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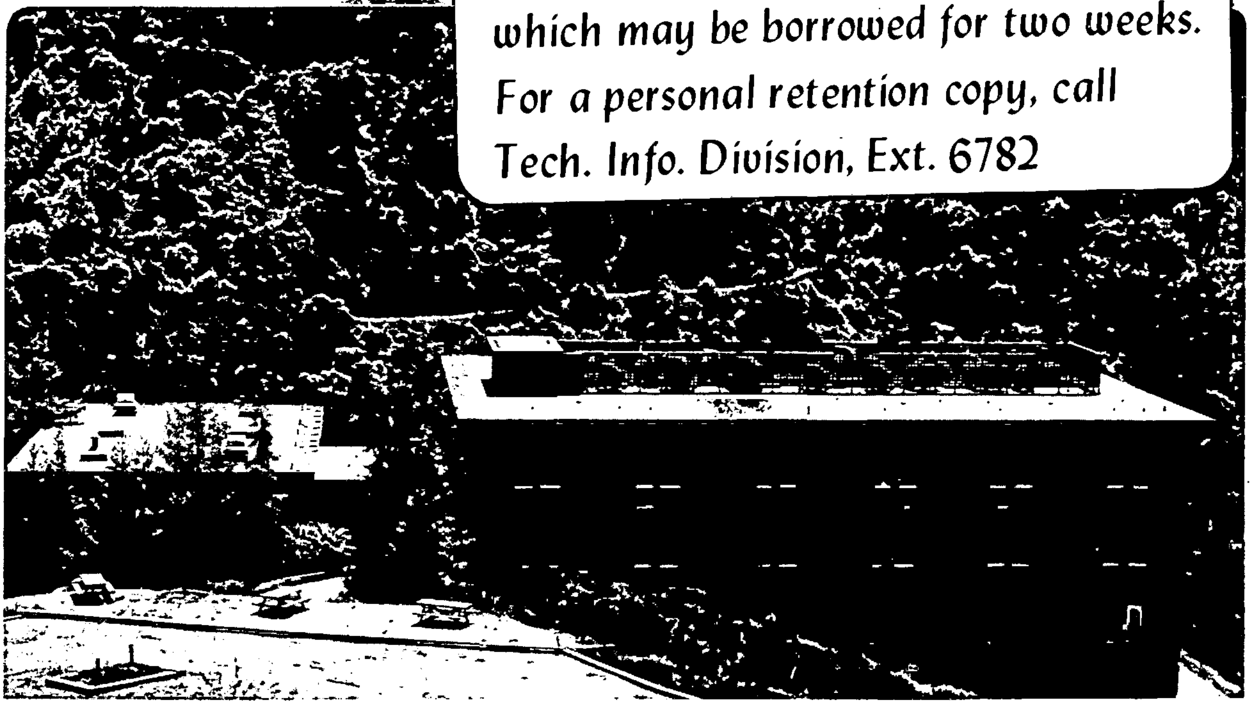

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On the Mechanism of the Reppe Cyclooctatetraene Synthesis From Ethyne: A Labeling Experiment

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Abstract

Singly ^{13}C-labeled ethyne may be cyclized to tetralabeled cyclooctatetraene under N_2 pressure (50-60 psig) by using nickel catalysts under conditions similar to those reported by Reppe. The resulting cyclopolyolefin is degraded to a C_4-fragment incorporated in dimethyl phthalate according to a literature procedure. The latter is analyzed through g.c. mass spectrometry. The peak ratios of the most intense $C_9H_7O_3$ peaks containing various amounts of label rule out cyclobutadienes and benzenes as intermediates, and metathesis mechanisms as part of the nickel catalyzed cyclic tetramerization of ethyne. The label distribution is, however, consistent with a concerted or stepwise coupling mechanism of the four alkyne units.

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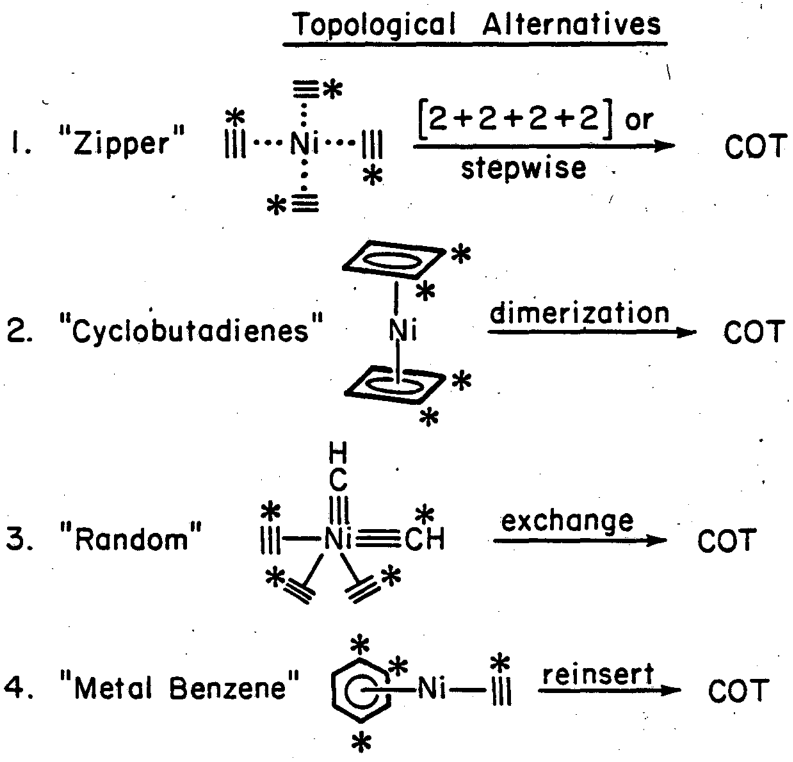
The mechanism of the remarkable nickel catalyzed cyclotetramerization of ethyne discovered by Reppe[1] is little understood, despite the synthetic significance of the reaction[2] and the mechanistic curiosity it has generated.[3] Originally formulated as a concerted "zipper" process,[4] recent work has suggested the possibility of the occurrence of a stepwise topological equivalent possibly involving dinuclear metallacycles.[5] Particularly significant has been the discovery of metal mediated alkyne-linking processes resulting in flyover bridges between two metal centers composed of four alkyne units,[5f,g] and the detection of a remarkably facile reversible cyclooctatetraene (COT) ring opening reaction.[5c,e]

Other work has implicated the intermediacy of nickel cyclobutadiene complexes.[6] Such intermediates were originally discounted as unlikely due to the stability of isolated representatives of this class of compounds.[7] Through the use of isotopic labeling they were also shown to be absent in a number of transition metal catalyzed alkyne cyclizations leading to aromatic compounds.[8] On the other hand, recently several cyclobutadiene nickel complexes have been isolated which appear to be good models for potential intermediates in COT synthesis,[6] particularly some which may be decomposed to COT under mild conditions.[6b]

In addition to the "zipper-stepwise" (hereafter called "zipper") and the "cyclobutadiene" mechanisms there are other major topological alternatives[9] (Scheme 1): a "random" process in which individual carbyne units are recombined arbitrarily,[10] and a "metal benzene" intermediate (formed by the stepwise process[8]) which inserts another molecule of ethyne en route to COT.[11] As indicated in Scheme 1 one might be able to distinguish between these possibilities by using singly labeled ethyne. A simple statistical analysis (neglecting ^{13}C-isotope effects) gives the expected distribution of the eight possible isomeric tetralabeled products (Table 1).



Scheme 1

One will note that in the zipper mechanism it is impossible to generate

Table 1. Theoretical Isomer Distribution of Labeled Cyclooctatetraenes According to Various Mechanisms of Formation.

								
zipper	0%	0%	0%	0%	50%	25%	12.5%	12.5%
cyclobutadiene	3.1	12.5	6.25	6.25	37.5	15.6	6.25	12.5
random	12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
metal benzene	0	6.25	6.25	6.25	43.75	18.75	6.25	12.5

three or four adjacent labels.

If one were to employ ethyne-1-^{13}C as starting material,[12] a possible way of interpreting the data arising from such a labeling experiment would be by inspection of the C_4H_4-fragment ion peak envelope. Unfortunately, we found that significant randomization of the COT carbon skeleton takes place prior to fragmentation.[13] A chemical degradation to a C_4-unit would lead to the label distribution depicted in Table 2 (assuming 100% label purity). In order to analyze results correctly, two further corrections have to be applied, one which takes into account the isotopic purity of both carbon atoms

Table 2. Calculated Relative Abundance of Labeled C_4-Fragments Derived From COT-$^*C_4$.

	zipper	cyclobutadiene	random	metal-benzene
$^*C_4$	0.00	0.39	1.56	0.00
C^*C_3	12.50	17.19	18.75	15.62
$C_2{}^*C_2$	75.00	64.84	59.37	68.75
$C_3{}^*C$	12.50	17.19	18.75	15.62
C_4	0.00	0.39	1.56	0.00

(^{12}C=98.89%, ^{13}C=97%[14]).[15] The other incorporates these numbers into the fragmentation pattern of the ions containing the C_4-unit originally derived from the labeled COT. We chose dimethyl phthalate as the target of degradation (vide infra) because the base peak in its mass spectrum at m/e 163 (M^+-OCH_3) is essentially isolated, i.e. it has no near neighbors except those due to natural ^2H, ^{13}C, ^{17}O and ^{18}O. The resulting theoretically expected label distributions for the various mechanisms are shown in Table 3 normalized to the most abundant fragment, m/e 165.[16]

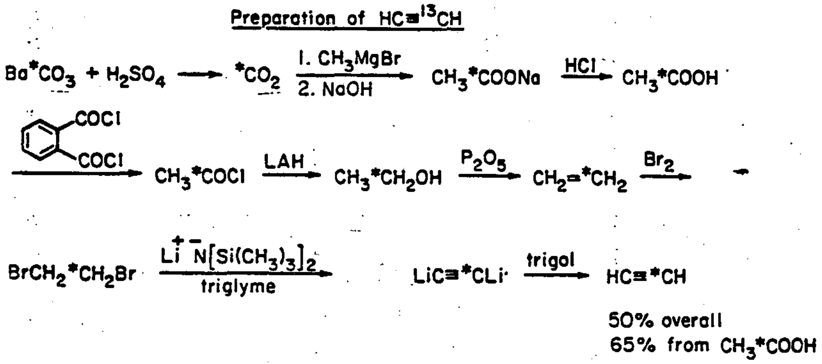
Table 3. Calculated and Experimental Relative Peak Intensities for the M^+-OCH_3 Ion Peak of Dimethyl Phthalate Containing Varying Amounts of Label According to Several Mechanisms

m/e	zipper	cyclobutadiene	random	metal benzene	Experimental[a]
163	0.6	1.5	3.6	0.8	2.9±0.1
164	22.4	31.7	36.5	28.2	21.1±0.6
165	100.0	100.0	100.0	100.0	100.0
166	23.6	32.6	37.3	29.2	22.8±0.4
167	1.9	3.1	5.2	2.3	1.3±0.5

[a] Average of five runs including standard deviations. The mass spectral line intensities ranged from 900-2200 counts for the smallest m/e = 167. This eliminates any significant ion statistical error in measuring the ratio of the ion peaks m/e 164-166 (B. J. Millard, "Quantitative Mass Spectrometry", Heyden, Philadelphia, Pa.,

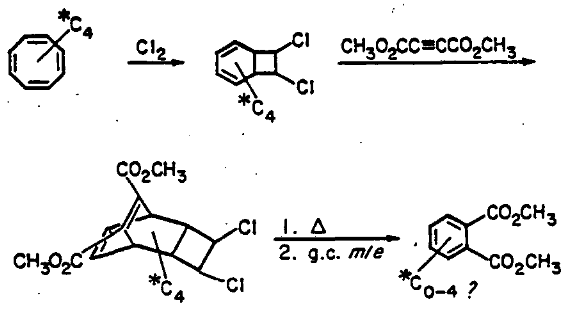
Chapter 3, "Sources of Error".) The deviation in m/e 167 could be ascribed to such errors while the disparity of the m/e 163 peak appears to be due to the presence of a small amount of impurity.

The required singly labeled ethyne[17] was prepared starting



Scheme 2

from commercially available $Ba^{13}CO_3$ or $CH_3{}^{13}COOH$[14] by literature methods[18] (Scheme 2) up to the 1,2-dibromoethane stage. Elimination and protonation was achieved as shown.[19] Cyclization[20] was followed by degradation[21] according to Scheme 3. The mass spectrum



Scheme 3

of the labeled COT revealed the absence of any COT-$^{13}C_5$ isomer in excess of the amount expected based on the natural abundance of ^{13}C in the ^{12}C-label. This rules out random carbon exchange processes of any kind in the cyclization. After degradation, the peaks for the dimethyl phthalate fragment m/e $C_9H_7O_3$ give the relative intensities shown in Table 3. The observed figures are clearly incompatible with the significant occurrence of cyclobutadiene, random, and metal benzene mechanisms or any other conceivable topologically equivalent sequence leading to COT. A separate experiment using a different catalytic system with less enriched ethyne-1-^{13}C is in remarkable agreement with these conclusions.[22] It follows that the predominant way in which four ethynes are linked by nickel catalysts en route to COT leaves the initial connectivity of the starting carbon pairs intact. This is currently best accommodated by the postulate of a zipper-stepwise type mechanism.

Acknowledgments

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† Camille and Henry Dreyfus Teacher-Scholar, 1978-1983.

(1) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *J. Liebigs. Ann. Chem.*, **560**, 1 (1948).

(2) A. C. Cope and H. C. Campbell, *J. Am. Chem. Soc.*, **74**, 179 (1952); A. C. Cope and D. S. Smith, *ibid.*, **74**, 5136 (1952); A. C. Cope and D. F. Rugen, *ibid.*, **75**, 3215 (1953); A. C. Cope and R. M. Pike, *ibid.*, **75**, 3220 (1953); J. R. Leto and M. F. Leto, *J. Am. Chem. Soc.*, **83**, 2944 (1961); P. Chini, N. Palladino, and A. Santambrogio, *J. Chem. Soc. (C)*, 836 (1967); G. A. Chukhadzhyan, E. L. Sarkisyan, and T. S. Elbakyan, *Zh. Obshch. Khim.*, **43**, 2302 (1973); V. K. Shitikov, T. N. Kolosova, V. A. Sergeev, V. V. Korshak, and P. O. Okulevich, *Zh. Org. Khim.*, **10**, 1007 (1974); L. H. Simons and J. J. Lagowski, *J. Org. Chem.*, **43**, 3247 (1978).

(3) For a review, see L. P. Yur'eva, *Russ. Chem. Rev.*, **43**, 48 (1974).

(4) G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 550 (1962); G. N. Schrauzer, P. Glockner, and S. Eichler, *Angew. Chem.*, **76**, 28 (1964); *Angew. Chem.*, *Int. Ed. Engl.*, **3**, 185 (1964); G. N. Schrauzer, *Adv. Organometal. Chem.*, **2**, 1 (1964); E.-A. Reinsch, *Theoret. Chim. Acta*, **17**, 309 (1970).

(5) See, (a) V. Hinrich-Dierks and H. Dietrich, *Acta Cryst.*, **B24**, 58 (1968); (b) D. J. Brauer and C. Krüger, *J. Organometal. Chem.*, **122**, 265 (1976); (c) G. Wilke, *Pure Appl. Chem.*, **50**, 677 (1978); (d) S. P. Kolesnikov, J. E. Dobson, and P. S. Skell, *J. Am. Chem. Soc.*, **100**, 999 (1978); (e) W. Geibel,

G. Wilke, R. Goddard, C. Krüger, and R. Mynott, *J. Organometal. Chem.*, **160**, 139 (1978); (f) S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M. J. Winter, and P. Woodward, *J.C.S. Chem. Comm.*, 221 (1978); (g) M. Green, N. C. Norman, and A. G. Orpen, *J. Am. Chem. Soc.*, **103**, 1269 (1981); (h) E.-A. Reinsch, *Theoret. Chim. Acta*, **11**, 296 (1968).

(6) (a) C. Fröhlich and H. Hoberg, *J. Organometal. Chem.*, **204**, 131 (1981); H. Hoberg and C. Fröhlich, *ibid.*, **197**, 105 (1980); P. Mauret, G. Guerch, and S. Martin, *Compt. Rend. Acad. Sc. Paris C*, **284**, 747 (1977); (b) H. Hoberg and C. Fröhlich, *Angew. Chem.*, **92**, 131 (1980); *Angew. Chem.*, *Int. Ed. Eng.*, **19**, 145 (1980); H. Hoberg and W. Richter, *J. Organometal. Chem.*, **195**, 355 (1980); see also H. Hoberg and W. Richter, *ibid.*, **195**, 347 (1980).

(7) P. M. Maitlis, *Adv. Organometal. Chem.*, **4**, 95 (1966); R. S. Dickson and P. J. Fraser, *ibid.*, **12**, 323 (1974); A. Efraty, *Chem. Rev.*, **77**, 691 (1977); see also J. R. Fritch and K.P.C. Vollhardt, *Angew. Chem.*, **91**, 439 (1979); *Angew. Chem.*, *Int. Ed. Engl.*, **18**, 409 (1979).

(8) G. M. Whitesides and W. J. Ehmann, *J. Am. Chem. Soc.*, **91**, 3800 (1969); **92**, 5625 (1970).

(9) Scheme 1 is not meant to imply specific mechanisms, but simply (as stated) topological variations of assembling four two-carbon fragments to give an eight-membered ring. However, there are numerous transition metal complexes, the structure of which

may or may not be relevant in this context: M. A. Bennett, Adv. Organometal. Chem., **4**, 375 (1966); L. A. Paquette, Tetrahedron, **31**, 2855 (1975); F. L. Bowden and A.B.P. Lever, Organometal. Chem. Rev., **3**, 227 (1968); A. Konietzny, P. M. Bailey, and P. M. Maitlis, J.C.S. Chem. Comm., 78 (1975); P. M. Bailey, B. E. Mann, I. D. Brown, and P. M. Maitlis, ibid., 238 (1976); P. F. Heveldt, B.F.G. Johnson, J. Lewis, P. R. Raithby, and G. M. Sheldrick, ibid., 340 (1978); M.E.E. Veldman, H. R. van der Wal, S. J. Veenstra, and H. J. de Liefde Meijer, J. Organometal. Chem., **197**, 59 (1980).

(10) Transition metals may convert alkynes to carbyne complexes: J. R. Fritch, K.P.C. Vollhardt, M. R. Thompson, and V. W. Day, J. Am. Chem. Soc., **101**, 2768 (1979); J. R. Fritch and K.P.C. Vollhardt, Angew. Chem., **92**, 570 (1980); Angew. Chem., Int. Ed. Engl., **19**, 559 (1980), and the references therein.

(11) We have cyclotetramerized ethyne in the presence of C_6D_6 and found no COT-d_6 (g.c.m.s.) in product, only a small amount of COT-$d_{1,2}$. This result suggests that, should the metal-benzene mechanism (Scheme 1) be operating, the metal may not reversibly dissociate benzene. Variations of the alternatives in Scheme 1 may be conceived of:

a. Metal cyclobutadienes which react further via metallacyclopentadienes in a stepwise manner; this is equivalent to the metal benzene process;

b. metal cyclobutadienes which convert to Dewar benzenes and subsequently tricyclo[4.2.0.$0^{2,5}$]octa-1,7-dienes en route to COT;

c. metal cyclobutadienes which add one ethyne to give a metal benzene complex which inserts the fourth ethyne to give COT. The last two possibilities produce numbers very close to the cyclobutadiene mechanism.

(12) Initial experiments were directed at using mono-deutero-ethyne. However, the results in ref. 11 and literature data discouraged this approach: L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, J. Org. Chem., **27**, 3930 (1962).

(13) See also: J. F. Franklin and S. R. Carroll, J. Am. Chem. Soc., **91**, 5940 (1969).

(14) We thank Dr. N. A. Matwiyoff (Stable Isotope Resource, Los Alamos Scientific Laboratory) for a generous sample of 99% ^{13}C labeled acetic acid.

(15) Label purity was ascertained at the stage of rigorously purified 1,2-dibromoethane.

(16) These numbers do not incorporate negligible effects due to natural abundance ^{2}H, or to ^{13}C-isotope effects. See, E. Buncel and C. C. Lee, eds., "Carbon-13 in Organic Chemistry", Vol. 3, Elsevier, 1977. Calculations were carried out using binomial statistics, both by hand and employing a simple BASIC program: R. E. Colborn, Ph.D. thesis, University of California, Berkeley, 1981.

(17) A more cumbersome and less efficient approach has been reported: R.F.C. Brown, F. W. Eastwood, and G. P. Jackman, Aust. J. Chem., **31**, 579 (1978).

(18) M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert, and P. F. Yankwich, "Isotopic Carbon", Wiley, New York, N.Y., 1949;

J. D. Cox and H. S. Turner, *J. Chem. Soc*., 3176 (1950); B. Bak, J. Christiansen, and J. T. Nielsen, *Acta Chem. Scand*., **14**, 1865 (1960); B. Bak, J. T. Nielsen, and M. Schöttlander, *ibid*., **16**, 123 (1962).

(19) Details will be published separately.

(20) $HC\equiv{}^{13}CH$ (5mmole), $Ni(acac)_2$ (2%), Et_2AlOEt (1-1.8%), THF, N_2 (85 psig), 1d, 85°C. Yield of COT: 50-60%.

(21) R. Pettit and J. Hennery, *Org. Syn*., **50**, 36 (1970). G. C. mass spectral data were obtained on a Finnigan 4000 instrument equipped with an Incos data system. Glass and fused silica capillary columns coated with SP-2250 or SE-54 served to separate products. All spectra were obtained at 70eV.

(22) $HC\equiv{}^{*}CH$ (90% labeled), $Ni(acac)_2$, CaC_2, THF, N_2 (50-60 psig), 2-3d, 85-90°C. For this label purity the following values are calculated (standardized to *m/e* 165 = 100%, ^{13}C in $^{12}C \sim 1\%$) (*m/e*, 163, 164, 166, 167)): zipper: 3.0, 38.2, 21.6, 1.7; cyclobutadiene: 4.6, 46.9, 29.3, 2.7; random: 7.3, 51.3, 33.5, 4.4; metal benzene: 3.6, 43.6, 26.3, 2.0. Found: 7.0, 36.5, 20.4, 1.2.

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