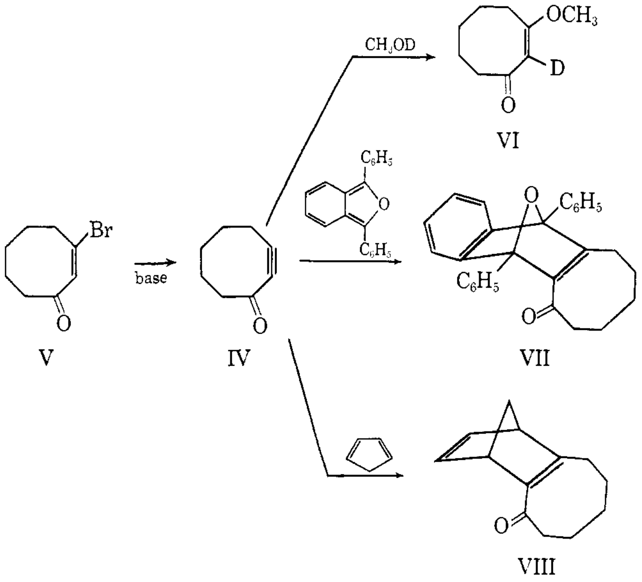
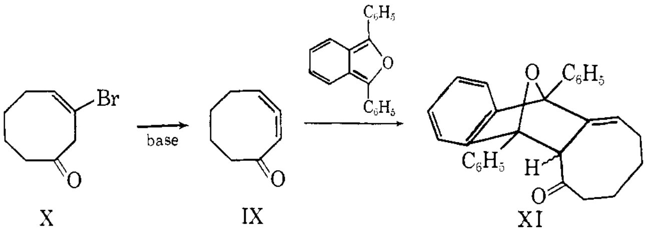
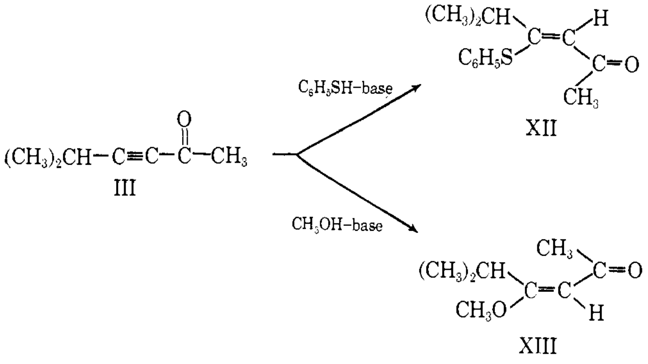
2,3-Cyclooctadienone (IX) is not an intermediate in these reactions. We have prepared this interesting cyclic allenone by reaction of 3-bromo-3-cyclooctenone (X) with base; it reacts with 1,3-diphenylisobenzofuran to give the two epimers of the expected Diels–Alder adduct XI, but none of VII.





The literature is rich with uses of conjugated acetylenic carbonyl compounds. Nucleophilic additions to the triple bond are of particular value. Most such reactions give *trans*-added products.[6] For example, the acetylenic ketone III reacts with sodium thiophenoxide in aqueous solvents to give the *trans*-β-thiophenoxy α,β-unsaturated ketone XII. It has been reported that primary and secondary amines add *cis* to activated triple bonds; it has been proposed that the proton carried into the reaction by the amine is transferred specifically to the α-vinyl carbon.[7] We have found, however, that *cis* addition to conjugated acetylenic carbonyl systems is not restricted to the addition of amines. The base-catalyzed addition of methanol to the acetylenic ketones we have studied takes the same course. For example, reaction of compound III with aqueous methanolic potassium carbonate gives only (by nmr) the *cis*-added *cis*-methoxy α,β-unsaturated ketone XIII. This is known to be the kinetically controlled product as the *trans* isomer of XIII is not isomerized under the reaction conditions. Much remains to be done before the factors that control the stereochemistry of such addition reactions are understood.



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(6) E. Winterfeldt, *Angew. Chem.*, **79**, 389 (1967); W. E. Truce and J. A. Simms, *J. Am. Chem. Soc.*, **78**, 2756 (1956).

(7) E. Winterfeldt and H. Preuss, *Ber.*, **99**, 450 (1966); R. Huisgen, H. Herbig, A. Siegl, and H. Huber, *ibid.*, **99**, 2526 (1966); R. Huisgen, B. Giese, and H. Huber, *Tetrahedron Letters*, 1883 (1967); B. Giese and R. Huisgen, *ibid.*, 1889 (1967). Compare W. E. Truce and D. G. Brady, *J. Org. Chem.*, **31**, 3545 (1966).

(8) Alfred P. Sloan Foundation Research Fellow.

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The Synthesis of a Stable Complex of a Macrocycle and a Threaded Chain

Sir:

Frisch and Wasserman[1] have commented on the expected stability of threaded molecular systems of the type **1** in which bulky groups A prevent the extrusion of a threaded chain B from a macrocycle C. We have synthesized substance **2** belonging to this novel system as described below. Similar methods may be applicable to the synthesis of catenanes[1] and other threaded compounds.

Reaction of 2-hydroxycyclotriacontanone (**3**) with succinic anhydride in pyridine gave the hemisuccinate ester **4**, mp 81–84° (methyl ester molecular ion 564 mass units) which was coupled, *via* the sodium salt, with Merrifield's peptide resin,[2] forming the resin adduct **5**. Treatment of a column of this resin-bound macrocycle with a solution of decane-1,10-diol and triphenylmethyl chloride in a mixture of pyridine, dimethylformamide, and toluene gave the ether **7** and only traces of the threaded complex **6**. The total yield of this complex was then improved by numerous repetitions of the process. After 70 treatments the column was extracted free of reagents and other soluble materials and the reaction products were hydrolyzed from the resin, by refluxing with sodium bicarbonate in methanol, yielding a mixture containing 6% of complex **2** which was readily purified by chromatography. Complex **2** was an oil, stable at temperatures up to 200°; the infrared spectrum [$\nu_{\max}$ 3440 (OH···O), 1710 (CO), 1070 (CH$_2$O–), 740 and 705 cm^{-1} (monosubstituted phenyl)] was very similar to that of a mixture of the ether **7** and acyloin **3** although chromatography demonstrated that there was no contamination by the latter two compounds.

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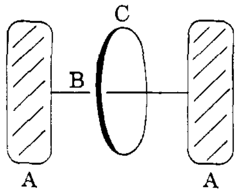
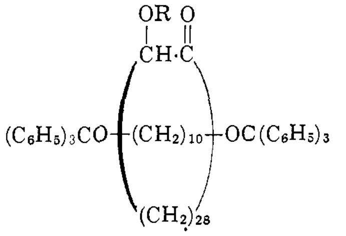
(1) H. L. Frisch and E. Wasserman, *J. Am. Chem. Soc.*, **83**, 3789 (1961). A rational synthesis of a member of this system has been mentioned in a preliminary note: G. Schill and H. Zollenkopf, *Angew. Chem.*, **79**, 149 (1967).

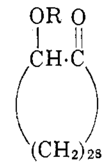
(2) R. B. Merrifield, *J. Am. Chem. Soc.*, **85**, 2149 (1963).



1



2, R = H
6, R = CO(CH$_2$)$_2$CO$_2$ resin



3, R = H
4, R = CO(CH$_2$)$_2$CO$_2$H
5, R = CO(CH$_2$)$_2$CO$_2$ resin

$(C_6H_5)_3CO(CH_2)_{10}OC(C_6H_5)_3$

7

Structure 2 was supported by degradation. Oxidation[3] with silver oxide gave octacosane-1,28-dicarboxylic acid, isolated as the dimethyl ester, mp 78–79°, and decane-1,10-diol bis(triphenylmethyl) ether (7), mp 73–75°. Since the latter compound has no reactive or polar functional groups its complex with the macrocycle clearly involved a novel type of binding. Cleavage of complex 2 with boron trifluoride ethereate in benzene gave decane-1,10-diol, mp 71–73°, triphenylmethanol, mp 164–165°, and the acyloin 3, mp 62–64°. All degradation products were isolated by chromatography, sublimed *in vacuo*, and identified through comparison with authentic samples by melting point and mixture melting point and by thin layer chromatography. In addition the infrared spectrum of the ether 7 was used for comparison.

Threaded compounds such as 2 can, at least in principle, be dissociated into two molecular species by simply stretching covalent bonds, *e.g.*, by expanding the macrocycle until the blocking groups can pass through. Chemical topology is therefore not involved.[1] The name hooplane is suggested; 2 is then the hooplane complex of 2-hydroxycyclotriacontanone (3) and decane-1,10-diol bis(triphenylmethyl) ether (7).

(3) M. Stoll and A. Rouvé, *Helv. Chim. Acta*, 30, 1822 (1947).

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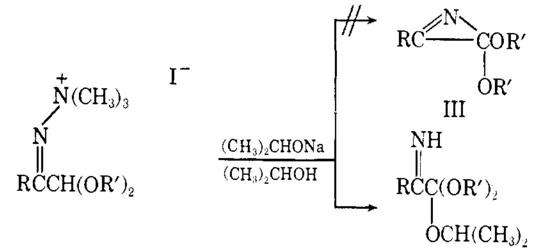
An Anomalous Neber Rearrangement. Synthesis of α-Imino Ortho Esters

Sir:

The Neber rearrangement of certain quaternary hydrazones has been shown to proceed through isolable azirine intermediates.[1,2] For example, treatment of isobutyrophenone N,N,N-trimethylhydrazonium iodide with sodium isopropoxide in isopropyl alcohol afforded 2,2-dimethyl-3-phenyl-2H-azirine in high yield.[1]

We wish to report the anomalous behavior of the hydrazonium iodide acetals Ia and Ib which, under Neber conditions, yielded a new class of compounds, the α-imino ortho esters IIa and IIb.[3] None of the anticipated 2,2-dialkoxyazirine III (an unsaturated α-lactam ketal[4]) was detected.



Ia, R = CH$_3$; R′ = CH$_3$CH$_2$
b, R = C$_6$H$_5$; R′ = CH$_2$

IIa, R = CH$_3$; R′ = CH$_3$CH$_2$
b, R = C$_6$H$_5$; R′ = CH$_2$

Treatment of pyruvaldehyde diethyl acetal N,N,N-trimethylhydrazonium iodide (Ia)[5] with sodium isopropoxide in isopropyl alcohol for 5.7 hr at room temperature afforded, after removal of the solvent *in vacuo* and extraction of the residue with ether, a 50%[6] yield of diethyl isopropyl orthopyruvate imine (IIa). Structure IIa is assigned on the basis of the following data: nmr spectrum $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.14 (12 H, multiplet, methyl protons), 1.87 (3 H, singlet, methyl protons), 3.34 (4 H, multiplet, methylene protons), 3.98 (1 H, broad multiplet, "tertiary" proton), and 9.62 ppm (1 H, broad singlet, imine proton); $\nu_{\mathrm{max}}^{\mathrm{film}}$ 3250 and 1660 cm^{-1}. *Anal.* Calcd for $C_{10}H_{21}NO_3$: C, 59.09; H, 10.41; N, 6.89. Found: C, 59.36; H, 10.54; N, 6.75.[7] Chemical evidence for the α-imino ortho ester structure was provided by the facile (air, room temperature) hydrolysis of IIa to the corresponding keto ortho ester. In addition, ethyl pyruvate and isopropyl pyruvate[8] were isolated from the room-temperature hydrolysis of IIa with 0.1 *N* hydrochloric acid.

Similarly, 2-benzoyl-1,3-dioxolane N,N,N-trimethylhydrazonium iodide (Ib) gave 2-benzoyl-2-isoproxy-1,3-dioxolane imine (IIb) in 56% yield. Structure IIb is assigned on the basis of the following data: nmr spectrum $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 1.08 (6 H, doublet, methyl protons), 3.84 (5 H, broad multiplet, "tertiary" plus methylene pro-

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(1) R. F. Parcell, *Chem. Ind.* (London), 1396 (1963).

(2) D. F. Morrow, M. E. Butler, and E. C. Y. Huang, *J. Org. Chem.*, 30, 579 (1965).

(3) Insofar as can be determined, no α-imino ester [RC(=NH)-COOR′] has ever been isolated and characterized. However, evidence for the existence of this class of compounds has been provided by the formation of various derivatives: (a) R. Appel and A. Hauss, *Z. Anorg. Allgem. Chem.*, 311, 290 (1961); (b) J. H. Boyer and D. Straw, *J. Am. Chem. Soc.*, 75, 1642 (1953); (c) E. Cioranescu, A. Bucur, and C. D. Neniescu, *Acad. Rep. Populare Romine, Studii Cercetari Chim.*, 8, 557 (1960); *Chem. Abstr.*, 56, 15500 (1962); (d) D. H. R. Barton and L. R. Morgan, Jr., *J. Chem. Soc.*, 622 (1962); (e) R. M. Moriarty and M. Rahman, *J. Am. Chem. Soc.*, 87, 2519 (1965).

(4) Saturated α-lactam ketals, *e.g.*, 2-methoxy-2-(*t*-butoxy)-3-phenylaziridine, have been proposed as reaction intermediates: H. E. Baumgarten, J. E. Dirks, J. M. Petersen, and R. L. Zey, *J. Org. Chem.* 31, 3708 (1966).

(5) Quaternary hydrazones Ia (mp 111–112° dec) and Ib (mp 129.0–129.5°) were prepared from pyruvaldehyde and phenylglyoxal, respectively, by way of intermediate keto acetals and N,N-dimethylhydrazone acetals. Satisfactory microanalytical and spectroscopic (infrared and nmr) data were obtained for all new compounds.

(6) Yield determination and product isolation were carried out by gas–liquid partition chromatography using a 1.5 m × 6 mm column of 10% SE-30 on 70–80 mesh Anakrom ABS.

(7) The nmr spectra were recorded with a Varian A-60A spectrometer. The infrared data were taken on a Perkin-Elmer Model 337 grating spectrophotometer. Microanalyses were carried out by Dr. Franz J. Kasler.

(8) We thank William A. White for the preparation of an authentic sample of isopropyl pyruvate; P. A. Leermakers, P. C. Warren, and G. F. Vesley, *J. Am. Chem. Soc.*, 86, 1768 (1964).