Synthesis and Pyrolysis of the Diels–Alder Adduct of Ditropyl and Dimethyl Acetylenedicarboxylate

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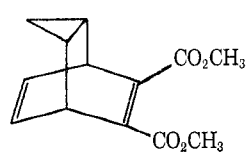
Dimethyl acetylenedicarboxylate (1) and ditropyl (3) react in a 2:1 mol ratio at 140° to produce a 24–42% yield of the Diels–Alder adduct 4. Adduct 4 was shown to possess two three-membered rings *formally* derivable from a bisnorcaradiene structure. Thermal decomposition of 4 proceeds in two stages, each of which produces dimethyl phthalate. Of the possible low-molecular-weight products only benzene was *tentatively* identified.

Cyclic conjugated trienes, when reacted with dieneophiles, generally produce Diels–Alder adducts in which considerable bond reorganization has taken place.[2] Thus the reaction of cycloheptatriene with dimethyl acetylenedicarboxylate (1) yields *mainly* dimethyl tricyclo[3.2.2.0^{2,4}]nona-6,8-diene-6,7-dicarboxylate[3,4] (2). Tetracyanoethylene produces an anal-



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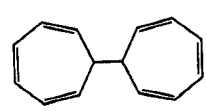

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ogous product.[5,6] It is therefore of interest to establish the structure of the Diels–Alder adducts of ditropyl (biscycloheptatrienyl) (3)[7a] with one or more dieneophiles, with particular emphasis on the question whether bond reorganization remains intraannular or involves the interaction of one ring with the other.[7b]

Experimental Section[8]

Dimethyl Acetylenedicarboxylate (1).—1, Eastman Organic Chemicals (Cat. No. 7235), was distilled and the fraction collected at 66–73° (6–7 mm), possessing n^{20}D 1.4466, was used.

Ditropyl (7,7′-biscycloheptatriene) (3) was prepared in quantity according to the method of Harrison, *et al.*,[7a] from tropylium fluoroborate[9] and zinc dust. The material thus obtained proved quite unstable during short periods of storage in the dark. However, after chromatography on Merck Alumina (No. 71707) using pentane as eluent, a white solid, mp 60.0–61.5° (lit.[7a] 61.0°), was obtained which remained unchanged after several years.

Adduct 4.—A mixture of compound 3 (5.0 g, 27 mmol), ester 1 (9.7 g, 68 mmol), and redistilled xylene (10 ml) was refluxed under nitrogen for 5 hr. Evaporation at 1–5 mm and room temperature overnight produced a red, viscous gel which on trituration with methanol yielded an off-white solid. Recrystallization from methanol furnished 3.0 g (24%)[10] of white crystals, mp 173.2–175.8°. Further recrystallization from the same solvent gave small, white, fluffy needles: mp 175.2–176.3°; uv (EtOH) end absorption with a shoulder at 241–242 mμ (log ε 3.78); ir (CCl_4) 3060, 3030, 2993, 2950, 2900, 2840 (C–H), 1720 (conjugated ester C=O, broad, intense, and complex), 1632, 1596 (C=C), 1432, 1342 ($COOCH_3$), 1260, 1057 cm^{-1} (C–O); nmr data are summarized in Table I.

TABLE I

60-MHz NMR DATA OF 4[a]

Chemical shift (τ)	Relative area	Signal appearance	Assignment
9.08	1	Unresolved multiplet (5.0)[b]	H-3; H-3′
8.77	2	Unresolved multiplet (5.8)[c]	H-2, 4; H-2′,4′
6.23	6	Singlet	$-OCH_3$
5.95	2	Unresolved multiplet (10)[d]	H-1,5; H-1′,5′
4.00	2	"Triplet"[e]	H-8,9; H-8′,9′

[a] Data were obtained with a $CDCl_3$ solution containing internal TMS. No simplification of the spectrum was apparent at 100 MHz. A spectrum obtained at 100 MHz using a C_6H_6 solution of compound 4 exhibited only the expected upfield shift (0.1–0.3 ppm) of all signals with no attendant simplification of the spectrum. CCl_4 and C_5H_5N also failed to resolve the resonances. The numbers in parentheses refer to peak widths at half-height in Hz. [b] Irradiation of this signal produces no change in the other signals except the τ 8.77 resonance which then resembles the τ 5.95 signal. [c] Irradiation of this signal causes the τ 9.08 resonance to sharpen and the τ 5.95 resonance to mirror the τ 4.00 signal (AA′XX′). [d] Irradiation of this signal causes the τ 9.08 and 8.77 resonances to sharpen and the τ 4.00 signal to collapse to a singlet. [e] Irradiation of this signal causes the τ 5.95 resonance to approximately mirror the τ 8.77 signal.

Anal. Calcd for $C_{26}H_{26}O_8$ (assuming 2 mol of 1 per mol of 3): C, 67.0; H, 5.6; O, 27.4; mol wt, 466.5. Found: C, 67.0; H, 5.7; mol wt, 442 (cryoscopic camphor solvent).

Hydrogenation of the Adduct.—An ethyl acetate solution of the adduct 4 (0.844 g, 1.8 mmol), stirred at room temperature in contact with 5% Pd–C catalyst (0.235 g) absorbed 97% of the theoretical quantity of hydrogen (assuming four double bonds per molecule) in 1.5 hr. Chromatography on Alumina (Woelm, neutral, activity grade I, chloroform eluent) and recrystallization from ethyl acetate produced glistening white crystals of the octahydro adduct 5, mp 224–225°. The nmr data are given in Table II.

Anal. Calcd for $C_{26}H_{34}O_8$: C, 65.8; H, 7.2; O, 27.0; mol wt, 474.5. Found: C, 65.8; H, 7.5; mol wt, 459 (cryoscopic camphor solvent).

(1) (a) Partial support of this work from the North Carolina State University Engineering Foundation and Faculty Research and Professional Development Fund is acknowledged with pleasure. (b) Author to whom correspondence should be addressed. (c) Partial support by a grant from the Gulf Research and Development Co. is gratefully acknowledged.

(2) A. S. Onishchenko, "Diene Synthesis," L. Mandel, Translator, Daniel Davey and Co., New York, N. Y., 1964, pp 373–383.

(3) (a) K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953); (b) M. J. Goldstein and A. H. Gevirtz, *Tetrahedron Lett.*, 4413 (1965); (c) M. J. Goldstein and A. H. Gevirtz, *ibid.*, 4417 (1965).

(4) Systematic nomenclature graciously supplied by Dr. Kurt L. Loening, Director of Nomenclature, Chemical Abstracts Service, Columbus, Ohio.

(5) N. W. Jordan and I. W. Elliott, *J. Org. Chem.*, **27**, 1445 (1962).

(6) G. H. Wahl, Jr., *ibid.*, **33**, 2158 (1968).

(7) (a) A. G. Harrison, L. R. Honnen, and H. J. Dauben, Jr., *J. Amer. Chem. Soc.*, **82**, 5598 (1960). (b) *E.g.*, R. S. Givens, *Tetrahedron Lett.*, 663 (1969). In a study of the photochemistry of 3, no product directly attributable to interannular reaction was isolated.

(8) All melting points are corrected. Ultraviolet spectra were obtained using a Beckmann DK-2 spectrophotometer. Infrared spectra were determined using a Perkin-Elmer 521 spectrophotometer. Elemental analyses were performed by Schwarzkopf Laboratories, Woodside, N. Y. Thermal analyses were obtained using DuPont 900 DTA and 950 TGA instruments. Nmr spectra were recorded with both Varian T-60 and HA-100 spectrometers.

(9) K. Conrow, *Org. Syn.*, **43**, 101 (1963).

(10) A yield of 42% was obtained by heating 0.5 g of compound 3 and 1.2 g of compound 1 at 140° for 2 hr under N_2 without solvent. *However, a similar reaction of 5.0 g of 3 and 12 g of 1 produced a violent explosion!*

TABLE II

100-MHz NMR DATA OF 5[a]

Chemical shift (τ)	Relative area	Signal appearance	Assignment
9.49	1	Unresolved multiplet (4.5)	H-3; H-3′
8.88	2	Unresolved multiplet (7.0)	H-2,4; H-2′,4′
8.78, 8.74	4	Two overlapping unresolved multiplets	H-$8_{ex,en}$,$9_{ex,en}$; H-$8'_{ex,en}$,$9'_{ex,en}$
7.72	2	Broad multiplet (9.5)	H-1,5; H-1′,5′
7.18	2	Singlet (3.5)	H-6,7; H-6′,7′
6.39	6	Singlet (3.5)	$-OCH_3$

[a] Data were obtained with a $CDCl_3$ solution containing internal TMS. The numbers in parentheses refer to peak width at half-height in Hz.

Saponification of the Adduct.—The adduct **4** (0.5 g) was refluxed for 5 hr with 25 ml of 20% aqueous KOH. Cooling, acidification with concentrated HCl, and stirring for 2 days produced a white solid which, after two recrystallizations from aqueous methanol furnished off-white crystals which do not melt, but turn brown and slowly decompose on heating above 100°.

Anal. Calcd for $C_{22}H_{18}O_8$: C, 64.4; H, 4.4; O, 31.2; neut equiv, 102.5. Found: C, 64.1; H, 4.3; neut equiv, 105.

Thermal Analysis of the Adduct 4.—A differential thermal analysis scan (10°/min, N_2 atmosphere) showed a sharp endotherm at the melting point and a broad exotherm beginning at 225° and peaking at about 265°. A shallow endotherm, peaking at about 290° was also noted.

A thermogravimetric scan (12.0 mg, 15°/min, N_2 atmosphere) indicated no weight loss until about 220°. These results are summarized in Table III.

TABLE III

THERMOGRAVIMETRIC ANALYSIS OF THE ADDUCT 4

Temperature °C	% wt loss
200	0
225	1.0
250	8.5
275	41.0
300	51.0
325	54.0
375	58.0
400	60.5
425	64.0
450	69.0
500	75.0

Decomposition of the Adduct 4. A. Under Nitrogen.—A flask containing 1.0 g of compound **4** which was connected to a trap at −78° was flushed with N_2 several times. It was then heated under an atmosphere of N_2 at 235–255° for 1 hr to produce a dark red, amorphous solid wet with a sweet-smelling liquid. Vacuum distillation followed by vpc and ir analyses clearly showed the volatile fraction to be predominantly (>90%) dimethyl phthalate (**6**). Approximately nine other minor products were detected by vpc. One of these products (~0.5%) is benzene as shown by vpc peak height enhancement experiments.

The solid product [ir (KBr) 1720, 1200 cm^{-1} (conjugated ester)] decomposes at about 280° without melting.

Anal. Calcd for $C_{16}H_{16}O_4$ (loss of 1 mol of **6** from **4**): C, 70.6; H, 5.9; O, 23.5. Found: C, 70.9; H, 6.2.

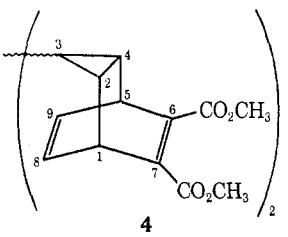
The 280° volatile decomposition product was also identified by ir and vpc as dimethyl phthalate (**6**). The nonvolatile product was a brittle, dark amorphous solid which was not further characterized.

B. In the Presence of Hydroquinone.—An experiment which differed from A only by the inclusion of 0.026 g of hydroquinone and by heating under vacuum gave essentially identical results.

C. Under High Vacuum.—An experiment similar to A, in which a vacuum of 10^{-4}–10^{-5} Torr was employed and in which the evacuated flask was immersed in a preheated oil bath at 240° for 1 hr produced a purer but lower yield of compound **6** and considerable sublimation of compound **4** into the tube connecting the flask to the receiver.

Discussion

Structure of the Adduct 4.—The elemental analysis and molecular weight data clearly indicate a 2:1 acetylenedicarboxylate–ditropyl addition product. The infrared absorption of the product and its saponification to a tetraacid further show that the ester grouping remains intact during the reaction. Finally, hydrogenation indicates the presence of only four double bonds per molecule. A centrosymmetric (C_{2h}) structure[11] of adduct **4** which is in accord with these results is given below.



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The nmr data (Table I) strongly confirm this assignment. Thus the presence of *only* five different types of hydrogens is evident. Furthermore, the low field, apparent triplet at τ 4.00 is strongly suggestive of a vinyl group in a symmetric bicyclic skelton. Its immediate environment is further established by the collapse of the signal to a singlet on irradiation of the τ 5.95 resonance. That this latter resonance is associated with bridgehead hydrogens is proven by its shape and location and by the decoupling experiments. The sharp resonance at τ 6.23 with relative area 6 is confidently assigned to the methyl hydrogens of the ester groups.

The two high-field resonances are completely consistent with a symmetrically substituted, cyclopropyl grouping. The lack of fine structure in these signals (in a variety of solvents) precluded a completely secure assignment of the relative configuration of H-3 with respect to H-2 and 4 (*i.e.*, cis or trans). However, the relatively small peak widths observed (5.0–5.8 Hz) argue strongly for a small (2–4 Hz) coupling constant ($^3J_{2,3}$). Thus the cyclopropyl hydrogens are most probably trans rather than cis since $^3J_{cis} > {}^3J_{trans}$.[12]

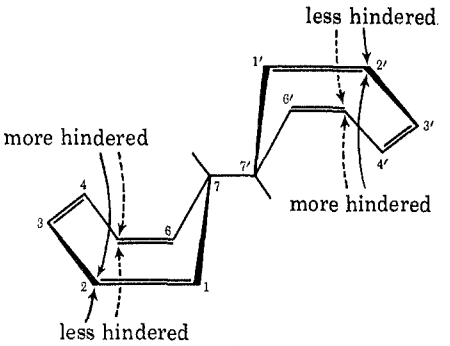
The sole remaining structural ambiguity concerns the orientation of the three-membered ring, *i.e.*, whether it is located over the substituted or over the unsubstituted double bond. Based on the steric control of approach argument which was originally proposed by Alder and Jacobs[3a] and confirmed by Goldstein and Gevirtz[3c] for the cycloheptatriene system, the most likely arrangement is as shown in **4**. Since **5** is very probably the most stable conformation of ditropyl (**3**),[13] approach of dieneophile **1** at carbons 2 and 5 (and at 2′ and 5′) to produce the adduct **4** will be substantially less hindered from the bottom of the "boat" than

(11) Systematic name:[4] Tetramethyl[3,3′-bitricyclo[3.2.2.$0^{2,4}$]nona-6,8-diene]-6,6′,7,7′-tetracarboxylate.

(12) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol 2, Pergamon Press, New York, N. Y., 1966, pp 692–695, and references cited therein.

(13) Conformation **5** is used without comment in G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, *J. Amer. Chem. Soc.*, **91**, 2823 (1969). Pertinent arguments concerning the conformations of seven-substituted cycloheptatrienes are given by R. W. Murray and M. L. Kaplan, *ibid.*, **88**, 3527 (1966), and by A. P. Ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **82**, 741 (1963).

from the top (see **5**). It is encouraging to note that this mode of attack also predicts a trans orientation of the two types of cyclopropyl hydrogens.



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Pyrolysis of the Adduct 4.—Cope has demonstrated that cyclobutene may be produced by pyrolysis of the Diels–Alder adduct of 1,3,5-cyclooctatriene and compound **1**,[14] and Wiberg[15] has shown that the similar decomposition of compound **2** results in detectable quantities of cyclopropene. Consequently, we felt that pyrolysis of **4** might yield one or more isomers of C_6H_6. The *concerted* loss of two molecules of dimethyl phthalate from adduct **4** would produce 3,3′-biscyclopropene which *might* be transformed further into other C_6H_6 isomers by various intramolecular rearrangements.[16]

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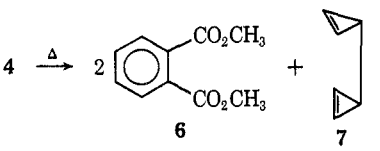
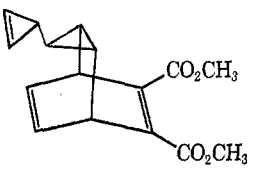


6 **7**

However, the thermal analysis data are not consistent with such a *concerted* decomposition. Apparently the loss of one molecule of ester **6** produces the reactive cyclopropene derivative **8** which polymerizes before a



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second molecule of **6** is lost. This interpretation, which is consistent with the reactivity of cyclopropene observed by Wiberg and Bartley,[15] is supported by the analytical and spectral data for the nonvolatile pyrolysis product and, also, by the further production of ester **6** on pyrolysis of the polymer at a higher temperature.

Registry No.—**4**, 25967-00-4; **5**, 25967-01-5; **8**, 25967-02-6.

Acknowledgment.—We are grateful to Mr. Russell J. Miller for initial nmr measurements.

(16) R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *ibid.*, **87**, 5139 (1965). A study of the rearrangement of several polyphenyl derivatives of **7** through the assumed intermediacy of Ladenburg and Dewar benzene structures.

Stable Carbonium Ions. CV.[1] Protonation of Sulfoxides and Sulfones in Fluorosulfuric Acid–Antimony Pentafluoride–Sulfuryl Chloride Fluoride Solution

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A series of sulfoxides and sulfones have been studied in HSO_3F–SbF_5 solution diluted with sulfuryl chloride fluoride. Protonation on sulfur was observed for sulfoxides by nmr spectroscopy. The site of protonation of sulfones is on oxygen. Protonated sulfoxides and sulfones in FSO_3H–SbF_5–SO_2ClF solution are stable up to 65° except protonated benzyl *tert*-butyl sulfone which cleaved to *tert*-butyl cation and phenylmethanesulfinic acid even at a temperature as low as −78°.

The interaction of sulfones and sulfoxides with Lewis acids has been studied by a number of investigations.[3–7] In some cases solid adducts could be obtained.[3,7] Cryoscopic studies of sulfoxides and sulfones in sulfuric acid solution have also been carried out.[8–11] Gillespie[8,10] showed that aryl sulfoxides are strong bases and aryl sulfones are weak bases in sulfuric acid. However, both cryoscopic and conductimetric measurements of Hall and Robinson[11] showed that diphenyl sulfone was a nonelectrolyte in sulfuric acid. These results do not agree with those of Gillespie.[8,10] Alkyl sulfones were found to behave as weak electrolytes in sulfuric acid.[11,12] It was also indicated that dimethyl sulfoxide has a cryoscopic *i* factor of slightly greater than two,[11] in agreement with complete protonation according to eq 1.

$$(CH_3)_2S{=}O + H_2SO_4 = (CH_3)_2\overset{+}{S}OH + HSO_4^- \qquad (1)$$

* To whom correspondence should be addressed.
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(9) H. H. Szmant and G. A. Brost, *J. Amer. Chem. Soc.*, **73**, 4175 (1951).
(10) R. J. Gillespie and R. C. Passerin, *J. Chem. Soc.*, 3850 (1956).
(11) S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42**, 1113 (1964).
(12) E. M. Arnett and C. F. Douty, *J. Amer. Chem. Soc.*, **86**, 409 (1964).