The chemistry of cyclo-octatetraene and its derivatives

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Foreword

The story of cyclo-octatetraene began in 1911–13 with Willstätter's multistep preparation from pseudo-pelletierine, surely one of the most hopeful synthetical projects ever undertaken in organic chemistry. Although for many years doubt was cast on the validity of this work it was proved in 1947 to have been correct. Yet in view of its inaccessibility, for thirty years after its discovery the likelihood of ever being able either to solve the fascinating theoretical speculation as to whether cyclo-octatetraene was an aromatic compound akin to benzene, or to investigate its properties in any detail, seemed wholly remote.

The writer recalls the almost incredible news reaching this country in 1945 that Reppe had prepared cyclo-octatetraene in kilogram quantities by the polymerisation of acetylene, and his wonder on seeing this beautiful yellow liquid in bulk. Since 1945, and indeed a few years before in Germany, the investigation of this remarkable compound has been pursued in chemical laboratories throughout the world, and has revealed an astonishing variety of chemical behaviour, little of which could have been foretold by application of chemical theory or by analogy with the behaviour of other substances, and in which, in contrast with benzenoid compounds, the cyclo-octatetraene nucleus seldom retains its original structure.

It has long been evident that a comprehensive account of the chemistry of cyclo-octatetraene was needed, not only to summarise the great volume of work that has been done with it but, on the basis of the information disclosed, to lay the foundations of a real knowledge of the chemistry of this hydrocarbon. This timely book by Dr G. I. Fray in collaboration with Dr R. G. Saxton fulfils both these objectives, and generations of chemists who will continue to investigate this versatile hydrocarbon will be grateful to be able to 'look it up in Fray and Saxton'.

W. BAKER

For
Joyce and Patricia

Preface

Z,Z,Z,Z-Cyclo-octatetraene (COT) (I) has played an outstanding role in many aspects of theoretical and synthetical chemistry. As [8]annulene, the next higher vinylogue of benzene, it is of fundamental importance for the understanding of cyclic alternating π-systems. As a medium-ring polyene, it undergoes a wide variety of reactions which are often accompanied by skeletal transformations, and it is the progenitor of a large number of interesting species including, for example, cyclobutadiene (II), semibullvalene (III), the homotropylium cation (IV), the dianion (V), 1H-azonine (VI), basketene (VII), bullvalene (VIII), [16]annulene (IX) and triamantane (X).

(I)   (II)   (III)   (IV)

(V)   (VI)   (VII)

(VIII)   (IX)   (X)
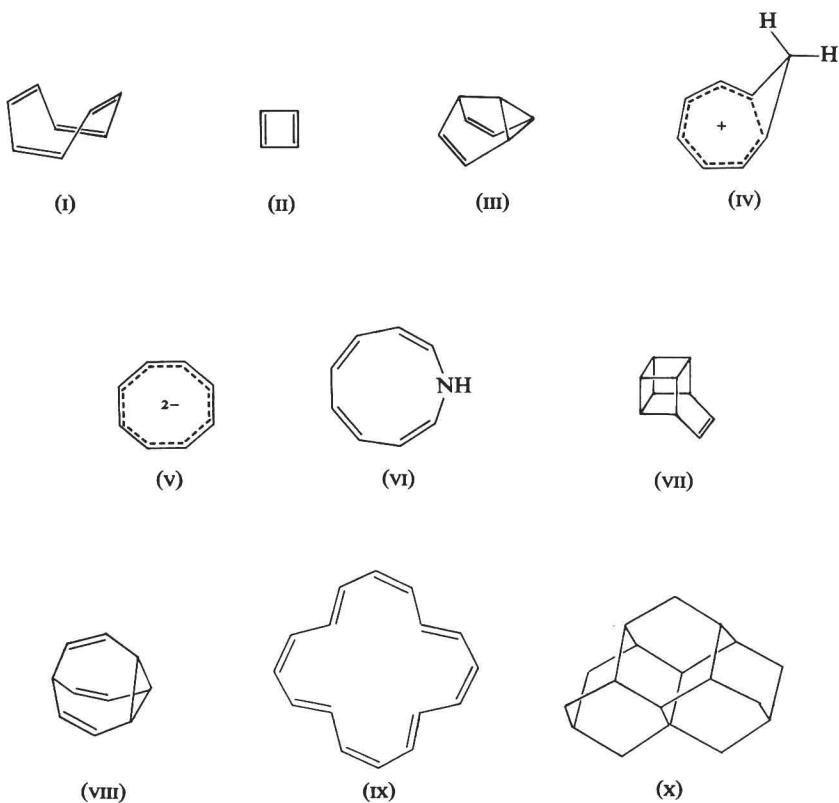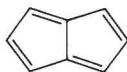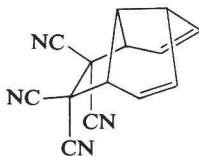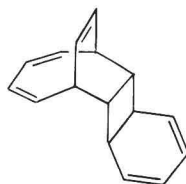
(XI)   (XII)   (XIII)

COT also forms an exceptional variety of complexes with transition metals. In addition to the interest, from the viewpoint of bonding theory, of these multifarious derivatives (some of which exhibit intriguing fluxional behaviour), modifications of the attached C_8H_8 ligand may occur, leading to systems such as pentalene (XI). Moreover, reactions of metal-coordinated COT can provide routes to systems which are not readily available by the conventional transformations of organic chemistry; examples include the dihydrotriquinacene-derivative (XII) and the COT dimer (XIII).

We feel that our interest in such a molecule needs no apology, and the rapid development of its chemistry during the last decade provides some justification for a new summary of existing knowledge. In chapter 1, the formation, physical properties and chemical reactions of COT are outlined, while chapter 2 deals with substituted (and annulated) derivatives of the parent compound; in order to keep the length of the book within bounds, benzo-derivatives and analogues containing hetero-atoms, e.g. azocines, have been omitted. Chapter 3 attempts to cover, as far as possible, the known chemistry of those compounds which are immediately derivable from COTs. By means of an appendix, prepared after the main typescript had been submitted, we have been able to include additional material from the later literature (up to the end of 1976).

We are indebted to previous reviewers of this field, notably the following:

L. E. Craig, *Chem. Rev.*, 1951, **49**, 103

R. A. Raphael, in *Non-Benzenoid Aromatic Compounds* (ed. D. Ginsburg), Interscience, 1959, chapter VIII

G. Schröder, *Cyclooctatetraen*, Verlag Chemie, Weinheim, 1965

H. P. Figeys, *Topics in Carbocyclic Chem.*, 1969, **1**, 269

L. A. Paquette, *Tetrahedron*, 1975, **31**, 2855.

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                                                        R.G.S

Contents

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Cyclo-octatetraene

1. Formation

Cyclo-octatetraene was first described in 1911 by Willstätter and Waser,[1] who obtained it from pseudo-pelletierine (**1**), an alkaloid from the bark of the pomegranate tree, by a lengthy degradation proceeding *via* cyclo-octa-1,3,5-triene (see also ref. 2). The resulting sample of COT probably contained *ca.* 30% of styrene,[3] and its authenticity did not go unchallenged (for a review of the evidence, see ref. 4). However, the original reaction sequence was repeated some thirty-six years later by Cope and Overberger[3, 5] (scheme 1), and Willstätter's claim was completely vindicated.

Scheme 1
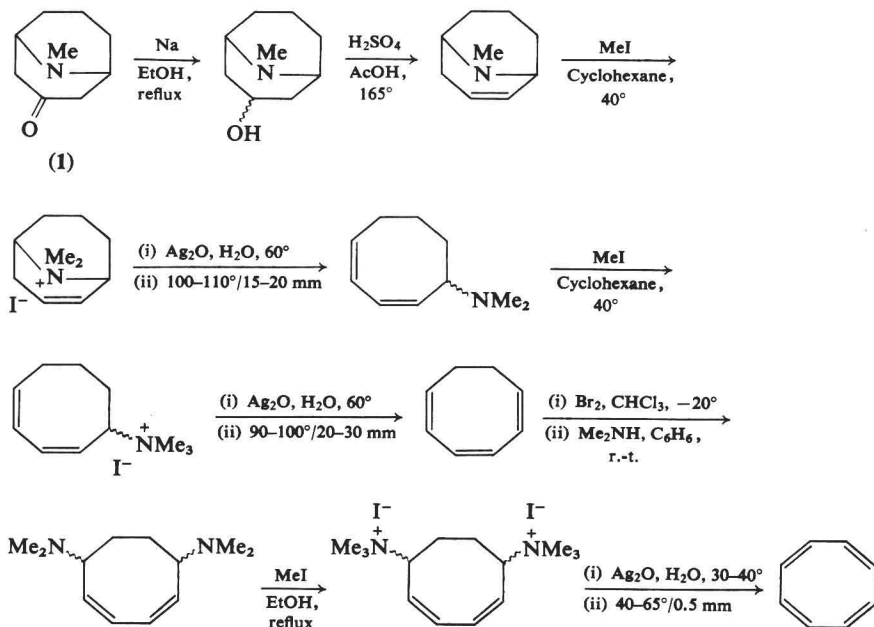
This type of approach to COT may be simplified by starting from the readily available cyclo-octa-1,5-diene, but the introduction of the additional double

bonds by means of the Hofmann elimination procedure,[6,7] or by dehydro-bromination,[8-10] results in poor yields of a product which is contaminated with styrene, benzocyclobutene etc.

In 1940, the important discovery that COT could be produced by the cyclo-tetramerisation of acetylene was made in the laboratories of Badische Anilin- & Soda-Fabrik AG, by Reppe *et al.*[11] The reaction is best carried out (up to 70% conversion) in dry tetrahydrofuran or dioxan at 85–90° and a pressure of 15–25 atmospheres, in the presence of nickel(II) compounds such as the cyanide or chelate 'ato' complexes from acetylacetone, acetoacetic esters, salicylaldehyde, *N*-alkylsalicylaldimines etc.[11-15] (a much less efficient conversion results from the use of $(CH_2=CH.CN)_2Ni$ [16]). The process has been reviewed,[17-19] and Schrauzer[15,18] has proposed a mechanism involving an intermediate octahedral nickel complex (**2**) (but see appendix). (For a discussion of bonding in this type of complex, see refs. 20, 21. An earlier hypothesis proposed the intermediacy of a cyclobutadiene complex (**3**)[22].)
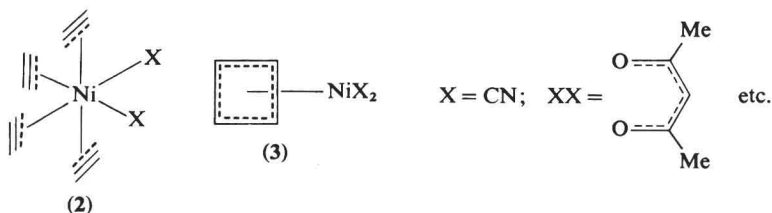

Among the by-products of the Reppe process are benzene, styrene, naph-thalene, azulene, *Z*-1-phenylbuta-1,3-diene, vinylcyclo-octatetraene, and a $C_{12}H_{12}$ fraction of unknown constitution.[23-26]

Octadeuteriocyclo-octatetraene may be prepared by similar cyclotetramer-isation of dideuterioacetylene.[27]

COT has been identified as one of the products of the thermal polymer-isation of acetylene,[28,29] and very low yields of COT result from u.v. irradiation of acetylene.[30,31]

COT is also formed by various isomerisation processes occurring in other C_8H_8 compounds. Reactions which generate bicyclo[4.2.0]octa-2,4,7-triene (**4**), unless carried out at low temperatures,[32] lead to COT *via* valence isomerism (see p. 10); examples are given in scheme 2.

Other skeletal rearrangements leading to COT are outlined in schemes 3 and 4.

Additionally, COT is a minor photo-product of basketene (**6**)[55] and of the dimethyl acetylenedicarboxylate adduct (**7**),[56] and it has been detected amongst the pyrolysis products of the *β*-lactone (**8**)[57] and of *α*-cellulose.[58]

Finally, COT has been identified as one of the constituents responsible for the odour of tomatoes,[59] and may therefore be a natural product!

Scheme 2
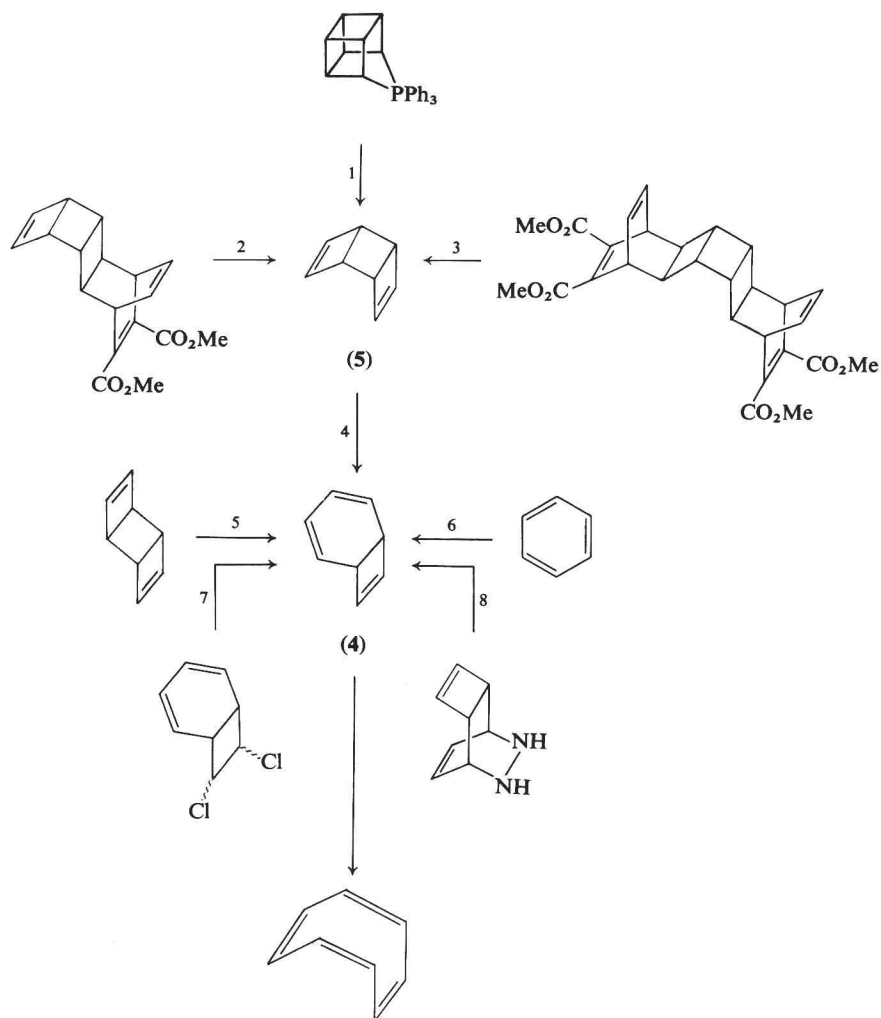
Reaction	Reagents and conditions	Yield (%)	Ref.
1	120°	85[a]	33
2	140–160°	—	34
3	*ca.* 150°	—	34
4	(>100°), 90–121°	—	(35), 36
5	{ *o*-Dichlorobenzene, 140°	100	35
	{ or e.g. AgBF$_4$, Me$_2$CO, reflux	100	37
6	HC≡CH, *hv*	(Very low)	38
7	NaI, NaHSO$_3$, Me$_2$CO, r.-t. → 50°	35	39
8	MnO$_2$, n-hexane, r.-t.	75–80	40

[a] Mixture of (5) and COT (4:1).
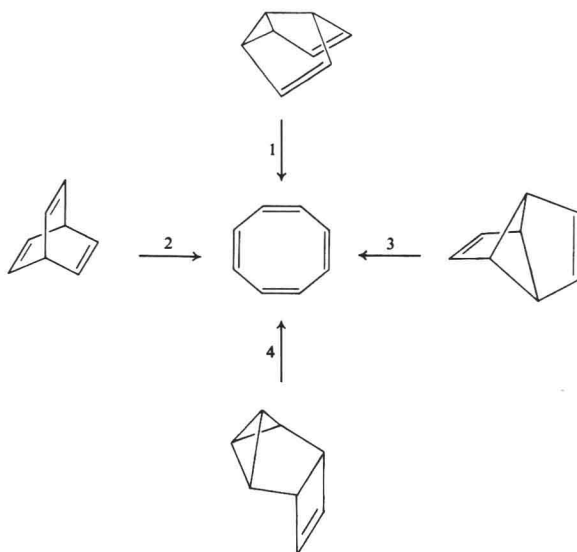
Reaction	Reagents and conditions	Yield (%)	Ref.
1	{ AgNO₃, MeOH(aq.), 80°	100	41
	{ or 427°/30 mm (flow system)	56	(42), 43
2	*hv*, methylcyclohexane	20	44
3	*hv* (Pyrex), e.g. isopentane, −60°	Up to 29	45
4	{ 400–500°	—	46
	{ or e.g. AgClO₄, Me₂CO, r.-t.	—	46

2. Purification

The purification of COT by fractional distillation and low-temperature crystallisation has been described in detail.[60]

For separation by liquid–solid column chromatography, see ref. 44.

For the use of gas–liquid chromatography, see e.g. refs. 9, 40, 44, 49; for other gas-chromatographic data see refs. 61, 62.

COT may also be purified *via* its silver nitrate complex $(COT)_2(AgNO_3)_3$ (see p. 51), from which it is readily regenerated by treatment with aqueous sodium chloride.[63]

COT forms an inclusion complex with thiourea,[64] but no use of this property appears to have been made.

COT is somewhat sensitive to air and light, and is best stored in the dark below room-temperature, in the presence of a free-radical inhibitor such as hydroquinone. Even so, samples of COT which have been kept for some time inevitably contain dimeric and polymeric material (see pp. 12–13, 34).

Scheme 4

Reaction	Reagents and conditions	Yield (%)	Ref.
1	*hv*	—	47
2	{ 345° (g.l.c.)	100	48
	{ or *hv* (Corex), Me$_2$CO, Et$_2$O^a	—	—
3	*hv* (Pyrex), Et$_2$O or THF	80–82	(50), 51, 52
4	*hv*	—	50
5	25°	100	41
6	*hv*	(Low)	53
7	240° (flow system)	100	54

^{a} Conditions used for 1,4-dideuteriocyclo-octatetraene (40%).[49]

(6)

(7)

(8)
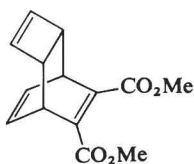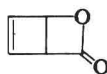
3. Physical properties

COT is a yellow liquid, with a strong distinctive odour.

Boiling-point (°C)	142–143	Pressure (mm Hg)	760		Ref. 11
	48		31		65
	42–42.5		17		11
Melting-point (°C)	−4.7				27, 66
	−4.5 to −3.5				63
Triple-point (K)	268.48				66
Density (g cm⁻³)	0.9382	Temperature (°C)	0		11
	(0.9206), 0.9209		20		(11), 60
	0.9196		25		60
	0.9117		30		60
Viscosity (cP)	1.42	Temperature (°C)	20		60
	1.30		25		60
	1.18		30		60

Heat capacity (12–330 K): see ref. 66

Vapour pressure (0–75 °C): see ref. 66

Heat of fusion (cal mol⁻¹) 2694.6   66

Heat of combustion (25 °C) (kcal mol⁻¹) −1084.9   67
                                        −1086.5   68

Heat of hydrogenation (25 °C) (kcal mol⁻¹) −97.96   69

|				
Refractive index (Na$_D$)[a]	1.5379	Temperature (°C)	20	60
	(1.5348), 1.5350		25	(63), 60, 69
	1.5323		30	60

[a] For measurements at other wavelengths, see ref. 60.

Dielectric constant (20 °C) 2.74   11

First ionisation potential (adiabatic)[a] (eV) 7.99   70
                                               8.0   71
                                               8.04   72
                                               8.06   73
[a] For higher ionisation potentials, see refs. 71, 72.

Electron affinity (kcal mol⁻¹) 13.3   74

Half-wave reduction potentials: see e.g. refs. 65, 75–82

Magnetic susceptibility (cm³ mol⁻¹) −0.0000539   83, 84

Magnetic rotation (μrad) 1009   85

The following have been calculated from thermochemical data:

Heat of vaporisation (25 °C) (cal mol^{-1})   10300   Ref. 66

Entropy (cal deg^{-1} mol^{-1})	(Liquid, 25 °C)	52.65	66
	(Gas, 25 °C, 1 atm)	78.10	66

Heat of formation (kcal mol^{-1})	(Liquid, 25 °C)	60.82	68
	(Gas, 25 °C)	71.0	86, 87
		71.1	88, 89
		71.12	90
		71.3	91
		71.9	69

Heat of isomerisation to styrene (kcal mol^{-1})	(Liquid, 25 °C)	−36.10	68
	(Gas, 25 °C)	−36.3	69

Empirical (thermochemical) resonance energy (stabilisation energy) (kcal mol^{-1})		
	2.4	69
	3.0	92
	3.3	93
	3.6	69
	4.8	67

For other calculations, see table 5, p. 11.

U.v. spectrum. COT exhibits a broad weak absorption band with a maximum near 280 nm (table 1), which tails into the visible region;[94,95] there is strong 'end-absorption', with a shoulder at *ca.* 205 nm[95,96] (ε 20000[97]). The absorption curve is reproduced in refs. 60, 94, 98. (Measurements have also been made in the gas phase[94,95].)

<div align="center">Table 1</div>

Solvent	$\lambda_{max.}$ (nm)	ε	Ref.
MeOH	280	350	94
EtOH	280	435	94
n-Heptane	280	235	94
CHCl$_3$	282	200	99
Cyclohexane	283	255	94
Iso-octane	283	250	98
CCl$_4$	288	320	94

I.r. spectrum. The C=C stretching vibration in COT gives rise to an absorption band with $\nu_{max.}$ (liquid film) 1634,[99] 1635[27] cm^{-1}. The spectrum is reproduced in refs. 27, 60; for complete lists of the principal absorption maxima, see refs. 27, 99. (Measurements have also been made in the gas phase[27,99].)

Raman spectrum. See refs. 27, 100, 101.