was held at 100-104° for 3 hr, cooled, and poured on ice. After the usual work-up ($CHCl_3$ solvent), distillation yielded 2.0 g (83%) of **13** as a colorless oil, bp 127-129° (0.3 mm).

Anal. Calcd for $C_{11}H_{19}NO_3$: C, 61.9; H, 8.9; N, 6.6. Found: C, 61.7; H, 8.8; N, 6.5.

Reactions of 8a with Cyclic Olefins.—In a typical reaction a stirred solution held at −10 to −5° of 4.5 g of **8a** in 25 ml each of pentane and cyclohexene containing 1 g of Aliquat-336[7] was treated dropwise with 50% sodium hydroxide. The theoretical amount of nitrogen was collected during 15 min. After the solution was warmed to 40° for 5 min the organic layer was worked up as usual. After solvent was removed the residue was chromatographed over Woelm neutral alumina to remove the Aliquat-336. Distillation afforded 3.1 g (80%) of **11**,[2b] bp 61-62° (0.3 mm). The reactions of **8a** with cycloheptene and cyclooctene were carried out essentially the same way to yield bicyclo[5.1.0]oct-8-ylidenecyclohexane[‡] (**16**), ir 5.58 μ, *m/e* 190 (calcd 190), and bicyclo[6.1.0]non-9-ylidenecyclohexane[‡] (**17**), ir, 5.58 μ, *m/e* 204 (calcd 204), respectively. The results are summarized in Table I.

Anal. Calcd for $C_{14}H_{22}$: C, 88.4; H, 11.6. Found: C, 88.3; H, 11.7. Calcd for $C_{15}H_{24}$: C, 88.2; H, 11.8. Found: C, 88.2; H, 11.8.

Reactions of 8a with Vinyl Ethers.[13]—The reactions of **8a** with ethyl vinyl ether and *tert*-butyl vinyl ether were carried out as described above for the reaction of **8a** with cyclic olefins except that the pentane was omitted. However, since on cooling a solution of **8a** in phenyl vinyl ether turbidity resulted, an equal volume of pentane was added.

2-Ethoxycyclohexylidenecyclopropane (19).—In a typical reaction 50% sodium hydroxide was slowly added dropwise to a stirred solution of 4.6 g of **8a** in 60 ml of ethyl vinyl ether and 1 ml of Aliquat 336[7] at −10 to −5°. The slow addition requires about 15 min in order that the temperature be maintained below −5°. During this time about the theoretical amount of nitrogen was collected. After 10 ml of water was added the organic layer was worked up as usual. The organic product was dissolved in pentane and chromatographed over 40 g of Woelm neutral alumina to remove the Aliquat 336. Distillation through a 12-in. Nester-Faust spinning band column afforded **19** in 80% yield: ir 5.59 μ; nmr (CCl_4) δ 3.65 (m, 1 H, $-CHOC_2H_5$), 3.52 (q, J = 6.8 cps, 2 H, OCH_2CH_3), 2.26 (m, 4 H, allylic CH_2 in cyclohexyl ring), 1.58 (m, 6 H, nonallylic CH_2 in cyclohexyl ring), 1.15 (t, J = 6.8 cps, 3 H, CH_2CH_3), 1.05 (m, 2 H, CH_2 in cyclopropyl ring); *m/e* 166 (calcd 166).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.5; H, 10.9. Found: C, 79.5; H, 10.7.

In a similar way 2-phenoxycyclohexylidenecyclopropane (**18**) and 2-*tert*-butoxycyclohexylidenecyclopropane (**20**) were isolated (see Table I). The nmr spectra of **18** and **20** were almost identical with that of **19** except for the number of methylene hydrogens in the bicyclic rings.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.1; H, 8.5. Found: C, 83.9; H, 8.4. Calcd for $C_{13}H_{22}O$: C, 80.3; H, 11.3. Found: C, 80.1; H, 11.5.

Registry No.—**7** (R = Me), 37150-62-2; **7a**, 37150-63-3; **8a**, 37150-64-4; **11**, 19690-02-9; **13**, 37150-66-6; **16**, 37150-67-7; **17**, 37150-68-8; **18**, 37150-69-9; **19**, 37150-70-2; **20**, 37150-71-3.

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[13] We acknowledge with thanks generous gifts of ethyl vinyl ether, *tert*-butyl vinyl ether, and phenyl vinyl ether from the General Aniline and Film Corp.

Cyclooctatetraene Derivatives from Bromocyclooctatetraene[1]

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N,N-Dimethylaminocyclooctatetraene, cyclopropylcyclooctatetraene, and cyclooctatetraenenitrile have been prepared for the first time. *N,N*-Diethylaminocyclooctatetraene has also been prepared, but was found to rearrange to α-*N,N*-diethylaminostyrene. In addition, *p*-anisylcyclooctatetraene, cyclooctatetraenealdehyde, and vinylcyclooctatetraene have been prepared in greatly improved yields over previously described procedures.

Since the Reppe synthesis of cyclooctatetraene in 1948 from acetylene,[2] numerous substituted cyclooctatetraenes have been prepared,[3] but for the most part the yields of these preparations have been at best fair. Recent work, however, has provided several cyclooctatetraenes[4] in good yield from the reaction of bromocyclooctatetraene[5] with organocopper(I) lithium reagents.[6]

In our continuing study of derivatives of bis(cyclooctatetraene)uranium(IV),[7] the need arose for preparing various substituted cyclooctatetraenes. Because of the lack of good general synthetic procedures, it was necessary to develop alternate routes to such compounds. We report the preparation of several substituted cyclooctatetraenes that were previously difficult to prepare. In addition, the syntheses of three new derivatives of cyclooctatetraene are described.

During the 1950's, Cope reported that substituted COT's could be prepared from the reaction of organolithiums with cyclooctatetraene.[8] Yields from these reactions were generally low (less than 25%) and gave side products which were difficult to separate from the desired material. In an extension of Cope's work, Paquette found that *p*-anisylcyclooctatetraene could be prepared from cyclooctatetraene and *p*-anisyllithium, but only in 3% yield.[9] We have found that the reaction of bromocyclooctatetraene with a fourfold excess of lithium di-*p*-anisylcopper(I) at −50° gives *p*-anisylcyclooctatetraene cleanly in 80% yield.

Cope and Fenton in 1951 reported the isolation of vinylcyclooctatetraene from accumulated residues of cyclooctatetraene preparations.[10] The procedure was tedious and gave only miniscule amounts of the derivative. When excess lithium divinylcopper(I) is allowed to react with bromocyclooctatetraene, the same product is obtained in 88% yield. Similarly, it was found

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[2] W. Reppe, O. Schlichting, and H. Meister, *Justus Liebigs Ann. Chem.*, **560**, 93 (1948).

[3] G. Schroder, "Cyclooctatetraen," Verlag Chemie, Wienheim, Germany, 1965.

[4] J. Gasteiger, G. Gream, R. Huisgen, W. Konz, and U. Schnegg, *Chem. Ber.*, **104**, 2412 (1971).

[5] W. Konz, Ph.D. Thesis, University of Munich, 1970.

[6] G. Whitesides, W. Fischer, Jr., J. San Filippo, Jr., R. Bashe, and H. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969).

[7] A. Streitwieser and U. Müller-Westerhoff, *ibid.*, **90**, 7364 (1968); A. Streitwieser and C. Harmon, *Inorg. Chem.*, in press.

[8] A. Cope and M. Kinter, *J. Amer. Chem. Soc.*, **73**, 3424 (1951); A. Cope and H. van Orden, *ibid.*, **74**, 175 (1952).

[9] L. Paquette, J. Malpass, and T. Barton, *ibid.*, **91**, 4714 (1969).

[10] L. Craig and C. Larrabee, *ibid.*, **73**, 1191 (1951); A. Cope and S. Fenton, *ibid.*, **73**, 1195 (1951).

that lithium dicyclopropylcopper(I) can be prepared and apparently is a versatile cyclopropylating agent.[11] This reagent, when used in a fourfold excess with bromocyclooctatetraene at −50°, gives a 95% yield of cyclopropylcyclooctatetraene.

Elix, Sargent, and Sondheimer have demonstrated that the reaction of bromocyclooctatetraene with base produces a transient cyclooctatrienyne that may be trapped to give cyclooctatetraene derivatives.[12] Making use of the analogous reaction of amines with benzynes, we found that *N*,*N*-dimethylaminocyclooctatetraene is prepared in 79% yield from the reaction of potassium *tert*-butoxide with bromocyclooctatetraene in the presence of dimethylamine. As expected, this compound is extremely sensitive toward acids, giving cyclooctatrieneone. In addition, the amine is air sensitive and decomposes rapidly at room temperature. In the course of preparing the amine, the first derivative prepared was the *N*,*N*-diethylaminocyclooctatetraene. However, attempted distillation, even at 1 μ, results in rearrangement (at times violently) to α-*N*,*N*-diethylaminostyrene. In contrast, the dimethyl derivative is easily distilled without rearrangement as an orange oil by evaporative distillation at 1 μ.

Cyclooctatetraene does not normally undergo electrophilic reactions without rearrangement or polymerization.[13] Recently, however, it has been demonstrated that iron-coordinated cyclooctatetraene does survive Vilsmeier conditions to give a formylated cyclooctatetraene.[14] Although the free formylcyclooctatetraene can be generated by ceric oxidation, isolation procedures and the preparation of starting material are time-consuming. Since large quantities of the aldehyde were desired, an alternative approach to this derivative was sought. Collman has reported that carbonyl compounds may be prepared from the reaction of organolithiums with iron pentacarbonyl at low temperatures.[15] We find that the reaction of cyclooctatetraenyllithium with iron pentacarbonyl under similar conditions gives an unexpected product. Instead of cyclooctatetraenealdehyde, a modest yield of (formylcyclooctatetraene)iron tricarbonyl was obtained. This apparently anomalous result may be rationalized by the following mechanism: cyclooctatetraenyllithium adds to a carbonyl group of the iron pentacarbonyl, and the product decomposes on hydrolysis to give cyclooctatetraenealdehyde and iron tetracarbonyl, which, in turn, combine *via* complexing at the double bonds with concomitant loss of carbon monoxide. Although this method did provide the desired formyl derivative, oxidation was still required to obtain the free ligand. The synthesis of the aldehyde can be accomplished, however, by the more traditional approach of treating cyclooctatetraenyllithium with methyl formate at 0°. This method gives the aldehyde cleanly in 79% isolated yield.

Corey and Hegedus[16] have reported briefly that *trans*-β-bromostyrene is converted into *trans*-β-cyanostyrene by reaction with potassium hexacyanodinickelate(I)[17] in methanol.[16] Despite several attempts we have not been able to transform bromocyclooctatetraene into the corresponding nitrile by this method except in low yield (8%). The nitrile can be prepared by an alternate route, however, from the interaction of cyclooctatetraenyllithium with cyanogen at low temperature. Although the nitrile can be obtained by either procedure, both have obvious drawbacks. The first method requires large amounts of the nickel complex and gives low yields, and, in the latter route, the extreme toxicity of cyanogen and the considerable polymerization of the product during reaction leave room for improvement.

Experimental Section

^{1}H nmr spectra were taken with a Varian Associates T-60 instrument. Ir spectra were obtained with a Perkin-Elmer 137 instrument. Commercial *n*-butyllithium, 15% in hexane, was used in cyclooctatetraenyllithium preparations. All reactions were run under a dry nitrogen atmosphere. Satisfactory mass spectra for all compounds have been obtained. Analyses were performed by the Analytical Services Laboratory, University of California. Bromocyclooctatetraene was distilled from an apparatus in which the bath covered the side arm such that there is minimal reflux of material back into the pot. This distillation procedure gave consistently high yields and bromocyclooctatetraene of >98% purity.

***p*-Methoxyphenylcyclooctatetraene.**—A solution of 0.20 mol of *p*-anisyllithium in 200 ml of ether, prepared from the reaction of *p*-bromoanisole in ether with an excess of lithium metal (1% Na), was added dropwise to 39.0 g (0.10 mol) of $CuI\cdot PBu_3$ in 150 ml of ether at −70°. After stirring for 0.5 hr, a solution of 4.6 g (0.025 mol) of bromocyclooctatetraene[4] in 50 ml of ether was added to the yellow complex over a period of 10 min. The mixture was stirred for an additional 5 hr at −40°, and allowed to warm to room temperature overnight. After hydrolysis and extraction with ether, the organic layer was extracted with 20% $AgNO_3$ (10 × 25 ml). Aqueous ammonia treatment freed the cyclooctatetraene derivative, which was taken up into ether and dried over $MgSO_4$. Solvent removal and subsequent chromatography over silica gel with pentane yielded 4.2 g (80%) of *p*-methoxyphenylcyclooctatetraene, nmr δ 3.6 (3 H, s), 5.8 (7 H, d), 6.8 (4 H, 2 d).

Anal. Calcd for $C_{15}H_{14}O$: C, 85.71; H, 6.66. Found: C, 85.60; H, 6.91.

Vinylcyclooctatetraene.—To 39 g (0.10 mol) of $CuI\cdot PBu_3$ in 100 ml of ether at −70° was added a solution of 0.20 mol of vinyllithium (commercial 2 *M* solution of vinyllithium in THF, Research Organic Corp.) dropwise over 20 min. After the clear yellow solution was stirred for an additional 20 min at −70°, a solution of 4.6 g (0.025 mol) of bromocyclooctatetraene in 25 ml of ether was added over a period of 10 min. The mixture was warmed to −40° and stirred for 5 hr at that temperature, then allowed to warm up overnight. Upon hydrolysis (100 ml of water), the product was taken up in ether and the ether solution was washed with water and dried with $MgSO_4$. Distillation of the residue after solvent removal gave 2.86 g (88%) of vinylcyclooctatetraene, bp 90–93° (30 mm), nmr δ 6.3 (1 H, q), 5.7 (7 H, s), 4.9 (2 H, m). This sample has properties identical in all respects with those reported by Cope[7] for vinylcyclooctatetraene isolated from high-boiling residues of cyclooctatetraene preparations.

Anal. Calcd for $C_{10}H_{10}$: C, 92.30; H, 7.70. Found: C, 92.52; H, 7.37.

Cyclopropylcyclooctatetraene.—An ether solution (100 ml) containing 0.2 mol of cyclopropyllithium (prepared from cyclopropyl bromide in the presence of an excess of lithium metal) was added dropwise over 30 min to 39 g (0.10 mol) of $CuI\cdot PBu_3$ in 100 ml of ether at −70°. After 20 min, 4.6 g (0.025 mol) of bromocyclooctatetraene in 25 ml of ether was added to the clear green solution. After stirring for 5 hr at −50°, the solution was warmed and hydrolyzed with 100 ml of water. The organic

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[11] A detailed study of the reactivity of this complex will be reported in a separate communication.

[12] J. Elix and M. Sargent, *J. Amer. Chem. Soc.*, **91**, 4734 (1969); J. Elix, M. Sargent, and F. Sondheimer, *ibid.*, **92**, 962 (1970).

[13] A. Cope, T. Liss, and D. Smith, *ibid.*, **79**, 240 (1957).

[14] B. Johnson, J. Lewis, and G. Randall, *J. Chem. Soc. A*, 422 (1971).

[15] W. Siegl and J. Collman, *J. Amer. Chem. Soc.*, **94**, 2516 (1972).

[16] E. Corey and L. Hegedus, *ibid.*, **91**, 1234 (1969).

[17] W. Burgess and J. Eastes, *Inorg. Syn.*, **5**, 197 (1957).

phase was separated and the aqueous layer was extracted with ether. The combined organic fractions were washed with water and dried over $MgSO_4$. Solvent removal followed by distillation gave 3.4 g (95%) of cyclopropylcyclooctatetraene, bp 40–43° (0.01 mm), nmr δ 5.8 (7 H, s), 1.6 (1 H, m), 0.7 (4 H, m).

Anal. Calcd for $C_{11}H_{12}$: C, 91.66; H, 8.34. Found: C, 91.33; H, 8.06.

***N*,*N*-Diethylaminocyclooctatetraene.**—Over a period of 1 hr, 5.6 g (0.05 mol) of potassium *tert*-butoxide was added in small portions to a solution of 9.2 g (0.05 mol) of bromocyclooctatetraene in a mixture of 50 ml of diethylamine and 150 ml of ether at 0°. The suspension was stirred for 3 hr at 0°, and allowed to warm overnight to room temperature. Rapid vacuum filtration to remove precipitated potassium bromide followed by solvent removal gave an orange-brown residue. Attempted distillation, even at 1 μ, resulted in rearrangement to α-*N*,*N*-diethylaminostyrene. However, the nmr spectrum of the crude preparation is consistent with the *N*,*N*-diethylaminocyclooctatetraene structure: δ 5.9 (6 H, d, COT protons), 4.5 (1 H, d, enamine proton), 3.2 (4 H, q), 1.2 (6 H, t, ethyls).

***N*,*N*-Dimethylaminocyclooctatetraene.**—Repetition of the above preparation, except that 200 ml of a saturated ether solution of dimethylamine was used, gave from 9.2 g of bromocyclooctatetraene 5.8 g (79%) of *N*,*N*-dimethylaminocyclooctatetraene by evaporative distillation (<30°) at 0.01 mm: nmr δ 5.8 (6 H, d), 4.4 (1 H, d), 2.6 (6 H, s). The analysis was poor but the assigned structure is supported by the nmr spectrum and by the mass spectral parent peak at *m/e* 147.

Anal. Calcd for $C_{10}H_{13}N$: C, 81.63; H, 8.84. Found: C, 81.11; H, 9.23.

Reaction of Cyclooctatetraenyllithium with Iron Pentacarbonyl.—A solution of 0.05 mol of cyclooctatetraenyllithium in 100 ml of ether at −70° was added dropwise to 19.5 g of iron pentacarbonyl in 100 ml of ether maintained at −70°. The deep red mixture was stirred for 3 hr at −70° and hydrolyzed with 15 ml of acetic acid. The solution was poured onto 250 ml of water and extracted with ether. The combined ether fractions were dried over $MgSO_4$ and the ether was removed under vacuum. The red residue was chromatographed over silica gel with a 5% methylene chloride-pentane mixture, giving 6.1 g (45%) of (formylcyclooctatetraene)iron tricarbonyl.

Cyclooctatetraenealdehyde.—To 100 ml of methyl formate at −30° was added a solution of 0.05 mol of cyclooctatetraenyllithium in 100 ml of ether over a period of 1 hr. The solution was stirred for 3 hr at 0° and hydrolyzed with 100 ml of water. The product was taken up in ether and dried with $MgSO_4$. Distillation of the orange residue after solvent removal gave 5.2 g (79%) of cyclooctatetraenealdehyde, bp 40–45° (0.5 mm), ir 1685 cm^{-1} (C=O).

Anal. Calcd for C_9H_8O: C, 81.81; H, 6.06. Found: C, 81.69; H, 5.98.

Cyclooctatetraenenitrile.—A mixture of 9.2 g of bromocyclooctatetraene, 7.8 g of potassium cyanide, and 22.2 g of $K_4Ni_2(CN)_6$ in 300 ml of absolute methanol was stirred for 8 hr at room temperature. The yellow suspension was poured into water and extracted with ether. The organic phase was washed with water and dried with $MgSO_4$. Solvent removal followed by chromatography of the residue with pentane over silica gel gave 0.52 g (8%) of cyclooctatetraenenitrile.

Cyclooctatetraenenitrile from Cyclooctatetraenyllithium.—Cyanogen was bubbled into 100 ml of ether until a saturated solution was obtained. This solution was cooled to −70°, and 0.05 mol of cyclooctatetraenyllithium in 100 ml of ether at −70° was added dropwise over a period of 20 min. The mixture was stirred for 2 hr at −70°, warmed to room temperature, and hydrolyzed with 200 ml of water. Upon standing overnight to decompose excess cyanogen, the organic phase was separated, washed with water, and dried. After the ether was removed, evaporative distillation of the residue at 1 mm (bath temperature, 40°) gave 1.6 g (25%) of cyanocyclooctatetraene. This sample was identical with the product obtained from $K_4Ni_2(CN)_6$, ir 2190 cm^{-1} (C≡N). Yields up to 40% have been obtained by first converting cyclooctatetraenyllithium to the corresponding Grignard reagent by the addition of anhydrous magnesium bromide.

Anal. Calcd for C_9H_7N: C, 83.72; H, 5.43. Found: C, 83.67; H, 5.51.

Registry No.—Bromocyclooctatetraene, 7567-22-8; *p*-methoxyphenylcyclooctatetraene, 23697-18-9; vinylcyclooctatetraene, 37164-12-8; cyclopropylcyclooctatetraene, 37164-13-9; *N*,*N*-diethylaminocyclooctatetraene, 37164-14-0; *N*,*N*-dimethylaminocyclooctatetraene, 37164-15-1; cyclooctatetraenealdehyde, 30844-12-3; cyanocyclooctatetraene, 37164-17-3.

A New Synthesis of 2-Hydroxy-3-methylcyclopent-2-en-1-one. III[1]

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A new synthesis of 2-hydroxy-3-methylcyclopent-2-en-1-one (**7**) is described. The Mannich reaction of cyclopentane-1,2-dione (**3**) with morpholine and formalin gave a Mannich base **6**, which was hydrogenolized to afford **7**. However, the Mannich reactions of keto enamines **5a–c**, which are enamino derivatives of **3**, gave the Mannich bases **9a–c**, respectively, which were similarly hydrogenolized to afford 3,5-dimethyl-2-hydroxycyclopent-2-en-1-one (**10**).

2-Hydroxy-3-methylcyclopent-2-en-1-one (**7**) is a flavor constituent, for example, in coffee aroma[2] and maple flavor.[3] Erickson and Collins[4] have utilized **7** as an intermediate in a synthesis of dihydrojasmone, which is useful in perfumery.

Previous papers[1,5] described several routes to synthesize **7** from 2-carbethoxy-2-methylcyclopentanone.[6] In this paper, we wish to report a new synthesis of **7** from cyclopentanone (**1**).

Cyclopentanone (**1**) is monobrominated with dioxane dibromide in ether and 2-bromocyclopentanone (**2**) is oxidized by ferric chloride to afford cyclopentane-1,2-dione (**3**), which exists almost entirely in the enolic form.[7]

In an earlier paper,[1] we reported that the treatment of 2,5-dibromocyclopentanone (**4**) with excess morpholine in ether gives 2-morpholinocyclopent-2-en-1-one (**5a**) in good yield. Cyclopentane-1,2-dione (**3**) is also obtained by the hydrolysis of **5a** in 20% hydrochloric acid.

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(1) For previous paper, see K. Sato, Y. Kojima, and H. Sato, *J. Org. Chem.*, **35**, 2374 (1970).

(2) M. A. Gianturco, A. S. Giammarino, and R. G. Pitcher, *Tetrahedron*, **19**, 2051 (1963).

(3) V. J. Filipic, J. C. Underwood, and C. O. Willits, *J. Food Sci.*, **30**, 1008 (1965).

(4) J. L. E. Erickson and F. E. Collins, Jr., *J. Org. Chem.*, **30**, 1050 (1965).

(5) K. Sato, S. Suzuki, and Y. Kojima, *ibid.*, **32**, 339 (1967).

(6) C. M. Leir has recently reported the synthesis of **7** from 2-carbomethoxy-2-methylcyclopentanone [*J. Org. Chem.*, **35**, 3203 (1970)].

(7) C. W. N. Cumper, G. B. Leton, and A. I. Vogel, *J. Chem. Soc.*, 2067 (1965).