removed by filtration under nitrogen, leaving a brown solution, Ia. Selected examples of proof of nitrogen incorporation follow.

Addition of Ia to dry ether yielded a cream solid that could not be redissolved without decomposition. An infrared spectrum of this material in a Nujol mull showed a weak band at 2260 cm^{-1}. When a solution comparable to Ia was prepared under helium, precipitation of the product with ether yielded only a sticky green tar which showed no discernible infrared bands in the 2700–2000-cm^{-1} region, where diazonium groups absorb.

Solution Ia reacted with compounds typically used in diazonium coupling reactions. Resorcinol dimethyl ether yielded a deep red oil with infrared and nmr spectra which were nearly superimposable on those of a red oil prepared from a diazonium salt of *o*-aminobenzenethiol and resorcinol dimethyl ether. The visible spectra differed, however, for the oil from Ia exhibited a maximum at 5400 A, while that from the authentic diazonium salt was at 5100 A.

Solution Ia reacted with azulene to give a black solid that decomposed upon all attempts at purification by crystallization or chromatography. Furthermore, this solid decomposed when heated above 120° with the evolution of quantities of gaseous material. The mass spectrum of the trapped gases consisted of six peaks at m/e 27, 28, 30, 44, 48, and 64, with m/e 28 being the largest. Under high resolution, appreciable quantities of molecular nitrogen were observed at m/e 28.

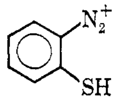
A solution analogous to Ia was prepared at -78° using silver perchlorate in the absence of nitromethane. The deep red methylene chloride solution was allowed to warm slowly in the presence of nitrogen to -10°, whereupon the color changed to deep blue. At this point, 1 equiv of resorcinol dimethyl ether was added, and the color of the solution changed to a light purple. After silver bromide was separated, the solution was concentrated *in vacuo*, leaving an oily, purple, ether-soluble residue. The visible spectrum of this oil exhibited a maximum at 5600 A. Elemental analysis was performed after extraction with pentane. *Anal.* Found: C, 56.2; H, 6.2; N, 2.5.

Since the only nitrogen in the system was in the molecular form, we have excluded the possibility that solvents or reactants were sources of incorporated nitrogen.

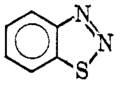
When the same process was carried out in an argon atmosphere the cold reaction mixture was also a deep red, but the "coupling" product was salmon pink. This residue was added to pentane, yielding a white emulsion. On standing overnight, exposed to air, a small amount of purple solid precipitated. The pentane solution yielded a heavy yellow syrup that would not crystallize. *Anal.* Found (for the solid): C, 34.0; H, 3.5; N, 0.6. Found (for the oil): C, 58.2; H, 5.5; N, 0.6. The nitrogen content was not significantly higher than that found in starting materials.

These results indicate that nitrogen is involved in the reaction during the preparation of solutions of I. It appears that the red color, similar to that observed by Kharasch, *et al.*,[7] may be ascribed to the benzenesulfenium ion, while the blue color formed at higher temperatures may represent the first nitrogen-containing intermediate.

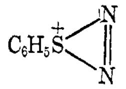
If nitrogen were incorporated into the aromatic ring, a conventional diazonium salt such as II would have formed. However, the visible spectrum of a known diazonium coupling product casts doubt on this possibility. Also, it has been shown[14] that II may easily be converted to a stable thiadiazole, III, but, under conditions in which it should form, it has been undetected in our system.



II



III



IV

$C_6H_5SN_2^+$

V

$(C_6H_5SN{=}NAr)H^+$

VI

The alternative to ring incorporation of nitrogen is bonding directly to sulfur. The most likely alternatives are then the cyclic and linear structures IV and V. The coupling products may then be represented as salts of the type VI.

Further studies are required in order to ascertain the nature of the coupling products and to investigate general applicability of the benzenesulfenium ion in the fixation of nitrogen.

Acknowledgment. This research was supported by Grant GP 5737 from the National Science Foundation.

(14) M. E. Ferrario, *Bull. Soc. Chem. France*, **9**, 536 (1911).

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A Structurally Selective Method for the Preparation of Certain Diels–Alder Adducts

Sir:

The Diels–Alder reaction[1] is probably the most general method for the synthesis of substituted cyclohexenes. Although characterized by high stereospecificity,[2] its structural selectivity is less pronounced. The combination of unsymmetrically substituted components usually leads to mixtures of structural isomers,[3] a situation causing chagrin in synthetic work, particularly when the minor isomer is the desired product.

We have developed a method which allows the preparation of certain Diels–Alder adducts in a structurally specific manner. Addition of α,β-unsaturated carbonyl compounds to dienes results in γ,δ-unsaturated products (*e.g.*, **3**) which in principle should be available by Claisen rearrangement of allyl vinyl ethers (*e.g.*, **1**). Support for the feasibility of a transition state with the geometry of **2** comes from the observation that the two aldehydes **4** and **5** are in thermal equilibrium.[4] Acrolein dimer[5] was transformed to the olefin **1**[6] by Wittig condensation

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

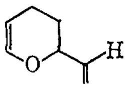
(2) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

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

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

(5) V. V. Fedorova, G. P. Pavlov, and I. D. Sinovich, *Chem. Abstr.*, **59**, 7361 (1963).

(6) The structures of the products obtained herein have been verified by infrared, ultraviolet, nmr, spectrometric, and elemental analyses. Purity was monitored by vapor chromatographic and quantitative nmr analyses.



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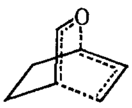

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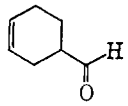

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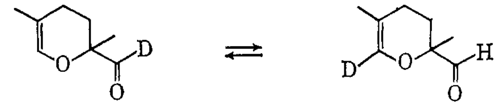
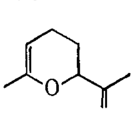


4 5

in dimethyl sulfoxide.[7] Pyrolysis of **1** in hexane solution in a flow system at 410° (contact time approximately 3 sec) yielded the known aldehyde **3**[1] in 68% yield. Wittig reaction using the readily available methyl vinyl ketone dimer[8] gave the olefin **6** which, on heating in a sealed tube (240°; 25 min), was isomerized to the pure ketone **7** (73%). In contrast, addition of methyl vinyl ketone to isoprene gives a mixture of adducts containing 29% **7** and 71% **8**.[9]



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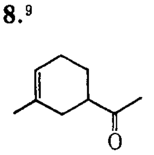

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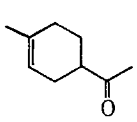
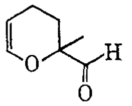


8

To study the effect of nuclear substituents on the course of the Claisen rearrangement, the *t*-butylimine (86% yield) of acrolein dimer was methylated and hydrolyzed[10,11] to the homolog **9** (80%).[12] Pyrolysis of the derived olefin **10** in hexane at 400° in a continuous-flow system furnished the known aldehyde **11**, semicarbazone mp 162–163.5° (lit.[13] mp 144°), as the only product (75–96%). Here again direct condensation of isoprene with acrolein produces a mixture consisting of 85% **11** and 15% "*meta*" isomer.[1]



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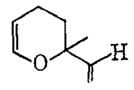

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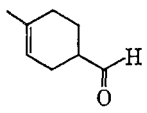
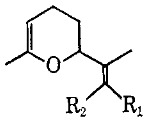
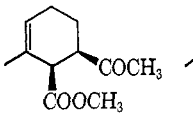


11

In cases where a substituent is present on the terminal carbon atom of the allylic double bond, the efficiency of the Claisen rearrangement is strongly affected by stereochemistry. Combination of the anion derived from methyl dimethylphosphonoacetate[14] with methyl vinyl ketone dimer resulted in a 2:1 mixture of the *trans* ester **12** and the *cis* ester **13**. Rearrangement of pure *trans* ester **12** in a sealed tube at 230° was complete in 20 min, and the stereochemical integrity of the starting material was essentially preserved in the product (83% yield) which consisted of 95% of the *cis* epimer **14** and 5% of the *trans* epimer **15**. Stereomodels show that the *cis* ester **13** leads to a much more crowded transition state, and this isomer was indeed more stable. Thermolysis of pure **13** at 285° for 35 min furnished a mixture of cyclohexenes (31%) containing 73% **15** and 27% **14**. Equilibration of the pure epimers in methanol solution containing some sodium methoxide was complete within minutes at 0° and led to a mixture of 68% of *trans* epimer **15** and 32% of *cis* epimer **14**. We have not yet exposed the pure epimers to the conditions used in the rearrangement of the *cis* ester **13**, and consequently do not know whether the starting material, the product, or both have undergone stereomutation.



12, $R_1 = COOCH_3$; $R_2 = H$
13, $R_1 = H$; $R_2 = COOCH_3$



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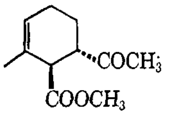
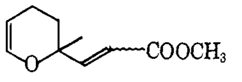


15

Rearrangement of an 83:17 mixture of *trans* and *cis* esters **16** in hexane at 450° yielded 85% of a 45:55 mixture of epimeric aldehydes **17**. In agreement with other work,[15] modified Wittig condensation[7] of ethylenetriphenylphosphorane with acrolein dimer yielded essentially pure *cis* olefin **18**. Its rearrangement at 230° was slow and furnished, in addition to polymeric material, only 8% of an 84:16 mixture of *trans* and *cis* epimers **19** and **20** (equilibrium at 25°; 86:14).[16] Similarly pyrolysis of a 9:1 mixture of stereoisomeric *cis* and *trans* olefins **21** in hexane at 460° produced 14% of a mixture of rearrangement products containing 55% *cis* epimer **22** and 45% *trans* epimer **23** (equilibrium at 25°; 30:70).



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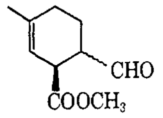

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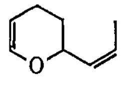

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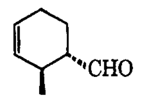

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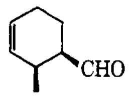

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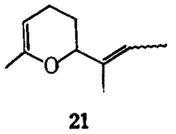

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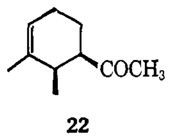

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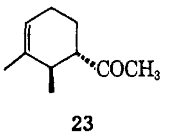

23

It is apparent that the Claisen rearrangement of 3,4-dihydro-2H-pyranylethylenes provides a useful method for the synthesis of cyclohexenes provided the bulky substituents on the aliphatic double bond are *trans* oriented.[17]

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

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

[9] E. F. Lutz and G. M. Bailey, *J. Am. Chem. Soc.*, **86**, 3899 (1964).

[10] G. Stork and S. R. Dowd, *ibid.*, **85**, 2179 (1963).

[11] G. Wittig and H. D. Frommeld, *Chem. Ber.*, **97**, 3548 (1964).

[12] Previously prepared by condensation of acrolein with methacrolein: R. R. Whetstone, U. S. Patent 2,479,283 (1949); *Chem. Abstr.*, **44**, 667 (1950).

[13] K. Alder and W. Vogt, *Ann.*, **564**, 109 (1949).

[14] W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

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

[16] *Cf.* equilibration of the corresponding methyl esters: T. Inukai and T. Kojima, *J. Org. Chem.*, **32**, 869 (1967).

[17] This work was generously supported by the National Institutes of Health (GM 09686-06).

[18] National Institutes of Health Predoctoral Fellow 1967–present.