anions.[7] These rapidly combine in THF solution;[8] *e.g.*, at 20° their concentration decreases from $\sim 10^{-3}$ to $\sim 10^{-4}$ in a few seconds,[9] and eventually equilibrium is established between dimers and the radical ions in which the former species is greatly favored. In HMPA the radical anions do not dimerize; neither their optical spectra nor the esr signal show any detectable change after 3 hr. Changes are observed after 24 hr; however, the products are then different from dimers.

(3) Electron transfer from biphenylsodium to quinoline in THF solution produces probably dimeric dianions, the concentration of free spins being only a few per cent of their initial value. Different behavior is observed in HMPA where a quantitative conversion of $B\cdot^{-},Na^{+}$ into quinoline radical ions takes place. The resulting radical anions remain stable; their uv and esr spectra were recorded. In contradistinction, the reaction with pyridine leads to radical ions which apparently dimerize and eventually are converted to dipyridyl through dehydrogenation in which sodium hydride is formed.

Acknowledgment. We gratefully acknowledge the financial support of these investigations by the National Science Foundation, the United States Air Force (Contract No. AF-33(615)-3788), and the Petroleum Research Fund administered by the American Chemical Society.

[7] (a) C. S. Johnson, Jr., and R. Chang, *J. Chem. Phys.*, **43**, 3183 (1965); (b) J. G. Broadhurst and E. Warhurst, *J. Chem. Soc., Sect. A*, 351 (1966); (c) R. E. Sioda, D. O. Cowan, and W. S. Koski, *J. Am. Chem. Soc.*, **89**, 230 (1967).

[8] D. Dadley and A. G. Evans, *J. Chem. Soc.*, 418 (1967).

[9] E. Franta, unpublished results from this laboratory.

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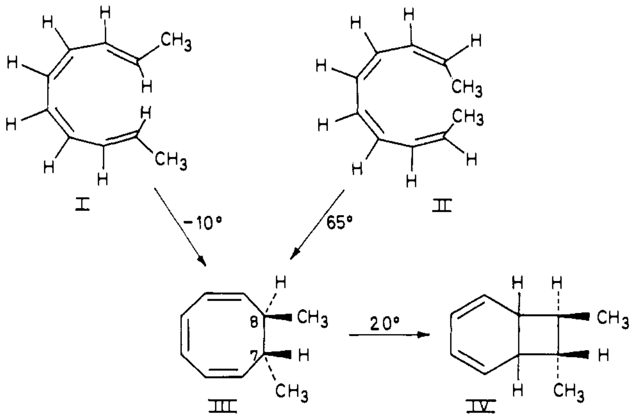
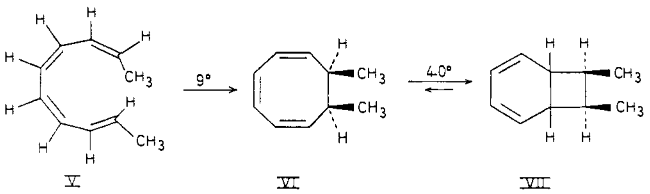
Stereospecific Conrotatory Valence Isomerization of Octatetraenes to Cycloocta-1,3,5-trienes

Sir:

cis,cis-Octa-1,3,5,7-tetraene cyclizes quickly at room temperature to give cycloocta-1,3,5-triene.[1] *all-cis*-1,8-Dimethoxyoctatetraene yields at 120° 7,8-dimethoxybicyclo[4.2.0]octadiene, for which the methoxy groups were suggested to be in *trans* position;[2] certainly the cyclooctatriene derivative is the intermediate.[3] A recent report[4] on the formation of *cis*- and *trans*-7,8-dimethylbicyclo[4.2.0]octadienes (VII and IV) provided indirect evidence that *trans,cis,cis,trans*- and *cis,cis,cis,trans*-deca-2,4,6,8-tetraene occurred as intermediates. The assumption of a conrotatory ring closure was based on nmr data of the bicyclo[4.2.0]-octadienes and on the pyrolysis (200°) of dimethyl acetylenedicarboxylate adducts which were not isolated from a multicomponent mixture. We now wish to report on the highly stereospecific cyclization of the three geometrically isomeric decatetraenes I, II, and V which were obtained crystalline. The structures of the pure products III and VI were based on conclusive evidence.



The valence isomerization of *trans,cis,cis,trans*-deca-2,4,6,8-tetraene (I) in chloroform was nearly complete at −10° after 30 hr.[5] The pure *trans*-7,8-dimethylcycloocta-1,3,5-triene (III) underwent at 20° in 8 hr a second tautomerization to give *trans*-7,8-dimethylbicyclo[4.2.0]octa-2,4-diene (IV).[6] The *all-cis* isomer II cyclized, likewise quantitatively, at 65°; here, of course, the bicyclic compound IV was the only isolable product.



The rate of cyclization of *cis,cis,cis,trans*-decatetraene (V) is between that of I and II. At 9°, 90% of the *cis*-7,8-dimethylcyclooctatriene (VI) and 10% of its bicyclic tautomer VII were obtained. After reaching thermodynamic equilibrium at 40°, an approximate ratio of 15:85 was established for VI and VII.

Thus, the electrocyclic conversions of the three decatetraenes are *conrotatory* as predicted by the Woodward–Hoffmann rules;[7] detection limits: nmr, $\leq 3\%$ IV in the presence of VII and *vice versa;* glpc, $\leq 0.05\%$ and $\leq 0.5\%$ VII in the product IV from I and II, respectively, and $\leq 0.5\%$ IV after the cyclization of V.

The *all-cis*-octatetraene system constitutes somewhat more than one turn of a helix and offers ideal conditions for a *conrotatory* cyclization. The model shows the increasing hindrance by one or two *cis*-methyl groups in V and II, respectively. Kinetic measurements have so far been completed for the slow cyclization II → III: $\Delta H^{\ddagger} = 21.7 \pm 1.0$ kcal/mole and $\Delta S^{\ddagger} = -12 \pm 3$ eu.[8] For comparison, the *disrotatory* cyclization of *trans,cis,trans*-octa-2,4,6-triene to give *cis*-5,6-dimethyl-

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[1] W. Ziegenbein, *Chem. Ber.*, **98**, 1427 (1965).

[2] H. Meister, *ibid.*, **96**, 1688 (1963).

[3] In contrast to M. Kröner's opinion (*ibid.*, **100**, 3172 (1967)) all our experimental evidence speaks against the assumed direct cyclization of octatetraenes to give bicyclo[4.2.0]octadienes which violates the Woodward–Hoffmann rules.

[4] E. N. Marvell and J. Seubert, *J. Am. Chem. Soc.*, **89**, 3377 (1967).

[5] Polymerization was best inhibited by using traces of dicyclohexylammonium picrate.

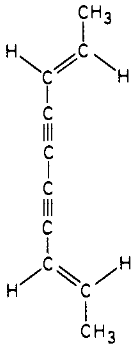
[6] Valence tautomeric equilibria of substituted cycloocta-1,3,5-trienes were investigated by R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, Special Publication No. 19, The Chemical Society, London, 1965, p 3.

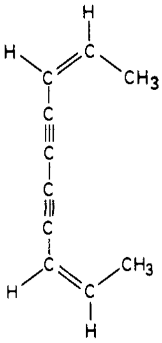
[7] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

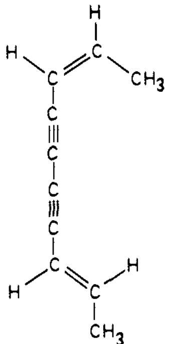
[8] Based on rate data at seven temperatures from 57.8 to 79.0° in $CDCl_3$.

cyclohexa-1,3-diene takes place at 130°;[9,10] the *trans,cis,-cis* and *all-cis* isomers are still less reactive.

Oxidative coupling with $Cu(OAc)_2$–pyridine converted *cis*- and *trans*-3-penten-1-ynes, and a mixture of these two, into the three stereoisomers VIII–X of 2,8-decadiene-4,6-diyne which were purified by preparative glpc (Apiezon L, 6-m column, 136°).[11]


VIII


IX


X

The hydrogenation of the pure (glpc) decadienediynes in pentane at −20° in the presence of Lindlar catalyst was stopped after uptake of 2.4 moles of hydrogen. Although glpc showed mixtures of at least 14 components,[12] at −70° the three decatetraenes I, II, and V crystallized in a pure state. The three tetraenes polymerized so rapidly in the presence of oxygen that all operations had to be carried out under nitrogen.

Some physical properties are: I: mp 30–32°; ir (CCl_4): *cis*-CH=CH 650 cm^{-1}, *trans*-CH=CH 947 cm^{-1}; uv (pentane): 307.5 mμ (log ε 4.48),[13] 294 (4.57), 281.5 (4.40), 272 and 261 shoulders (4.15, 3.89); nmr ($CDCl_3$):[14] τ 8.20 (d, J = 6.6 cps, further split by long-range coupling) for two methyls, 3.0–4.7 (m) for eight vinyl hydrogens; II:[15] mp 61–63°; ir (CCl_4): *cis*-CH=CH 685 cm^{-1}; uv (cyclohexane): 317 mμ (log ε 4.48), 302.5 (4.58), 289.5 (4.44), 280 and 269 shoulders (4.24, 4.02); nmr ($CDCl_3$): τ 8.23 (d, J = 6.9 cps, further split by long-range coupling) for two methyls, 4.46 ($\propto$) for 2- and 9-H, ≈3.7 (s, broad) for six vinyl hydrogens; V: mp below 0°; ir (CCl_4): *cis*-CH=CH 698 cm^{-1}, *trans*-CH=CH 950 cm^{-1}; uv (cyclohexane): 313 mμ (log ε 4.28), 299 (4.40), 286.5 (4.29), 277 and 264 shoulders (4.09, 3.99); nmr ($CDCl_3$): τ 8.18 (d, J = 6.0 cps, broad signals) for two methyls, 2.9–4.7 (m) for eight vinyl hydrogens.

Cyclization of I gave III:[5] nmr ($CDCl_3$): τ 9.0 (three signals, partial coalescence) for two methyls, ≈7.6 (m) for 7- and 8-H, 3.39–4.38 (m) for six vinyl hydrogens. Ozonolysis in ethyl acetate at −60°, peracetic acid treatment, and reaction of acidic products with diazomethane yielded dimethyl *rac*-2,3-dimethylsuccinate, bp 95° (12 mm), identical with an authentic specimen (ir, glpc retention time).

The isomerization III → IV[16] in $CHCl_3$ at 20° went to completion; IV: bp 49° (10 mm); ir (CCl_4): *cis*-CH=CH 710 cm^{-1}; uv (cyclohexane): 274 mμ (log ε 3.40), spectrum similar to that of the unsubstituted compound;[17] nmr ($CDCl_3$): τ 8.93 (d, J = 6.3 cps) and 8.98 (d, J = 5.9 cps) for two methyls. IV combines with TCNE at 0° in ethyl acetate to give a Diels–Alder adduct,[11,18] mp 205–206°; nmr ($CDCl_3$): τ 9.03 (d, J = 8.0 cps) and 8.97 (d, J = 8.0 cps) for two methyls, 8.20 (q, 1 H), 7.67 (q, 1H).

The conversion II → IV was completed in $CDCl_3$ at 65° after 14 hr.[5] Kinetic measurements were conducted in sealed nmr tubes by following the disappearance of the methyl doublet of II (II + IV = 100%): 10^4k (sec^{-1}) at 72.1°: benzene 3.70, CCl_4 3.45, $CDCl_3$ 2.92.

From the mixture of 90% VI and 10% VII, which was obtained from V at 9° in $CDCl_3$ after 155 hr, the bicyclic tautomer VII was removed at −10° by reaction with azodicarboxylic acid N-phenylimide as a crystalline Diels–Alder adduct; nmr of pure VI ($CDCl_3$): τ 8.95 (d, J = 6.9 cps) for two methyls, 7.25 (m) for 7- and 8-H, ≈4.15 (s, broad) for six vinyl hydrogens.

The equilibrium mixture of VII and VI showed bp 50–53° (11 mm) and *cis*-CH=CH wagging at 690 cm^{-1}; nmr ($CDCl_3$) of *cis*-7,8-dimethylbicyclo[4.2.0]octa-2,4-diene (VII): τ 8.97 (d, J = 6.4 cps) for two methyls, 7.44 (s, broad) for 7- and 8-H, 7.25 (m) for 1- and 6-H, 4.28 (s, broad) for four vinyl hydrogens; TCNE adduct of VII,[11,18] mp 223–224°; nmr (acetone-d_6): τ 8.92 (d, J = 6.6 cps) for two methyls, 7.90 (m, 2 H).

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(9) E. N. Marvell, G. Caple, and B. Schatz, *Tetrahedron Letters*, 385 (1965).

(10) E. Vogel, W. Grimme, and E. Dinné, *ibid.*, 391 (1965).

(11) Nmr and infrared spectra are in accordance with the structures. A full account of these data will be published later.

(12) The hydrogenation products contained 52% I, 52% II, and 38% V, respectively.

(13) Extinction coefficients are not reliable because of fast rearrangement to III with its weaker absorption.

(14) Determined on a Varian A-60 with TMS as internal standard, I, II, III, and V at −40°; s denotes singlet, d doublet, q quadruplet, $\propto$ octuplet, m multiplet.

(15) D. Holme, E. R. H. Jones, and M. G. Whiting, *Chem. Ind.* (London), 928 (1956).

(16) D. A. Bak and K. Conrow, *J. Org. Chem.*, 31, 3958 (1966), described mixtures enriched in IV + VII.

(17) A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Trumbull, *J. Am. Chem. Soc.*, 74, 4867 (1952).

(18) Satisfactory elementary analyses have been obtained.

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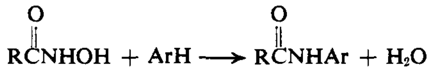
Direct Amidation. A New Aromatic Substitution Process

Sir:

A traditional method for the preparation of acyl derivatives of aromatic amines employs sequential nitration, reduction, and acylation of an aromatic starting material. We report here a new and promising method for the direct introduction of an acylamido group onto a moderately reactive aromatic ring in a single step.

We have found that an aromatic compound and a hydroxamic acid interact in hot polyphosphoric acid to furnish directly an acylamido derivative of the aromatic compound. In the simplest cases, the products are



$$R\overset{\overset{\displaystyle O}{\|}}{C}NHOH + ArH \longrightarrow R\overset{\overset{\displaystyle O}{\|}}{C}NHAr + H_2O$$

easily obtained from the diluted reaction mixture by extraction. Moreover, the operation is simple and can be completed in a short time.

One of the more successful examples that we have uncovered involves an intramolecular ring closure. Specifically, when hydrocinnamohydroxamic acid[1] was

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(1) C. D. Hurd and L. Bauer, *J. Am. Chem. Soc.*, 76, 2791 (1954).