6.05 μ (weak, C=N) and 8.35 and 8.85 μ. Five recrystallizations from acetonitrile gave an analytical sample, mp 175–183°, whose ^1H nmr spectrum (D_2O) contained peaks at δ 2.3–3.6 (m, 8 H, CH_2) and 2.15 (d, 3 H, J_{PH} = 13 Hz, P-CH_3).

Anal. Calcd for $C_6H_{12}NO_2P$: C, 44.72; H, 7.60; N, 8.69; P, 19.22. Found: C, 44.56; H, 7.43; N, 8.52; P, 18.96.

Reaction of Tri-*n*-butylphosphine with Hydroxylamine.—A mixture of 10 ml of absolute ethanol, 1.0 g (0.014 mol) of hydroxylamine hydrochloride, and 1.3 ml (1.1 g, 0.0055 mol) of tri-*n*-butylphosphine was refluxed for 2 hr. The mixture was filtered under nitrogen and the filtrate was poured into saturated ammonium chloride solution. The mixture was extracted with two 25-ml portions of tetrahydrofuran. The combined extracts were washed with saturated sodium chloride solution and dried over sodium sulfate under nitrogen. The solvent was evaporated and the residue was dried *in vacuo* over phosphorus pentoxide to give 0.78 g (66%) of tri-*n*-butylphosphine oxide. The sample contained an ir peak (Nujol) at 8.65 μ for $P \rightarrow O$; its ^{31}P nmr peak (5 *M* in tetrahydrofuran) was at −42.7 ppm (lit.[4] −43.2, −45.8 ppm).

This reaction was repeated using a 1:1 (*v/v*) pyridine–absolute ethanol solution. Work-up afforded a 50% yield, bp 126–130° (0.8 mm) [lit.[10] bp 300° (760 mm)].

Reaction of Triphenylphosphine with Hydroxylamine.—A mixture of 10.0 g (0.038 mol) of triphenylphosphine, 2.72 g (0.038 mol) of hydroxylamine hydrochloride, and 60 ml of pyridine was refluxed under nitrogen for 16 hr. The mixture was cooled and poured into 125 ml of saturated ammonium chloride solution. The two-phase mixture that formed was extracted with two 60-ml portions of benzene. The aqueous layer was filtered and extracted with a third 60-ml portion of benzene. The combined extracts were dried over sodium sulfate, and the solvent was removed to give 8.0 g (75%) of crude triphenylphosphine oxide, mp 151–159°, ^{31}P nmr signal (5.5 *M* in $CDCl_3$) at −27.6 ppm (lit.[4] −23.0 to −27.0 ppm). After recrystallization from benzene–cyclohexane, it melted at 158–161° (lit.[11] mp 156°).

Registry No.—Hydroxylamine, 7803-49-8; Ib thiosemicarbazone, 20817-03-2; IIa, 20797-90-4; IIb, 20797-91-5; tri-*n*-butylphosphine, 998-40-3; triphenylphosphine, 603-35-0.

Acknowledgment.—We are indebted to Stephen W. Dale for the ^{31}P nmr spectra.

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A Study of Some Substituted Cycloheptatrienecarboxylic Acids by Nuclear Magnetic Resonance Spectroscopy

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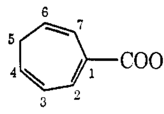
The thermal decomposition of ethyl diazoacetate in the presence of aromatic hydrocarbons, originally reported in 1885 by Buchner and Curtius,[3,4] constitutes one of the more direct preparative routes to cycloheptatriene derivatives. Since the pioneering work of Doering and his coworkers,[5,6] who were the first to recognize the existence of the cycloheptatrienyl (tropylium) cation in organic chemistry, there has been a sustained interest in this class of nonbenzenoid "aromatic" hydrocarbons. An added incentive has been the recognition that the thermal reaction of ethyl diazoacetate with aromatic hydrocarbons proceeds by a carbene mechanism.[7] Although the chemistry of cycloheptatriene has been adequately discussed in the literature,[4,8] the synthesis of substituted cycloheptatrienecarboxylic acids seems to have been confined to those members which are derived from methyl and methoxyl benzenes. Thus, in a series of papers following the initial discovery of the reaction, Buchner prepared alkylcycloheptatrienecarboxylic acids from the reaction of ethyl diazoacetate with toluene,[9] 1,3-dimethylbenzene,[10] and mesitylene.[11] In their extensive work, Johnson and coworkers described the preparation of alkoxycycloheptatrienecarboxylic acids resulting from the reaction of ethyl diazoacetate with anisole,[12] 1,3-dimethoxybenzene,[13,14] 1,4-dimethoxybenzene,[15] and 1,2,4-trimethoxybenzene.[14] Although the positions of the substituents in these products were established by chemical means, in few cases were the positions of the double bonds located. The lability[16] of the triene system under acidic conditions and also heat would preclude any definitive assignments based on chemical transformations.

We have recently had the occasion to prepare several of these known acids in connection with another problem,[17] and it became desirable to reinvestigate the structural assignments by nmr spectroscopic techniques. The monocyclic seven-membered-ring structure of the simplest member, β-cycloheptatrienecarboxylic acid **1**,[18,19] had been unambiguously established in 1956 by the same technique.



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The acids were prepared by published procedures with some minor modifications in some cases. Their melting points and nmr parameters are listed in Table I. Nearly all of the compounds gave first-order spectra with some long-range coupling being observed in certain cases. Their interpretation was based on the observations made on β-cycloheptatrienecarboxylic acid as well

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[2] Geigy Research Laboratories, Switzerland.

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TABLE I

NMR DATA OF CYCLOHEPTATRIENE CARBOXYLIC ACIDS

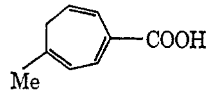
		Chemical shift[a,b]							
Acid	Mp, °C	C-2	C-3	C-4	C-5	C-6	C-7	OMe	Me
1	143–144	474 d ($J_{2,3}$ = 6.0)	387[c] ($J_{3,2}$ = 6.0; $J_{3,4}$ = 9.4)	344[d] ($J_{4,3}$ = 9.4; $J_{4,5}$ = 6.5)	140 t (J = 7.0)	330[d] ($J_{6,7}$ = 9.4; $J_{6,5}$ = 6.5)	410 d ($J_{7,6}$ = 9.4)		
2	99–100	462 d ($J_{2,3}$ = 6.5)	372 d ($J_{3,2}$ = 6.5)		142 d (J = 6.5)	327 m ($J_{6,7}$ = 9.0; $J_{6,5}$ = 7.0)	404 d ($J_{7,6}$ = 9.0)		124 s
3	143–144	468 d ($J_{2,3}$ = 7.5)	338 d ($J_{3,2}$ = 7.5)		155 d (J = 7.0)	328 m ($J_{6,7}$ = 9.6; $J_{6,5}$ = 7.0)	410 d ($J_{7,6}$ = 9.5)	221 s	
4	149–150	457 d ($J_{2,3}$ = 6.5)	368 d* ($J_{3,2}$ = 6.5)		139 s		391 s		122 s
5	189	455 d ($J_{2,3}$ = 7.0)	334 d ($J_{3,2}$ = 7.0)		164 s*		361 s*	223 s	
6	141–142		358 s		136 s		388 s		140 s 120 s (2Me)
7	116–117	455 d ($J_{2,3}$ = 6.3)	370 d ($J_{3,2}$ = 6.3)		136 q (J = 7.0)		395 s		122 s, 63 d (J = 7.0)

[a] Chemical shifts and coupling constants are expressed in hertz. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. J values are within ±0.3 Hz. [b] An asterisk indicates the existence of long-range coupling. [c] Center of a quartet. [d] Center of two triplets; J values were obtained by decoupling.

as on the expected effects of methyl and methoxyl groups on the chemical shifts of the neighboring ring protons.

The spectrum of **1** was recorded at 100 MHz and the peaks corresponding to individual ring protons were assigned by means of spin-decoupling techniques. Irradiation of the C-2 proton doublet ($J_{2,3}$ = 6 Hz) caused the C-3 proton quartet to collapse to a doublet ($J_{3,4}$ = 9 Hz). Irradiation of the methylene triplet simplified the pattern of the multiplet given by the C-4 and C-6 protons from four triplets to a pair of doublets of approximately equal coupling (J = 9.4 Hz). Definitive assignment of the origin of the high field and low field portions of the complex multiplet was achieved by irradiating the C-7 proton. Thus the two triplets in the high field portion were simplified to a triplet ($J_{6,5}$ = 6.5 Hz), while the low field portion of the multiplet remained essentially unchanged. This indicates that the C-6 proton signal is in the high field portion of the multiplet. In this manner all of the peaks in the nmr spectrum of **1** were attributed to the respective ring protons.

The low field doublet in the nmr spectrum of 4-methyl-1,3,6-cycloheptatrienecarboxylic acid (**2**) is



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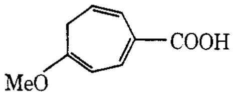
assigned to the C-2 proton. Signals appearing at progressively higher fields are due to the C-7, C-3, C-6, and C-5 protons, respectively. The C-4 methyl group causes some shielding[20,21] of the C-3 proton, while the adjacent C-5 protons remain unaffected compared with those of **1**. The spectrum of the monomethoxycycloheptatrienecarboxylic acid[12] **3** can be interpreted



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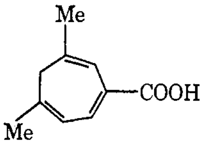
in much the same terms. While the chemical shifts and coupling constants of the C-2 and C-7 protons remain relatively unchanged compared with those of **1**, the C-3 proton is shielded considerably (49 Hz) owing to the delocalization effect[22,23] exerted by the C-4 methoxyl group.

The C-5 methylene protons centered at 155 Hz are somewhat deshielded compared with the doublet in **1**, owing to the inductive effect of the C-4 methoxyl group. Johnson and coworkers[12] had postulated a 1,3,5-triene structure for this compound, based on the mode of formation of anisic acid by degradation. The present nmr data indicate that the actual structure is that of 4-methoxy-1,3,6-cycloheptatrienecarboxylic acid (**3**).

Two 4,6-dimethylcycloheptatrienecarboxylic acids have been obtained by Buchner and coworkers[10] from the reaction of ethyl diazoacetate with 1,3-dimethylbenzene, and subsequent hydrolysis of the derived ester and amide derivatives, respectively. The acid obtained by hydrolysis of the ester can be designated as 4,6-dimethyl-1,3,6-cycloheptatrienecarboxylic acid (**4**), based on nmr spectral considerations. It is of



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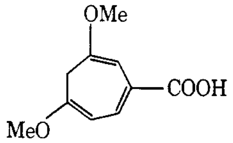
(22) See ref 20, p 721.

(23) J. Feeny, A. Ledwith, and L. H. Sutcliffe, *J. Chem. Soc.*, 2021 (1961).

interest to note that the same structure was proposed some 60 years ago, based on purely chemical methods. Inserting a second methyl group at C-6 causes little change in the chemical shifts of the ring protons compared with those of **2**, except for some additional shielding of the C-3 and C-7 protons. The dimethoxy analog of **4**, which is prepared by the reaction of 1,3-dimethoxybenzene and ethyl diazoacetate, exhibits strong shielding effects in its nmr spectrum. Thus the C-3 and C-7 protons are shielded to the extent of 53 Hz and 49 Hz, respectively, relative to **1**. The C-5 methylene protons which are flanked by the two methoxyl groups are now more deshielded compared with those of **3**. The data are consistent with structure **5**.



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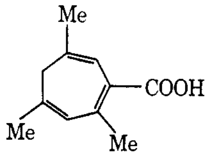
Of the seven isomeric 2,4,6-trimethylcycloheptatrienecarboxylic acids that could result from the reaction of ethyl diazoacetate with 1,3,5-trimethylbenzene, Buchner and Schottenhammer[11] had selected the 1,3,6- and 1,4,6-triene structures as the most compatible with the observed chemical properties. Consideration of the nmr data also leads to these two possible structures, namely 2,4,6-trimethyl-1,3,6-cycloheptatrienecarboxylic acid (**6**) and the isomeric 1,4,6-triene structure (not shown). A peak in the region expected of the C-3 proton appears at higher field than in the spectrum of the monomethyl derivative **2**, presumably because of the presence of a second α-methyl group. Two of the three methyl groups seem to be equivalent. Unfortunately the available data at 60 MHz cannot distinguish between the two isomeric triene structures. The thermal reaction between ethyl diazoacetate and 1,2,3-trimethylbenzene led, after hydrolysis of the resulting ester, to a crystalline acid which is designated as 4,5,6-trimethyl-1,3,6-cycloheptatrienecarboxylic acid (**7**). The slight shielding of the C-3 and C-7 protons is consistent with the presence of methyl groups on C-4 and C-6, respectively (compare **2** and **6**). The presence of a high field quartet and a three-proton doublet due to the C-5 proton and methyl group, respectively, is also consistent with the structural assignment.



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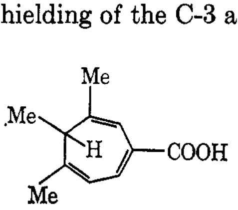

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Experimental Section

Melting points are uncorrected. Nmr spectra were obtained on 60-MHz[24] and 100-MHz[25] instruments in deuteriochloroform, using tetramethylsilane as internal reference. Compounds **1**, **3**, and **5** were prepared by published procedures.

4-Methyl-1,3,6-cycloheptatrienecarboxylic Acid (2).—A mixture of ethyl diazoacetate[26] (40 g) and toluene (1 l.) was gradually heated to 150° in an atmosphere of nitrogen at 25 atm. The pressure was then raised to 40 atm and the mixture was maintained at 150° for 4 hr. Cooling and evaporation of the solvent afforded a dark oil which was fractionated by distillation. A fraction boiling at 60° (0.17 mm) was collected (42.6 g) and was found to be a mixture of at least five components by vpc analysis. A portion of this mixture was dissolved in 60 ml of 10% aqueous methanol containing 10% potassium hydroxide and the solution was stirred overnight at room temperature. Acidification with 3 *N* hydrochloric acid, followed by extraction with ether and processing in the usual way, gave a pale yellow syrup which crystallized partially after standing at 0° for 2 weeks. The product was recrystallized from a mixture of ether and petroleum ether: yield 0.5 g; mp 99–100° (lit.[9] mp 107–108°); λ_{max} 290 mμ (MeOH, aqueous HCl), 283 (MeOH, aqueous NaOH).

Anal. Calcd for $C_9H_{10}O_2$: C, 71.95; H, 6.72. Found: C, 71.88; H, 6.69.

4,6-Dimethyl-1,3,6-cycloheptarienecarboxylic Acid (4).—Ethyl diazoacetate (40 g) was added dropwise to 500 ml of *m*-xylene while the solution was gradually heated. After the addition was complete, the solution was refluxed for 16 hr, the solvent was removed, and the residual dark oil was fractionated by distillation. A fraction boiling at 69–76° (0.17 mm) was collected (40 g) and showed at least five peaks in a vpc analysis. A portion (10 g) of this oil was dissolved in 60 ml of 10% aqueous methanol containing 10% potassium hydroxide, and the solution was heated at 70° for 2 hr. After cooling, acidification, extraction with ether, and processing, a crystalline solid was obtained which was filtered from petroleum ether (bp 30–60°). Recrystallization from a mixture of chloroform and petroleum ether gave the product (3 g): mp 149–150° (lit.[10] mp 148°); λ_{max} 273 mμ (MeOH, aqueous HCl), 267 (MeOH, aqueous NaOH).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.11; H, 7.38. Found: C, 72.96; H, 7.43.

4,5,6-Trimethyl-1,3,6-cycloheptatrienecarboxylic Acid (7).—Ethyl diazoacetate (40 g) was gradually added to 1,2,3-trimethylbenzene (400 ml) while the solution was slowly heated to 145°. The solution was stirred at this temperature for 6 hr after the addition was complete, and then it was cooled. The solution was evaporated and the residual yellow oil was fractionated by distillation. The fraction boiling at 85–90° (0.16 mm) (36 g) was collected and a portion (20 g) was hydrolyzed with aqueous methanolic potassium hydroxide at room temperature. Acidification and processing as described above, gave a light yellow oil which was fractionally crystallized from petroleum ether. A crop (1.7 g) had mp 108–111° and proved to be 2,3-dimethylphenylpropionic acid. A second and third crop of crystals obtained from the mother liquors corresponded to the desired product: yield 4 g; mp 114–115° (recrystallization from chloroform-petroleum ether afforded material with mp 116–117°); λ_{max} 290 mμ (MeOH, aqueous HCl), 284 (MeOH, aqueous NaOH).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.15; H, 7.92. Found: C, 74.17; H, 7.91.

2,4,6-Trimethyl-1,3,6-cycloheptatrienecarboxylic Acid (6).—Ethyl diazoacetate (40 g) was added dropwise to mesitylene (450 ml) with stirring and gradual heating to 150° during 3 hr. The mixture was stirred at the same temperature for an additional 6 hr, cooled, and evaporated. The dark oily residue was fractioned by distillation to give a fraction boiling at 60–82° (0.2 mm): yield 37 g. A portion (10 g) of this mixture was dissolved in aqueous methanolic potassium hydroxide and the solution was heated at 70° for 2 hr. Careful acidification of the chilled solution afforded a precipitate which was filtered and washed with petroleum ether: yield 4 g; mp 141–142° (lit.[11] mp 142°)

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[24] We thank Mr. R. B. Scott of Parke, Davis & Co. for recording the 60-MHz spectra.

[25] We are grateful to Mr. D. F. Williams, Department of Chemistry, University of Montreal, for recording the 100-MHz spectra and for decoupling experiments, and to Dr. M. St-Jacques of the same department for helpful discussions.

[26] A product of Aldrich Chemical Co., Milwaukee, Wis.

(recrystallization from aqueous methanol did not change the melting point); λ_{max} 279 mμ (MeOH, aqueous HCl), 273 (MeOH, aqueous NaOH).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.15; H, 7.92. Found: C, 74.06; H, 8.06.

Registry No.—**1,** 21297-55-2; **2,** 21297-56-3; **3,** 21297-57-4; **4,** 21297-58-5; **5,** 21297-59-6; **6,** 21297-60-9; **7,** 21297-61-0.

Raney Nickel Desulfurization of Cyclooctyl Mercaptan and Cyclooctyl Sulfide

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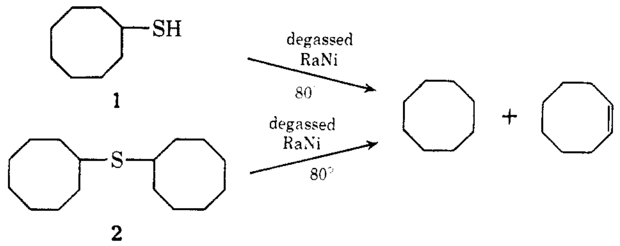
It has been suggested that the Raney nickel desulfurization of an organic mercaptan or sulfide proceeds through a free-radical intermediate which is subsequently hydrogenated or recombines to form a coupled product.[3-7] The following equation illustrates the process by which such reactions are believed to take place.[8]

$$\begin{tikzcd}
 & & RH + R'H \\
RSR' \arrow[r, "Ni(H)"] & R\cdot + \cdot R' \arrow[ur] \arrow[dr] & \\
 & & RR + RR' + R'R'
\end{tikzcd}$$

In view of our interest in the free-radical reactions of medium sized ring compounds,[9] we undertook a brief study of the desulfurization of cyclooctyl mercaptan and cyclooctyl sulfide. If a cycloalkyl mercaptan or sulfide of this type is desulfurized with degassed Raney nickel with the subsequent formation of cycloalkyl radicals, one would expect these radicals to undergo characteristic disproportionation and coupling reactions rather than being hydrogenolyzed to a hydrocarbon.

For this study, cyclooctyl mercaptan (**1**) was prepared in 43% yield by the reaction of cyclooctyl bromide with thiourea followed by basic hydrolysis of the intermediate isothiouronium salt. Cyclooctyl sulfide (**2**) was prepared in 41% yield by the reaction of sodium sulfide nonahydrate with cyclooctyl bromide. The desulfurization reactions were carried out by refluxing a benzene solution of mercaptan or sulfide with a tenfold excess of degassed Raney nickel for time intervals up to 48 hr. The desulfurization of cyclooctyl mercaptan gave a 80–85% yield of a product mixture containing only cyclooctane and *cis*-cyclooctene. The relative amounts of these products varied over a wide range depending on the length of time the Raney nickel was degassed. Generally, the product mixture contained about 80% cyclooctane and 20% *cis*-cyclooctene. However, if the Raney nickel was vigorously degassed for periods of 24 hr or more, the yield of *cis*-cyclooctene approached 80% whereas the yield of cyclooctane dropped to 20%. The desulfurization of cyclooctyl sulfide proceeded very slowly and always gave back on the order of 70% unchanged starting material. From the sulfide which did decompose there was obtained a 71% hydrocarbon yield which consisted principally of *cis*-cyclooctene. No bicyclooctyl could be isolated from desulfurization of either **1** or **2**, lending some doubt as to whether these particular desulfurizations proceed through a conventional free-radical intermediate under the experimental conditions employed. In addition, the relative amounts of cyclooctane and *cis*-cyclooctene which are formed in these desulfurizations indicate that disproportionation of cyclooctyl radicals is not an important reaction pathway. The cyclooctane formed in these desulfurizations does not arise by hydrogenation of *cis*-cyclooctene since a sample of *cis*-cyclooctene was unaffected when refluxed with degassed Raney nickel in benzene. Cyclooctane is apparently formed by partial hydrogenolysis of the mercaptan or sulfide and is dependent on the amount of hydrogen bound to the surface of the degassed Raney nickel. The formation of *cis*-cyclooctene, however, is presumably due to elimination of the elements of hydrogen sulfide from cyclooctyl mercaptan or elimination of a mercaptan moiety from cyclooctyl sulfide.



Because of the highly complex nature of metallic surfaces, it is difficult to postulate an exact mechanism for these elimination reactions. In the case of a Raney nickel catalyst, a further complicating factor is the presence of substantial amounts of basic oxides.[10] One possible explanation would involve coordination of the sulfur with a metal surface followed by a homolytic weakening of the carbon–sulfur bond. Hydrogenolysis of the carbon–sulfur bond would yield cyclooctane as expected. Abstraction of a hydrogen atom on the 2 position of the ring at the metal surface, together with complete homolytic cleavage of the carbon–sulfur bond, would yield *cis*-cyclooctene. Further work on the desulfurization of alkyl mercaptans and sulfides would be useful to better understand the nature of this reaction.

Experimental Section

Boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses. Gas chromatography was carried out with 190 × 0.8 cm Pyrex columns containing 25–30% by weight liquid stationary phase on 60–80 or 80–100 mesh Johns-Manville Chromosorb. Samples were eluted with helium gas at 15 psi and detected by use of a thermal conductivity cell.

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[1] Deceased, June 4, 1966.

[2] (a) National Science Foundation Cooperative Predoctoral Fellow 1959–1960. (b) To whom inquiries should be addressed: Esso Agricultural Products Laboratory, Linden, N. J.

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