tube containing a solution of diphenyl disulfide (0.79 g; 3.62 mmol) in olefin **12** (9.00 g; 72.50 mmol) under an argon atmosphere was heated at 225° for 1 hr. Distillation provided 2.54 g of a colorless liquid, bp 43–65° (0.4 mm). Analysis by vpc[28a] revealed that the product mixture consisted of 20% of **13**, 57% of **14**, and 23% of a by-product identified as octa-4,6-dienal. When collected by preparative vpc[28a] this by-product exhibited the following spectral features: n^{19}D 1.4990 (lit.[34a] n^{25}D 1.4957); ir[34b] (CCl_4) 3010, 2910, 2810, 2710, 1735, 1440, 1410, 1040, 985, 945, and 920 cm^{-1}; uv max (95% ethanol) 228 nm (ϵ 24,600); nmr[34b] (CCl_4) δ 9.54 (1 H, t, J = 1), 6.25–5.00 (4 H, m), 2.44 and 2.40 (4 H, two overlapping s), and 1.71 (3 H, d, J = 5.5).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.06; H, 9.56.

2-(2-Buten-2-yl)-6-methyl-3,4-dihydro-2H-pyran (15). This olefin prepared in 87% yield as described for **2** was a colorless liquid composed of two (9:1) overlapping components on vpc:[28a] bp 58.5–60.5° (5.5 mm); nmr (CCl_4) δ 5.21 (1 H, m), 4.62–4.18 (2 H, m), and 2.50–1.40 (13 H, m with a very strong peak at 1.62 and a weaker one at 1.52).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.27; H, 10.72.

***cis*- and *trans*-1-Acetyl-2,3-dimethyl-3-cyclohexene (16 and 17). (a) Flow-System Pyrolysis.** Pyrolysis of **15** in hexane at 460° gave 14% of a liquid, bp 88–93° (10 mm), shown to be a mixture of **16** and **17** in the ratio 55:45 by vpc.[28a] Preparative vpc[28a] gave pure samples of each component, and when equilibrated separately with potassium *t*-butoxide in dry *t*-butyl alcohol at 25°, each gave the same equilibrium mixture of 30% of **16** and 70% of **17**. The *trans*-epimer **17** had nmr (CCl_4) δ 5.42 (1 H, broadened s), 2.70–0.90 (15 H, multiple absorptions with prominent peaks at 2.14 (3 H, s), 1.72 (3 H, s), and 0.98 (3 H, d, J = 7)).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.69; H, 10.73.

The *cis*-isomer **16** exhibited nmr (CCl_4) δ 5.42 (1 H, broadened s), 2.85–0.80 (15 H, multiple absorptions with prominent peaks at 2.12 (3 H, s), 1.75 (3 H, s), and 0.86 (3 H, d, J = 7)).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.69; H, 10.66.

(b) Sealed Tube Thermolysis. A sealed tube thermolysis of olefin **15** under argon at 240° for 2.5 hr gave 32% of a mixture composed of 6% of **15**, 51% of **16**, 38% of **17**, and 4% of several other materials by vpc analysis.[28a]

Methyl *cis*- and *trans*-3-(3,4-Dihydro-2H-pyran-2-yl)acrylate (19 and 18.)[33] The Wadsworth–Emmons procedure[14] was employed. To a slurry of sodium hydride (8.38 g; 0.21 mol of a 60.2% mineral oil dispersion) in dry 1,2-dimethoxyethane (500 ml) in a one-liter three-necked flask, equipped with a dropping funnel, a thermometer, and a mechanical stirrer, was added dropwise methyl dimethylphosphonoacetate[35a] (38.20 g; 0.21 mol). Water bath cooling was used to maintain the reaction temperature below 20°. After complete addition and 0.25 hr of further stirring, acrolein dimer (**1**) (22.40 g; 0.20 mol) was added dropwise at $\leq$20°. Stirring was continued for 1 hr before the reaction mixture was diluted with water (1 l.) and extracted with ether. The combined organic phases were washed with water and saturated salt solution, dried ($MgSO_4$), and concentrated *in vacuo*. Distillation provided 31.04 g (93%) of a colorless liquid, bp 68–82° (0.7 mm), which was by vpc analysis[28d] an 82:18 mixture of isomers **18** and **19** easily separated on a 40-cm spinning-band column. In this manner 4.07 g (12%) of the

---

(31) This anomaly has been discussed by Roberts.[20]

(32) D. Motskus and P. Kaikaris, *Liet. TSR Mokslu Akad. Darb., Ser. B*, (3), 95 (1964); *Chem. Abstr.*, **62**, 2717e (1965).

(33) J. Cologne and P. Jeltsch, *Bull. Soc. Chim. Fr.*, 1292 (1963).

(34) (a) M. Jacobson, *J. Amer. Chem. Soc.*, **77**, 2461 (1955); data for the pure *trans,trans* isomer; (b) these spectral data agree closely with those reported for this compound obtained in another unusual manner: W. G. Dauben and G. W. Schaffer, *Tetrahedron Lett.*, 4415 (1967).

(35) (a) This reagent was prepared according to the procedure[35b] used in the preparation of methyl diethylphosphonacetate. Formed in >60% yield, the reagent was obtained as a colorless oil: bp 95–96° (1.3 mm), nmr (CCl_4) δ 3.83 and 3.64 (6 H, two unequally populated s), 3.72 (3 H, s), 2.94 (2 H, d, J = 21.5); (b) H. O. House, V. K. Jones, and G. A. Frank, *J. Org. Chem.*, **29**, 3327 (1964).

pure *cis*-isomer **19** was obtained: bp 54–57° (0.65 mm); $n^{27}D$ 1.4790; nmr (CCl_4) δ 6.35 (1 H, d of d, *J* = 11.5, 7.0), 6.31 (1 H, d of t, *J* = 6.5, 1.5), 5.75 (1 H, d of d, *J* = 11.5, 1.5), 5.32 (1 H, m), 4.65 (1 H, m), 3.68 (3 H, s), and 2.2–1.5 (4 H, m).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.22; H, 7.37.

The pure *trans*-isomer **18** (22.76 g; 68%) had bp 65–68° (0.65 mm); $n^{27}D$ 1.4848; nmr (CCl_4) δ 6.90 (1 H, d of d, *J* = 16.0, 4.0), 6.38 (1 H, d of t, *J* = 6.5, 1.5), 5.98 (1 H, d of d, *J* = 16.0, 1.5), 4.65 (1 H, m), 4.45 (1 H, m), 3.72 (3 H, s), and 2.2–1.5 (4 H, m).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 63.88; H, 7.30.

Thermolysis of Methyl *trans*-3-(3,4-Dihydro-2H-pyran-2-yl)-acrylate (18). Thermolysis of **18** under argon at 250° for 10 min in a sealed Pyrex tube gave 87% of product, bp 71–73° (0.36 mm). Analysis by vpc[28e] revealed a mixture of 77% of **20**, 19% of **21**, and 4% of **22**. Analysis of the spectral data[36] for the three components collected separately by vpc and for the original reaction product showed, however, that the reaction mixture was in fact free of *trans*-epimer **21**. The *cis*-isomer **20** clearly epimerized partially under the vpc conditions; the *trans*-isomer **21** was stable under these conditions.

The pure *cis*-epimer **20** had nmr (CCl_4) δ 9.62 (1 H, s), 5.82 (2 H, two overlapping s), 3.64 (3 H, s), 3.42 (1 H, m), 2.55 (1 H, m), and 2.1 (4 H, m).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.06; H, 7.37.

The pure *trans*-epimer **21** showed nmr (CCl_4) δ 9.50 (1 H, s), 5.74 (2 H, overlapping s), 3.66 (3 H, s), 3.40 (1 H, m), 2.88 (1 H, m), and 2.2–1.5 (4 H, m).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.26; H, 7.25.

The conjugated isomer **22** had ir (CCl_4) 1730, 1715, 1645 cm^{-1}; uv max (95% ethanol) 218 nm (ε 8100); nmr (CCl_4) δ 9.64 (1 H, s), 7.20 (1 H, t, *J* = 3.5), 3.74 (3 H, s), 3.40 (1 H, m), 2.4–1.4 (6 H, m).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.08; H, 7.20.

Treatment of pure isomers **20** and **21** separately with methanolic sodium methoxide at 0° produced in each case a mixture of 15% of **20** and 85% of **21**.

Thermolysis of Methyl *cis*-3-(3,4-Dihydro-2H-pyran-2-yl)acrylate (19). The *cis*-α,β-unsaturated ester **19** when heated at 250° for 3 hr in a sealed Pyrex tube gave 18% of product bp 72–82° (0.38 mm). Analysis by vpc[28e] indicated a mixture of 3% of **19**, 14% of **20**, 47% of **21**, 24% of **22**, and 12% of two unknown components.

The course of the rearrangement of **19** at 250° was monitored by vpc;[28e] the results are shown in Table I.

Table I

T, min	Product composition (%)				
	19	20	21	22	Others
10	96	<1	2	0	2
45	74	4	20	0	2
90	43	10	40	3	4
135	20	13	42	19	6
165	10	15	37	34	4

Methyl *cis*- and *trans*-3-(6-Methyl-3,4-dihydro-2H-pyran-2-yl)-crotonate (24 and 23). These compounds were prepared by the method described for **18** and **19** and obtained as a mixture of 63% of **23** and 37% of **24** (by vpc[28b]) separable by spinning-band distillation.

cis-Unsaturated ester **24** had bp 72–74.5° (1.05 mm); uv max (95% ethanol) 214 nm (ε 15,400); nmr (CCl_4) δ 5.60 (1 H, q, *J* = 1.5), 5.45 (1 H, d of d, *J* = 9.5, 3.0), 4.42 (1 H, m), 3.62 (3 H, s), 2.22–1.15 (10 H, multiplet with prominent peaks at 1.92 (3 H, d, *J* = 1.5), and 1.70 (3 H, d, *J* = 1.0)).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.53; H, 8.29.

trans-Unsaturated ester **23** had bp 82–83° (0.93 mm); uv max (95% ethanol) 214 nm (ε 16,800); nmr (CCl_4) δ 5.83 (1 H, q, *J* = 1.5), 4.42 (1 H, m), 4.16 (1 H, broadened d, *J* = 9.5), 3.62 (3 H, s), 2.30–1.30 (10 H, m with prominent peaks at 2.10 (3 H, d, *J* = 1.5), and 1.72 (3 H, broadened s)).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.50; H, 8.26.

Thermolysis of Methyl *trans*-3-(6-Methyl-3,4-dihydro-2H-pyran-2-yl)crotonate (23). A sample of *trans*-α,β-unsaturated ester (**23**) under argon was heated at 230° for 20 min. Analysis by vpc[28b] showed a product composition of 7% of **23**, 88% of **25**, and 5% of **26**. The *cis*-epimer **25** had bp 70–71° (0.18 mm); nmr (CCl_4) δ 5.54 (1 H, broad s), 3.58 (3 H, s), 3.20 (1 H, broad s), 2.64–1.62 (11 H, m with prominent peaks at 2.12 (3 H, s) and 1.74 (3 H, broadened s)).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.63; H, 8.28.

The *trans*-epimer **26** (isolated by preparative vpc[28b]) possessed the following properties: bp 65–66° (0.14 mm); nmr (CCl_4) δ 5.45 (1 H, broad s), 3.66 (3 H, s), 3.42–2.75 (2 H, m), 2.32–1.40 (10 H, m with prominent peaks at 2.14 (3 H, s), and 1.67 (3 H, broadened s)).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.39; H, 8.27.

Treatment of **25** and **26** separately with methanolic sodium methoxide at 0° produced in each case an equilibrium composition of 32% of **25** and 68% of **26**.

Thermolysis of Methyl *cis*-3-(6-Methyl-3,4-dihydro-2H-pyran-2-yl)crotonate (24). A sample of *cis*-α,β-unsaturated ester **24** under argon was heated at 285° for 35 min in a sealed Pyrex tube giving a product whose composition upon vpc analysis[28b] was 3% of **24**, 26% of **25**, and 70% of **26**. The course of the rearrangement of **24** at 285° was monitored by vpc;[28b] the results are given in Table II.

Table II

T, min	Product composition (%)		
	24	25	26
5	40	13	47
15	4	27	69
35	1	28	71

Methyl 3-(2-Methyl-3,4-dihydro-2H-pyran-2-yl)acrylate (27). This product was prepared from the aldehyde **8** and methyl dimethylphosphonoacetate[35a] as described for **18–19**. The ester **27** (77%) was a colorless liquid: bp 86.5–90.5° (3 mm); vpc analysis[28b] indicated that this material was a 83:17 mixture of two components presumed to be the *trans*- and *cis*-geometrical modifications of structure **27**; nmr (CCl_4) δ 6.76 (1 H, d, *J* = 16), 6.26 (1 H, d of t, *J* = 6.5, 1.5), 5.82 (1 H, d, *J* = 16), 4.60 (1 H, m), 3.66 (3 H, s), 1.80 (4 H, m), and 1.32 (3 H, s).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.15; H, 8.04.

Pyrolysis of Methyl 3-(2-Methyl-3,4-dihydro-2H-pyran-2-yl)-acrylate (27). Pyrolysis of a hexane solution of **27** at 410° gave 85% of product, bp 101–103° (2.5 mm). Analysis of this material by vpc[28b] revealed a mixture of 55% of **28** and 45% of **29**. Analysis of the spectral data[37] for these two epimers collected separately by vpc[28b] and the original reaction product showed, however, that the reaction product was in fact essentially free (<10%) of *trans*-epimer **29**. The *cis*-epimer **28** clearly epimerized partially under the vpc conditions; *trans*-isomer **29** was stable under these conditions. Pure *cis*-epimer **28** obtained by preparative vpc:[28b] ir (CCl_4) 1740 cm^{-1}; nmr (CCl_4) δ 9.60 (1 H, s), 5.58 (1 H, m), 3.64 (3 H, s), 3.40 (1 H, broad s), 2.38 (1 H, m), 2.04 (4 H, m), and 1.70 (3 H, m).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 66.17; H, 7.76.

The pure *trans*-stereoisomer **29** showed the following spectral characteristics: nmr (CCl_4) δ 9.65 (1 H, s), 5.45 (1 H, m), 3.68 (3 H, s), 3.40 (1 H, broad s), 2.80 (1 H, m), 2.00 (4 H, m), and 1.70 (3 H, m).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.97; H, 7.76.

When both **28** and **29** were separately treated with methanolic sodium methoxide each generated an equilibrium composition of 21% of **28** and 79% of **29**.

Diethyl Methylphosphonate. The following procedure was adapted from a similar *Organic Syntheses* preparation.[38] Methyl

---

(36) Note particularly the nmr δ values for the methine hydrogen on the carbon α to the carboxaldehyde function: δ 2.55 for **20** and δ 2.88 for **21**. The original reaction product showed no absorption at δ 2.88.

(37) The methine hydrogens on the carbon α to the carboxaldehyde function appear at δ 2.38 in **28** and δ 2.80 in **29**. The original reaction product showed no absorption at δ 2.80.

(38) "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 325.

iodide (500 g; 3.55 mol) was placed in a 2-l. three-necked flask equipped with a dropping funnel and a reflux condenser. The addition funnel was charged with triethyl phosphite (415 g; 2.50 mol), and about 50 ml was introduced into the reaction vessel along with several pieces of porous clay plate. The reaction solution was heated gently with a flame until an exothermic reaction commenced. The remainder of the phosphite was then added at a rate sufficient to maintain vigorous reflux. After addition was complete, the solution was refluxed for 1 hr and then concentrated *in vacuo* to give 390 g of colorless liquid, which was vacuum distilled to afford 370 g (97%) of diethyl methylphosphonate: bp 38–38.5° (1.1 mm); lit.[38] bp 51° (1 mm); > 99% purity by vpc;[28b] nmr (CCl_4) δ 4.04 and 3.90 (4 H, two overlapping q, $J = 7$ for each), 1.34 (3 H, d, $J = 17.5$), and 1.28 (6 H, t, $J = 7$).

Diethyl Acetonylphosphonate (32). A 2-l., three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a drying tube was charged with 500 ml of dry tetrahydrofuran (THF) and cooled to −70°. Then 141 g (0.50 mol) of butyllithium (as a 22.7% solution in hexane) was added and followed by the dropwise introduction of 76.0 g (0.50 mol) of diethyl methylphosphonate. After complete addition the resultant semisolid mass was stirred at −70° for 30 min before 900 ml of ethyl acetate (cooled to −70°) was introduced rapidly. The resultant clear solution was stirred at −70° for 30 min and then allowed to warm slowly to room temperature. The reaction solution was concentrated *in vacuo* to a semisolid mass which was diluted with ethyl acetate and extracted with 10% aqueous acetic acid, saturated sodium bicarbonate solution, and water. The aqueous extracts were made basic and back extracted with ethyl acetate. The combined organic layers were washed with saturated salt solution, dried ($MgSO_4$), and concentrated *in vacuo* to give 76.5 g of liquid which on fractional distillation through a 10-cm Vigreux column provided 53.6 g (56%) of **32**: bp 106–111° (1.8 mm); 98% purity by vpc;[28b] ir (CCl_4) 2980, 2920, 2880, 1715, 1615, 1475, 1430, 1390, 1360, 1255, 1230, 1165, 1115, 1095, 1055, 1025, 975, and 955 cm^{-1}; nmr (CCl_4) δ 4.08 and 3.94 (4 H, two overlapping q, $J = 7$ for each), 2.98 (2 H, d, $J = 22.5$), 2.20 (3 H, s), and 1.28 (6 H, t, $J = 7$).

***trans*-3-Buten-2-one-4-(3,4-dihydro-2H-pyran-2-yl) (30).**[39] A 1-l. three-necked flask fitted with a thermometer, a dropping funnel, an argon inlet, and a magnetic stirring bar was charged with 300 ml of dry 1,2-dimethoxyethane (DME) and cooled to −70°. Then 98.7 g (0.23 mol) of butyllithium solution (15.20% in hexane) was added and followed by the dropwise introduction of a solution of 44.6 g (0.23 mol) of diethyl acetonylphosphonate **32** in DME (100 ml) over 2 hr. After complete addition, stirring was continued at −70° for 15 min before the dropwise addition of 25.8 g (0.23 mol) of acrolein dimer (**1**) in DME (50 ml) over 1 hr. Stirring was continued for an additional 30 min at −70° before the cold solution was poured into 1 l. of water. The phases were separated and the aqueous layer was extracted with ether. The combined organic layers were washed with water and saturated salt solution, dried ($MgSO_4$), and concentrated *in vacuo* to give 47.1 g of liquid. This material was vacuum distilled to yield 20.9 g (69%) of a colorless liquid, bp 69–70° (0.62 mm), which by vpc[28d] appeared to be 92% pure, contaminated with acrolein dimer (**1**) (2%) and an unknown impurity (6%, perhaps the *cis* form of **30**). An analytical sample of **30** showed: uv max (95% ethanol) 218 nm (ϵ 15,000); nmr (CCl_4) δ 6.62 (1 H, d of d, $J = 16, 4$), 6.24 (1 H, d of t, $J = 6.5, 1.5$), 6.08 (1 H, d of d, $J = 16, 1.5$), 4.58 (1 H, m), 4.40 (1 H, m), 2.18 (3 H, s), 1.95 (4 H, m).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.84; H, 7.75. Semicarbazone showed mp 136–137.5°.

Anal. Calcd for $C_{10}H_{15}N_3O_2$: C, 57.40; H, 7.23; N, 20.08. Found: C, 57.53; H, 7.55; N, 20.34.

2-Acetyl-2-cyclohexene-1-carboxaldehyde (31). A sealed Pyrex tube containing the α,β-unsaturated ketone **30** in an argon atmosphere was heated for 4.25 hr at 190–195°. Vacuum distillation gave 0.82 g (33%) of colorless liquid, bp 76–80° (0.4 mm), whose vpc analysis[28f] showed 7% **30**, 72% **31**, and 21% of six other components. Preparative vpc[28f] provided **31** in a state of 90% purity and this material exhibited the following spectral characteristics: ir (CCl_4) 1730, 1675 cm^{-1}; uv max (95% ethanol) 231, 300 nm (ϵ 9600, 440); nmr (CCl_4) δ 9.50 (1 H, d, $J = 1.0$), 6.96 (1 H, d of t, $J = 4.0, 1.5$), 3.35 (1 H, m), 2.40–1.20 (9 H, m with sharp singlet at 2.23 (~3 H)).

Anal. Calcd for $C_{12}H_9O_2$: C, 71.02; H, 7.95. Found: C, 70.81; H, 7.71.

2-(Buta-1,3-dien-1-yl)-2,5-dimethyl-3,4-dihydro-2H-pyran (33). Phenyllithium (0.22 mol; 110 ml of a 2.01 *M* solution in benzene–ether (70:30)) was added dropwise to an ice–water cooled slurry of allyltriphenylphosphonium bromide[40] (84.3 g; 0.22 mol) in 250 ml of benzene, and the resultant dark red mixture was stirred under argon for 1 hr. Employing an argon atmosphere the mixture was filtered and the red solution was transferred to another flask.[41] Then with water bath cooling a solution of methacrolein dimer[42] (28.0 g; 0.20 mol) in 200 ml of benzene was introduced dropwise into the stirred ylid solution. The reaction mixture was stirred overnight at room temperature under argon. The mixture was diluted with 200 ml of water, and the organic layer was separated and concentrated *in vacuo* to a semisolid mass which was mixed with pentane and suction filtered. The pentane filtrate was washed with 50:50 dimethyl sulfoxide–water, water, and saturated salt solution, dried ($MgSO_4$), and concentrated *in vacuo* to give 46.8 g of crude product. Vacuum distillation provided 18.2 g (55%) of triene **33** as a colorless liquid:[43] bp 56–66° (1.7 mm); uv max (95% ethanol) 223 nm (ϵ 17,900); nmr (CCl_4) δ 7.30–6.20 (1 H, m), 6.06 (1 H, q, $J = 1.5$), 5.90–4.90 (4 H, m), 1.80 (4 H, m), 1.52 (3 H, d, $J = 1.5$), and 1.35 and 1.25 (3 H, two s in ratio 4:1).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.31; H, 10.12.

1,4-Dimethyl-2-vinyl-3-cyclohexene-1-carboxaldehyde (34). Pyrolysis of triene **33** in an argon atmosphere for 2.25 hr at 190° gave 60% of a product, bp 52–60° (1.1 mm), containing 96% of **34** by vpc;[28d] nmr (CCl_4) δ 9.52 and 9.42 (1 H, two s in ratio 2:3), 6.10–4.80 (4 H, m), 3.15–2.55 (1 H, very broad s), 2.20–1.40 (7 H, m with prominent broadened s at 1.70 (~3 H)), and 1.05 and 0.90 (3 H, two s in ratio 2:3).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.23; H, 9.72.

4-Methyl-3-pentenyltriphenylphosphonium Bromide. A solution of triphenyl phosphine (205 g; 0.782 mol) and 5-bromo-2-methyl-2-pentene[44] (127.5 g; 0.782 mol) in benzene (180 ml) containing a few seed crystals of the phosphonium salt from a previous run was refluxed for 84 hr. After cooling the crystalline product was collected by suction filtration and washed with ether. Drying *in vacuo* left 310.6 g (94%) of small white crystals, mp 178–184°. Recrystallization of a sample from acetone gave large colorless rhomboids: mp 183–185°; nmr ($CDCl_3$) δ 7.82 (15 H, m), 5.20 (1 H, m), 3.66 (2 H, broad m), 2.38 (2 H, broad m), and 1.58 and 1.44 (6 H, two overlapping s).

2-(2,6-Dimethylocta-2,5,7-trien-8-yl)-3,4-dihydro-2H-pyran (35). A 5-l., three-necked flask fitted with an argon inlet, a mechanical stirrer, and a rubber septum was charged with a mixture of 4-methyl-3-pentenyltriphenylphosphonium bromide (170.0 g; 0.40 mol) and dry ether (3.5 l.) and cooled in an ice–water bath. Then 168 g (0.40 mol) of butyllithium solution (15.22% in hexane) was introduced *via* a cannula so as to maintain a reaction temperature of 5–10°. The orange-red reaction mixture was stirred for 1 hr before the dropwise addition of a solution of ketone **30** (55.4 g; 0.364 mol) in ether (200 ml), maintaining a reaction temperature of 1–2°. After stirring overnight at room temperature the reaction mixture was filtered, and the filtrate was concentrated *in vacuo* to a semisolid mass which was extracted with pentane. The pentane solution was washed with 1:1 dimethyl sulfoxide–water solution (2 × 200 ml), water, and saturated salt solution, dried ($MgSO_4$), and concentrated *in vacuo* to leave 61.0 g of a liquid which was fractionally distilled to give 42.7 g (54%) of tetraene **35** as a colorless liquid: bp 90–93° (0.04 mm); 99% pure by vpc;[28e,45] uv max (95% ethanol), 237 nm (ϵ 28,400); nmr (CCl_4) δ 6.30 (1 H, d of t, $J = 6.5, 1.5$), 6.22 (1 H, d, $J = 16.5$), 5.52 (1 H, d of d, $J = 16.5$,

---

(39) The preparation of this compound *via* aldol condensation between acrolein dimer and acetone is reported. We were unable to duplicate this preparation, and the physical constants for the compound prepared in the present work and those found in this literature report differ drastically: see J. Cologne and P. Jeltsch, *Bull. Soc. Chim. Fr.*, 1262 (1963).

(40) G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954).

(41) Lithium bromide was removed in an attempt to maximize the yield of the *trans*-olefin in the Wittig condensation. See ref 12.

(42) G. N. Koshel and M. I. Farberov, *Chem. Abstr.*, **62**, 3997e (1965).

(43) While vpc[28a,d] showed only a single component, this material is probably a mixture of geometrical isomers (nmr suggests a 4:1 isomer mixture). At a column temperature of 180° in the vpc, partial rearrangement of **33** to **34** took place; at 120° this could be avoided.

(44) M. Julia, S. Julia, and R. Guegan, *Bull. Soc. Chim. Fr.*, 1072 (1960).

(45) The temperature necessary for analysis caused some rearrangement of **35** to **36**.

6.0), 5.50 (1 H, finely split t, $J = 7.5$), 5.08 (1 H, finely split t, $J = 7.5$), 4.58 (1 H, m), 4.30 (1 H, m), 2.78 (2 H, t, $J = 7.5$), and 2.25–1.50 (13 H, complex absorptions with strong, finely split peaks at 1.75–1.65 for approximately 9 H).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.88; H, 10.15.

Thermolysis of Tetraene 35 to Triene 36. Tetraene **35** (19.15 g; 87.80 mmol) under an argon atmosphere was heated in a sealed tube for 2.5 hr at 190°. Fractional distillation gave 12.80 g (67%) of triene **36** as a pale yellow liquid: bp 96–100° (0.03 mm); 99% pure by vpc;[28c,46] nmr (CCl_4) δ 9.65 (1 H, d, $J = 1.5$), 5.85–4.85 (4 H, m), 3.0 (1 H, broad s), 2.68 (2 H, t, $J = 7.5$), and 2.4–1.5 (14 H, m with two finely split singlets at 1.68 and 1.60 in the ratio 1:2 for a total of 9 H).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.51; H, 10.19.

Acknowledgment. This work was generously supported by the National Institutes of Health and by the Hoffmann-La Roche Anniversary Foundation.

[46] A mixture of three stereoisomers in a ratio of 17:72:11.

Stable Carbonium Ions. XCVII.[1a] Protonation of 3-Phenylsydnone, Its Derivatives, and Related Model Compounds

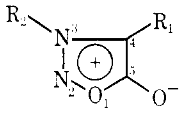
George A. Olah, David P. Kelly,[1b] and Nausicaa Suciu[1c]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

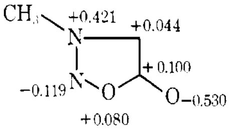
Received October 2, 1969

Abstract: Protonation of the mesoionic 3-phenylsydnone and 1,1-disydnonylethylene in FSO_3H-SbF_5 solution is shown to occur on the carbonyl oxygen atom, by analogy with protonation of regular carbonyl groups. Unlike diphenylmethyl- and triphenylcarbinols, 4,4′-bis(3-phenylsydnonyl)methyl- and phenylcarbinols do not form tertiary carbonium ions in FSO_3H-SbF_5 solution, indicating poor stabilizing ability by the adjacent positively charged sydnonyl rings. 4,4′-Bis(3-phenylsydnonyl) ketone and the corresponding α-diketone protonate on the exocyclic carbonyl oxygen atoms in preference to the sydnone carbonyl oxygens.

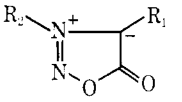
Due to their unique mesoionic character, sydnones have been the subject of continued study since their discovery in 1935.[2] The aromatic 6π-electron system obtained by removal of one π electron onto the exocyclic oxygen atom[3] (I) is unequally distributed around the ring as shown by the relatively high-field nmr absorption of the 4 proton,[4] molecular orbital calculations (II),[5,6] and their behavior as 1,3 dipoles.[7] Both the proton shift and dipolar reactivity can be rationalized in terms of the localized azomethine–imine system III. Recently Roche and Kier used ω-HMO calculations to study the chemical reactions of sydnones.[6] By a comparison between the π-electron energies of the protonated and nonprotonated heteroatomic system, they concluded that protonation of 3-methylsydnone (I, $R_1 = H$, $R_2 = CH_3$) should occur preferentially on the number two nitrogen atom. This conclusion is surprising (even when supported by the observations of a weak N–H stretch in the infrared) in view of previous electron density calculations,[5] which showed a greater negative charge on the exocyclic oxygen atom (II).[8]



I



II



III

We have examined the nmr spectra of 3-phenylsydnone (I, $R_1 = H$, $R_2 = C_6H_5$) and some of its derivatives[9] in super acid solutions in order to clarify the site of protonation and also to study the effect of sydnonyl groups as neighboring substituents in carbonium ions.

Results and Discussion

3-Phenylsydnone. In trifluoroacetic acid solution at −10 to +10°, fine structure appears for the phenyl group absorption, and the sydnone ring methine proton (H_4) is shifted downfield by 0.71 ppm from that in $CDCl_3$ solution (Table I). No separate OH or NH signal was observed due to exchange with the solvent. However, in HSO_3F-SbF_5-SO_2 solution at −60–90°, a one-proton, temperature-dependent signal is observed at δ 10.24, the phenyl protons are slightly shifted, and the sydnone 4-H signal is downfield of the phenyl protons at δ 8.33 (Figure 1). The temperature-dependent signal at δ 10.24 is not an N–H proton since protonation of nitrogen lone pairs in sp^2 orbitals gives rise to signals at around δ 14, which, even at −90°, are generally broad.[10] Both the chemical shift and the temperature dependence of the observed proton indicate that it is of intermediate character between

---

[1] (a) Part XCVI: J. M. Bollinger, J. M. Brinich, and G. A. Olah, *J. Amer. Chem. Soc.*, in press; (b) Postdoctoral Research Associate, 1969; (c) Institute of Inframicrobiology; Acad. R.S.R., Bucharest 1, Rumania.

[2] J. C. Earl and A. W. Mackney, *J. Chem. Soc.*, 899 (1935). For review articles see: (a) W. Baker and W. D. Ollis, *Quart. Rev.* (London), **11**, 15 (1957); (b) F. H. C. Stewart, *Chem. Rev.*, **64**, 129 (1964); (c) N. Suciu, *Stud. Cercet. Chim.*, **16**, 117 (1968).

[3] W. Baker and W. D. Ollis, *Chem. Ind.* (London), 910 (1955).

[4] F. H. C. Stewart and N. Danieli, *ibid.*, 1926 (1963).

[5] (a) C. B. Kier and E. B. Roch, *J. Pharm. Sci.*, **55**, 807 (1966); (b) K. Sundaram and W. P. Purcell, *Int. J. Quantum Chem.*, **2**, 145 (1968); (c) J. A. Singer and W. P. Purcell, *J. Med. Chem.*, **10**, 754 (1967).

[6] E. B. Roche and L. B. Kier, *Tetrahedron*, **24**, 1673 (1968).

[7] R. Huisgen, "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 51.

[8] A more recent calculation,[5b] indicates less difference between the N-2 and the O-6 atoms.

[9] (a) N. Suciu, Gh. Mihai, M. Elian, and E. Stroescu, *Tetrahedron*, **21**, 1369 (1965); (b) N. Suciu and Gh. Mihai, *ibid.*, **24**, 33 (1968); (c) *ibid.*, **24**, 37 (1968).

[10] (a) G. A. Olah and D. P. Kelly, *J. Amer. Chem. Soc.*, in press; (b) G. A. Olah and G. D. Mateescu, *ibid.*, **92**, 1430 (1970).