Chemical Transformations of Substituted Bicyclo[2.1.1]hexan-2-ones. Ring Contraction Studies and Synthesis of Tricyclo[2.2.0.0^{2,6}]hexan-3-one

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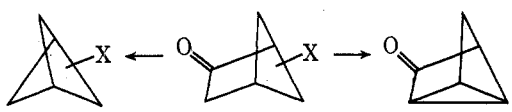
The synthesis of 3-formylbicyclo[2.1.1]hexan-2-one and 3-diazobicyclo[2.1.1]hexan-2-one has been accomplished. The latter, under ring contraction conditions, gives low yields of methylbicyclo[1.1.1]pentane carboxylate but primarily solvent insertion products. 2,3-Epoxybicyclo[2.1.1]hexane gives only bicyclo[2.1.1]hexan-2-one with base. Tricyclo[2.2.0.0^{2,6}]hexan-3-one has been prepared by dehydrochlorination of *exo*-5-chlorobicyclo[2.1.1]hexan-2-one.

One of the major reasons for our interest in the synthesis of functionally substituted bicyclo[2.1.1]hexan-2-ones, 1,[1] was to investigate their further chemical transformation into either tricyclo[2.2.0.0^{2,6}]hexan-3-one (**2**) or into functionalized bicyclo[1.1.1]pentanes (**3**). The parent hydrocar-



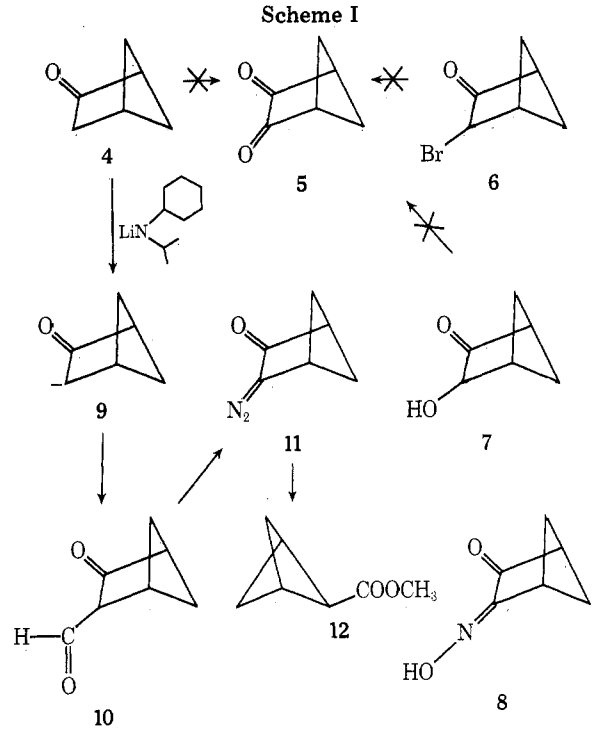
3 **1** **2**

bon of **2** is known,[2] and is now readily prepared,[3] but only two simple functionalized derivatives have been prepared,[4] and their chemistry has been virtually ignored. Substituted bicyclo[1.1.1]pentanes, **3**, have been prepared via free-radical substitution on the parent hydrocarbon,[5] itself available only in very low yield via either Wurtz cyclization[6] or decarbonylation of bicyclo[2.1.1]hexan-2-one.[7] In particular, since free-radical substitution on bicyclo[1.1.1]pentane gives predominantly 1-substituted products, we sought a ring contraction route to the 2-substituted derivatives.[8] In this paper we report the successful preparation of **2**,[9] the results of ring contraction studies on difunctional bicyclo[2.1.1]hexanes, and formation and chemistry of the enolate anion of bicyclo[2.1.1]hexan-2-one.

Synthesis of 3-Diazobicyclo[2.1.1]hexan-2-one (11). Our initial efforts were directed toward the preparation of diazo ketone **11**, an obvious precursor to both **2** and **3**. In particular, since the well-studied ring contraction of α-diazobicyclo[2.2.1]hexanones has resulted in numerous 5-substituted bicyclo[2.1.1]hexanes,[10] **11** was expected to give **12** on photolysis. The obvious route to **11** (Scheme I) was via α-diketone **5** and its mono-*p*-toluenesulfonylhydrazone. Unfortunately, selenium dioxide oxidation of **4**[11] under a variety of conditions[12] which produced bicyclo[2.2.1]heptane-2,3-dione from bicyclo[2.2.1]hexan-2-one all failed to give **5**. These conditions included heating at reflux in acetic acid, chlorobenzene, or *p*-xylene. This presumably reflects difficulty in preparing the highly strained[13] enol of **4**, since an even more highly strained, though heavily substituted, α-diketone has been reported.[14] Oxidation[15] of α-bromo ketone **6** or of **7**[16] all afforded recovered starting material. A variety of routes[17] to the α-oximino ketone **8**, a second possible precursor of **11**, were also unsuccessful. Likewise we were unable to prepare the enol ether, enol acetate, or any enamine of **4** under a wide range of conditions which were successful with the homologous bicyclo[2.2.1]heptan-2-one.

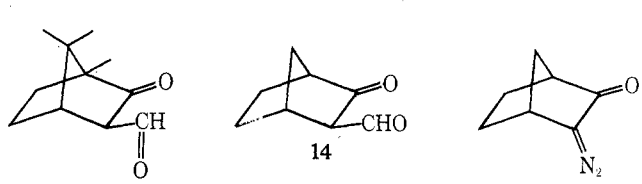
Although normally α substitution of ketones is more favorable via the enol (or enol acetate or enamine), our total lack of success forced us to attempt formation and trapping of enolate **9**. A variety of bases (potassium *tert*-butoxide in *tert*-butyl alcohol, sodium amide in ammonia, and sodium

Scheme I



hydride in benzene) proved of little use, but lithium cyclohexylisopropylamide in THF was successful as demonstrated by trapping of **9** with D_2O, bromine,[1] and, for the purposes of ring contraction studies, with ethyl formate to give **10**.

The structure of **10** was easily assigned from its physical properties. One interesting feature was that NMR showed the α-formyl ketone to be essentially nonenolized in chloroform.[18] Even in Me_2SO-d_6,[19] the product is predominantly the 1,3-dicarbonyl tautomer. Comparison with 3-formylcamphor (**13**) and 3-formylnorcamphor (**14**) is given in Table I. The increase in strain resulting from introduction of two sp^2-hybridized centers into the bicyclo[2.1.1]hexane nucleus is obvious. Treatment of **10** with *p*-toluenesulfonyl



13 **14** **15**

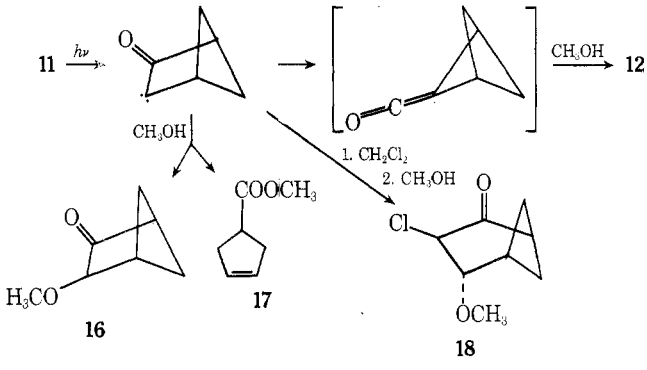
azide and triethylamine[20] gave a 61% yield of crude **11**, the physical properties of which compared well with those of **15**.[10a] Attempted distillation of **11** resulted in extensive decomposition.[21]

Table I. Percent Enol (by NMR)

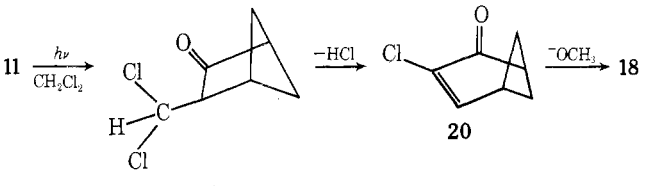
Compd	Solvent	
	$CHCl_3$	Me_2SO-d_6
10	0	12
13	55	100
14	33	91

Ring Contraction of 11. Photolysis of 11 was carried out under a wide variety of conditions,[10] summarized in Scheme II. In all cases a very low (<2%) yield of the desired ring contraction ester 12[5,22] could be obtained, but the major products, 16 from irradiation in basic methanol, the corresponding alcohol from aqueous dioxane, and 18 from irradiation in dichloromethane[23] at −78 °C, all appear to arise from insertion of the α-diazo ketone into solvent taking preference over ring contraction to the highly strained ketene. Low yields of ring contraction products have been noted in other cases.[24] Apparently this route to 2-substituted bicyclo[1.1.1]pentanes is even less satisfactory than the original.[5]

Scheme II

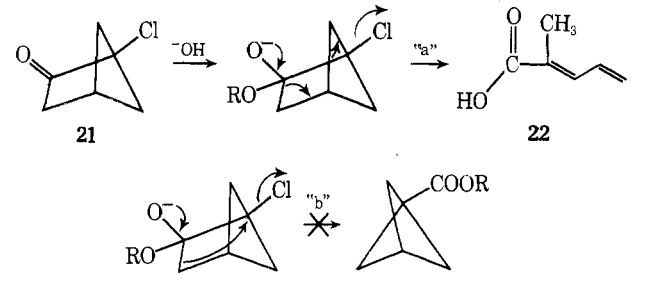


Compound 18 was the major product under conditions used by Eaton and Temme for a similar ring contraction synthesis of a highly strained [2.2.2]propellane.[23] The origin of 18 appears to be ring expansion of the carbene insertion product 19 to give 20 which, upon methoxide workup,[23] gives 18. Indeed a compound with the molecular ion



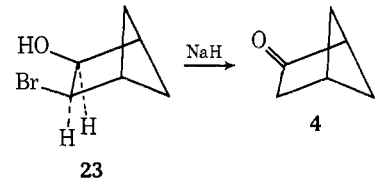
(GC–mass spectrum) expected for 20 could be detected in the crude photolysis product, but was not further characterized.

Other Ring Contraction Attempts. The availability of a number of bicyclo[2.1.1]hexane derivatives led us to attempt a series of ring contractions,[25,26] although the high strain of the desired products and less than favorable geometry for the quasi-Favorskii type pathways worked to prevent the desired reaction. Thus chloro ketone 21[1] on

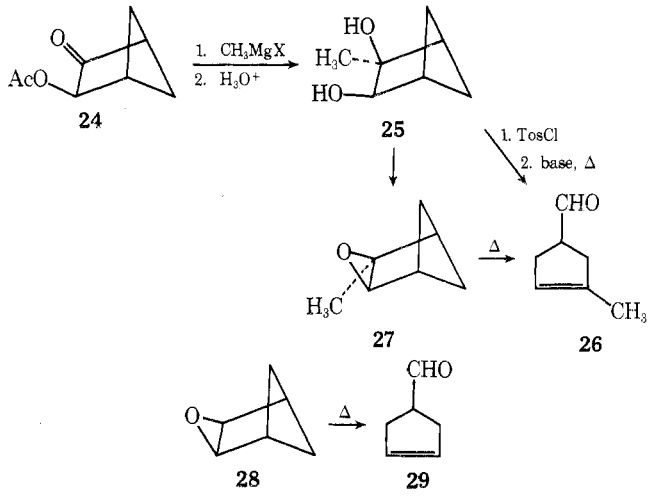


treatment with base gave the anion of 22 via path a followed by rearrangement, rather than ring contraction (path b).

Sodium borohydride reduction of 6 gave selectively the cis bromo alcohol 23, which on treatment with sodium hydride gave only hydride shift product 4. Acetoxy ketone 24[1]

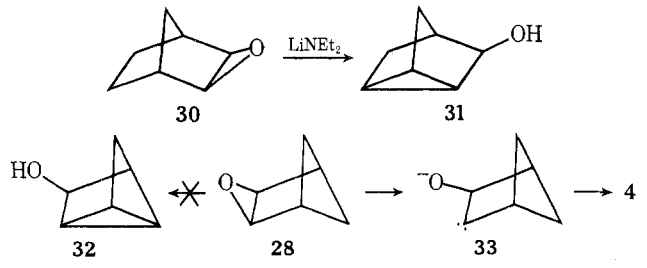


gave a single diol upon treatment with methyl Grignard reagent. The cis structure 25 is tentatively suggested in analogy with the results obtained in hydride reduction of 6 and on the basis of a strong intramolecular hydrogen bonded OH region in the infrared spectrum of 25. Treatment of 25



with tosyl chloride gave a monotosylate which with base gave two products, one of which was 26, the other not yet identified but not a ring contraction product. Aldehyde 26 is presumably formed by thermolysis of 27. Thermolysis of 28, obtained by epoxidation of bicyclo[2.1.1]hex-2-ene[27] gives 29. This thermal behavior has ample precedent.[28,29]

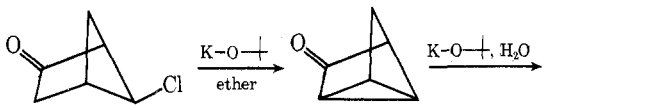
Tricyclo[2.2.0.0^{2,6}]hexan-3-one. Our initial attempt to prepare a derivative of the tricyclo[2.2.0.0^{2,6}]hexane ring system involved treatment of 28 with lithium diethylamide, a reaction known[29] to convert 30 into 31. None of the de-



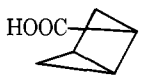
sired 32 was obtained; the only isolated product was bicyclo[2.1.1]hexan-2-one (4). The presumed intermediate, 33, must therefore insert into the α C–H bond in preference to the β. The geometry for such β insertion in the bicyclo[2.1.1]hexane system is apparently far less favorable than that in the [2.2.1]heptanes, since the carbene derived from 4 gives only bicyclo[2.1.1]hex-2-ene and not tricyclo[2.2.0.0^{2,6}]hexane.[27b]

A successful synthesis of 2[9] was obtained by base treatment of *exo*-5-chlorobicyclo[2.1.1]hexan-2-one (34)[1] under carefully controlled conditions (see Experimental Section). Such intramolecular displacements have become a valuable

route[4a,30] to strained bicyclic systems. The structure of **2** was supported by its particularly revealing NMR spec-



34 **2**



35

trum,[9] its mass spectrum, and infrared carbonyl absorption at 1775 and 1759 cm^{-1}. The latter compares well with that of the homologous nortricyclanone (1768 and 1755 cm^{-1}).[31] Haller–Bauer cleavage of **2** gave *endo*-bicyclo[2.1.0]pentane-2-carboxylic acid (**35**), the spectral properties of which were identical with those of authentic material.[32] The microwave spectrum of **2** has now been recorded[33] along with its high dipole moment (3.67 ± 0.02 D). A complete microwave study on the parent hydrocarbon has also been reported recently.[34] The chemistry of compound **2**, a dehydro derivative of already strained bicyclo[2.1.1]hexan-2-one,[11] bicyclo[2.2.0]hexan-2-one,[35] and bicyclo[2.1.1]hexan-5-one,[10a] is under present investigation.

Experimental Section[36]

3-Formylbicyclo[2.1.1]hexan-2-one (10). A 2-l. three-necked flask equipped with two addition funnels and a mechanical stirrer was connected by a glass tube to a 3-l. three-necked flask equipped with a mechanical stirrer. The system was thoroughly dried and kept under an argon atmosphere. THF (ca. 1 l.) and 72.5 ml (0.4 mol) of cyclohexylisopropylamine[37] were added to the first flask and cooled to 0 °C. With stirring and continued cooling, a solution of *n*-butyllithium in hexane was added dropwise over a 40-min period. After stirring at 0 °C for 1 h, the solution was further cooled via a dry ice–acetone bath after which bicyclo[2.1.1]hexan-2-one (**4**, 14.5 g, 0.15 mol) in 600 ml of THF was added dropwise over a 2-h period. Stirring at −78 °C was continued for 1 h. The resulting enolate solution was then transferred slowly using argon pressure, into the second flask which contained 54 ml (0.692 mol) of ethyl formate in 500 ml of dry THF at −78 °C. The addition took approximately 90 min, after which stirring was continued for 1 h at −78 °C followed by addition of 220 ml of 10% HCl. After warming to room temperature the organic layer was separated, the aqueous layer extracted five times with ether, and the combined organic layers worked up in the usual manner. The crude product was distilled through a 5-in. Vigreux column. After recovery of 1.5 g of **4** there was obtained 5.02 g (27%) of **10**, bp 57–60 °C (0.5 mm). There was a large pot residue of products which appeared to be aldol derived from attack of **9** on **4**.

Compound **10** has characteristic infrared absorption at 2825, 2730, 1769, and 1722 cm^{-1}. The mass spectrum shows the molecular ion at *m/e* 124 and the base peak at *m/e* 95. The NMR spectrum in $CDCl_3$ shows 1.64 (d of d, J = 7.5, 7.0 Hz, 1 H), 1.85 (d of d, J = 7.5, 7.0 Hz, 1 H), 2.31 (m, 2 H), 2.89 (m, 1 H), 3.10 (m, 1 H), 3.27 (d, J = 4 Hz, 1 H), and 9.75 ppm (s, 1 H). Anal. Calcd for $C_7H_8O_2$: C, 67.73; H, 6.50. Found: C, 67.59; H, 6.60.

3-Diazobicyclo[2.1.1]hexan-2-one (11). In a 500-ml round-bottom flask were mixed 9.90 g (0.08 mol) of **10**, 250 ml of methylene chloride, and 15.7 g (0.08 mol) of *p*-toluenesulfonyl azide. The flask was cooled to 0 °C and 55.8 g of triethylamine was added with stirring over a 30-min period. The mixture was stored overnight at 4 °C. A cold solution of 5.0 g of potassium hydroxide in 60 ml of water was added and the mixture stirred for 15 min at 0 °C. The methylene chloride layer was separated, the aqueous layer extracted twice with cold methylene chloride, and the combined methylene chloride layers washed with cold 1.4% KOH and cold water and dried in the refrigerator over sodium sulfate. The solvent was removed at 15 °C (5 mm) to give 11.61 g of crude diazo ketone. This material proved to be quite unstable and was best stored in solution at 0 °C.

The infrared spectrum shows significant bands at 2115, 2079, and 1727 cm^{-1}. The NMR spectrum has signals at 2.3 (m, 2 H), 2.47–2.80 (m, 3 H), and 3.27–3.5 ppm (m, 1 H).

Photolysis of 11. A. In Methanol. A solution of crude **11** (ca. one-fifth of the above solution) was concentrated in vacuo at 15 °C and dissolved in 1 l. of methanol containing 6.0 g of sodium bicarbonate.[38] The solution was irradiated at 0 °C with stirring through a Corex filter using a 450-W Hanovia lamp. The irradiation was followed by the disappearance of the diazo ketone bands in the infrared and required 6 h. Most of the solvent was removed through a 24-in. Vigreux column under reduced pressure and the yellow-brown residue worked up with pentane in the usual manner and evaporated to give 1.12 g of brown product. GLC analysis (10 ft, 10% NPGS) showed three peaks, A (10%), B (30%), and C (60%). Pure compounds were collected by preparative GLC.

Compound A was methylbicyclo[2.1.1]pentane 2-carboxylate (**12**). The infrared and NMR spectra were identical with those of the authentic compound.[5,22]

Compound B was methylcyclopent-3-ene carboxylate (**17**). The NMR spectrum has signals at 1.68 (d, J = 8.0 Hz, 4 H), 3.16 (d, J = 8.0 Hz, 1 H), 3.73 (s, 3 H), and 5.70 ppm (s, 2 H). The infrared spectrum exhibits absorption bands at 3060 (w), 3030 (w), 3000, 2965, 2860, and 1728 cm^{-1}. The mass spectrum shows the molecular ion at *m/e* 126.

Compound C was 3-methoxybicyclo[2.1.1]hexan-2-one (**16**), as established by its spectral data. The NMR spectrum has signals at 1.38–1.46 (t, J = 7.5 Hz, 1 H), 1.86–1.95 (t, J = 7.5 Hz, 1 H), 2.16–2.28 (m, 2 H), 2.76–2.86 (m, 1 H), 2.87–2.95 (m, 1 H), 3.56 (s, 3 H), and 3.74 ppm (s, further splitting, 1 H). The infrared spectrum indicates absorption bands at 2995, 2965, 2880, 2830, and 1766 cm^{-1}. The mass spectrum has its molecular ion at *m/e* 126.

B. In Dioxane–Water. Approximately one-tenth of the solution of **11** was concentrated and dissolved in 216 ml of purified dioxane and 108 ml of water containing 3.75 g of sodium bicarbonate. Irradiation was carried out followed as above. Most of the solvent was removed at 40 °C (5 mm) and the remaining aqueous layer extracted three times with ether to remove neutral products. Work-up of this material afforded 0.39 g of a yellow liquid shown by GLC (10 ft, 10% NPGS) to contain at least three products, the major one of which was identical in retention time and mass spectrum with 3-hydroxybicyclo[2.1.1]hexan-2-one.[1]

The basic layer from above was acidified with 6 N HCl and worked up with methylene chloride. Evaporation of the solvent afforded 0.11 g of crude material which was treated with excess ethereal diazomethane. GLC analysis, as above, showed A and B in an approximate 1:1 ratio. The components were identified by their retention times and mass spectra.

C. In Methylene Chloride. A solution of 9.0 g of crude **11** was dissolved in 1 l. of methylene chloride and irradiated at −78 °C for 5 h. The methylene chloride solution at this time showed a peak at 2381 cm^{-1} in the infrared. The cold solution was then treated at −78° with sodium methoxide prepared from 1.84 g of sodium and 200 ml of methanol. The resulting solution was stirred for 24 h and worked up with ether to give 7.14 g of crude residue. Short-path distillation afforded two fractions and a large tarry residue. The first, 0.19 g, bp 80–90 °C (35 mm), consisted mainly of **12** contaminated with a second component (GLC). The second fraction, 1.53 g (11%), bp 75–78 °C (3.0 mm), was assigned the structure *trans*-3-chloro-4-methoxybicyclo[3.1.1]heptan-2-one (**18**) on the basis of its spectral data.

The infrared spectrum shows carbonyl absorption at 1727 cm^{-1}. The mass spectrum has its molecular ion at *m/e* 174, 176 ($C_8H_{11}O_2Cl$). The NMR spectrum shows 2.27–2.46 (m, 4 H), 2.84–3.14 (m, 2 H), 3.61 (s, 3 H), 5.16 ppm (s, 2 H). Anal. Calcd for $C_8H_{11}O_2Cl$: C, 55.02; H, 6.35. Found: C, 54.84; H, 6.33.

(*E*)-2-Methyl-2,4-pentadienecarboxylic Acid (22). A mixture of 77.5 mg (0.6 mmol) of **21**[1] and 39 ml of 2 M KOH was placed in a glass pyrolysis tube, sealed under nitrogen, and heated at 155 °C for 18 h. The cooled solution was extracted with methylene chloride and worked up to give 34.6 mg (48%) of a light yellow solid. Pure **22** was collected by preparative GLC (10 ft, 10% FFAP) as a white solid, mp 63–65 °C, infrared and uv spectrum as reported[39] (mp 64–65 °C). The NMR spectrum was also consistent: 1.96 (s, 3 H), 5.3–5.7 (m, 2 H), 6.33–7.40 (m, 2 H), 10.66 ppm (s, 1 H).

***cis*-3-Bromobicyclo[2.1.1]hexan-2-ol (23).** A solution of 1.05 g (6 mmol) of **6** in 20 ml of absolute ethanol was treated for 1 h with 0.074 g (1.8 mmol) of sodium borohydride, quenched with 0.3 ml of acetone, and worked up with ether to give 0.83 g of a light yellow liquid. Short-path distillation gave 0.75 g (72%) of **23**, bp 41–42 °C (0.4 mm). GLC analysis (8 ft, 5% FFAP, 15 ft SE-30, or 10 ft 5% DEGS) indicated the presence of only one compound. The NMR spectrum shows 1.05 (t, some further splitting, 1 H), 1.80 (m, 3 H), 2.47 (d, 1 H), 2.55 (m, 1 H), 2.7 (m, 1 H), 4.12 (t, J = 6 Hz, 1 H), and 4.55 ppm (d, J = 6 Hz, 1 H). The 6-Hz coupling between C_2H and C_3H is consistent with the assigned cis stereochemistry.[40]

Anal. Calcd for C_6H_9BrO: C, 40.91; H, 5.12 Found: C, 40.51; H, 5.20.

2-Methylbicyclo[2.1.1]hexane-2,3-diol (25). An ice-cold solution of 2.5 g (16 mmol) of **24**[1] in 20 ml of dry ether was treated with 80 mmol of methylmagnesium bromide, and the solution was then heated at reflux for 4 hr, cooled, acidified, and worked up in the usual manner. Removal of solvent gave 1.91 g (92%) of **25** as an oily liquid, molecularly distilled to give 1.15 g of **25** [bp 59 °C (0.05 mm)]. The infrared spectrum was as expected. The NMR shows 0.7–1.9 (m, 4 H), 1.37 (s, 3 H), 2.3 (m, 2 H), 3.50 (s, 1 H), 4.2 ppm (broad, 2 H).

3-Methyl-3-cyclopentenecarboxaldehyde (26). A solution of 1.91 g (0.015 mol) of **25** in 15 ml of dry pyridine was treated with 2.99 g (0.016 mol) of *p*-toluenesulfonyl chloride at 0 °C for 35 h, then acidified and worked up to give 2.83 g of oily tosylate. Without purification this material was dissolved in 50 ml of *tert*-butyl alcohol, 1.12 g (0.01 mol) of potassium *tert*-butoxide was added, and the solution was heated at reflux for 5 h. Work-up afforded 0.80 g of a yellow liquid. GLC (10 ft, 10% Carbowax 20M) showed two components, A and B, in approximately equal amounts. Both were collected by preparative GLC.

Component A was assigned structure **26** on the basis of its spectral data. Important infrared bands are at 3020, 2855, 2700, and 1725 cm^{-1}. The NMR spectrum has 1.79 (s, 3 H), 2.20–2.30 (m, 5 H), 5.30 (m, 1 H), and 9.61 ppm (s, 1 H). The mass spectrum has the molecular ion at *m/e* 110 and base peak at *m/e* 95.

Component B has not yet been identified but was clearly not the desired 1-acetylbicyclo[1.1.1]pentane.

2,3-Epoxybicyclo[2.1.1]hexane (28). Bicyclo[2.1.1]hex-2-ene[27b] (2.20 g, 0.0275 mol), 5.83 g of sodium carbonate, and 35 ml of methylene chloride were cooled to 0 °C with stirring and treated with 5.88 g (0.029 mol) of *m*-chloroperbenzoic acid over an 80-min period. The solution was stirred for an additional 2 h, filtered, and worked up to give 3.0 g of crude **28** which proved to be unstable above 40 °C. Pure material was obtained by preparative GLC from a 5 ft 3% SE-30 column at 40 °C.The NMR spectrum has broad absorption from 1.20–2.40 (4 H), 2.48 (s, 2 H), and 3.66 ppm (s, 2 H). Anal. Calcd for C_6H_8O: C, 74.97; H, 8.38. Found: C, 74.75; H, 8.42.

3-Cyclopentene-1-carboxyaldehyde (29). The epoxide **28** was isomerized to **29** under a variety of conditions: neat at 80 °C for 18 h; in solution in THF at reflux overnight; or in benzene at 60 °C for 6 h in the presence of anhydrous zinc bromide.

The aldehyde **29** has ir, NMR, and mass spectral data identical with those of authentic **29**.[41] The spectra of **29** and **26** were similar, and were used in the assignment of structure to **26.**

Bicyclo[2.1.1]hexan-2-one (4). A. From 23. A mixture of 1.77 g (0.01 mol) of **23** and 0.425 g (0.01 mol) of sodium hydride in 7 ml of dry diglyme was heated at 80 °C for 2 days under nitrogen which was swept into a dry ice–acetone trap. The trap contained no aldehyde (infrared). The reaction mixture was poured onto ice and worked up in the usual manner to give 1.41 g of a residue which showed (GLC, 10 ft, 10% DEGS) the presence of starting material **23,** and **4** in a ratio of 2:1. Component **4** was collected and identified by its characteristic spectra.

B. From 28. Seventeen milliliters of a 22% solution (2.67 M) of commercial *n*-butyllithium in hexane was added to an ice-cold solution of 3.8 g (0.045 mol) of diethylamine in 15 ml of dry benzene and then stirred for 20 min. A solution of 1.44 g (0.015 mol) of **28** in 12 ml of benzene was added dropwise over a 30-min period and the solution stirred for an additional 65 h at room temperature. After work-up in the normal manner, most of the solvent was removed in vacuo at room temperature. GLC analysis of the residue showed only one product, **4,** in 46% yield. Ketone **4** was collected and characterized by its infrared and NMR spectra.

Under essentially these same conditions **31** was obtained from **30** in 43% yield.

Tricyclo[2.2.0.0^{2,6}]hexan-3-one (2). To a 250-ml flask was added 1.37 g (12.2 mmol) of freshly prepared potassium *tert*-butoxide and 60 ml of dry ether. The suspension was stirred and cooled in an ice–salt bath while adding 0.774 g (5.95 mmol) of **34**[1] in 30 ml of ether dropwise over a 90-min period. The mixture was maintained at −5 °C and became yellow-brown. After 6 h the suspension was filtered, and the ether was washed immediately with five 5-ml portions of saturated salt solution and dried over magnesium sulfate. The drying agent was removed and the ether distilled at 10 °C and aspirator pressure to give 0.46 g of crude product. GC and NMR analysis showed this to contain a small amount of *tert*-butyl alcohol. Pure **2** was collected by preparative GLC using a 5 ft glass column of 6.2% SE-30 with a column temperature of 58 °C. The compound is thermally unstable and base labile. The infrared spectrum has significant bands at 3060, 3030, 2950, 2870, 1775, and 1759 cm^{-1}. The ultraviolet spectrum has λ_{max} (cyclohexane) at 254 nm (ϵ 30). The NMR spectrum at 220 MHz has been reported in detail.[9] The mass spectrum shows the molecular ion as the parent peak at *m/e* 94. Anal. Calcd for C_6H_6O: C, 76.57; H, 6.43. Found: C, 76.66; H, 6.64.

***endo*-Bicyclo[2.1.0]pentane-2-carboxylic Acid (35).** To a 25-ml flask under an argon atmosphere was added 0.97 g (8.7 mmol) of freshly sublimed potassium *tert*-butoxide, 2.6 ml of dimethyl sulfoxide, and 45 μl of water. A solution of **2** (0.104 g, 1.1 mmol) in 0.5 ml of dimethyl sulfoxide was added dropwise from a syringe to the stirred suspension. Stirring at room temperature was continued for 4 h after which the mixture was poured onto ice, acidified, extracted four times with ether, and worked up to give 0.065 g (52%) of **35** which has an NMR spectrum identical with that of authentic **35**.[32,42]

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Registry No.—2, 54096-50-3; **4,** 5164-64-7; **6,** 58191-34-7; **10,** 58191-35-8; **11,** 58191-36-9; **12,** 22287-39-4; **16,** 58191-37-0; **17,** 58101-60-3; **18,** 58191-38-1; **21,** 58191-39-2; **22,** 58191-40-5; **23,** 58191-41-6; **24,** 58191-42-7; **25,** 58191-43-8; **26,** 58191-44-9; **28,** 58191-45-0; **29,** 20145-35-1; **34,** 54096-48-9; **35,** 58191-46-1; *p*-toluenesulfonyl azide, 941-55-9; bicyclo[2.1.1]hex-2-ene, 822-41-3; *m*-chloroperbenzoic acid, 937-14-4.

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(36) Melting points and boiling points are uncorrected. Analyses were carried out by Galbraith Laboratories Inc. NMR spectra were run on a Varian T-60 or HR220 instrument in $CDCl_3$ or CCl_4 with Me_4Si as internal standard and are reported as parts per million (δ). Ir spectra were obtained on a Perkin-Elmer Model 257 spectrometer. Mass spectra were obtained on an LKB 9000 mass spectrometer. GLC experiments were performed on a Varian Aerograph Model A-90P.
(37) Diisopropylamine could also be used but a side product, diisopropylformamide, was difficult to separate from **10** by distillation.
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Molecular Design by Cycloaddition Reactions. XXIV.[1] Stereospecific Cycloaddition Reactions of Dibenzo[4,5-*c*]furotropone

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Marked differences in reactivities between [4,5-*c*]furotropone and dibenzo[4,5-*c*]furotropone in their cycloaddition reactions are observed. Reactions of dibenzo[4,5-*c*]furotropone, readily prepared from 3,6-epoxy-3,6-dihydrotribenzocycloheptatrienone with 3,6-diphenyltetrazine, with some electron-deficient and -rich dienophiles gave [4 + 2] adducts in good yields. The structures of these adducts were determined by spectral means and supported by mechanistic considerations.

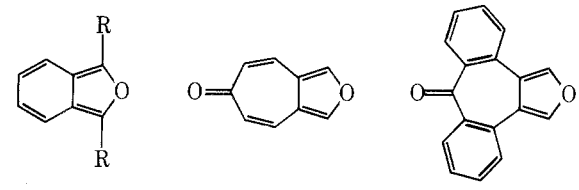
We have already investigated the photochemical and thermal cycloaddition reactions of benzoheterocycles such as isobenzofuran derivatives with some cyclic diene and triene compounds.[2]

Synthesis of a highly reactive isobenzofuran (**1a**) has also been reported; however, it rapidly polymerizes.[3] 1,3-Diphenylisobenzofuran (**1b**) is commercially available and has been used extensively as a trapping agent for reactive dienes but is very sensitive to oxygen.[4] By contrast, [4,5-*c*]furotropone (**2**) has proved to be inert to the Diels–Alder reactions even with a highly reactive dienophile as tetracyanoethylene.[5]

Therefore, it was of interest to prepare derivatives of these ring systems and to examine their reactivities.

The present paper describes a ready method for the preparation of dibenzo[4,5-*c*]furotropone (**3**) (dibenzo[*a*,*e*]furo[3,4-*c*]-8*H*-cycloheptatrienone),[6] and its reactivity in cycloaddition reactions with some dienophiles.

Chart I



1a, R = H
b, R = Ph

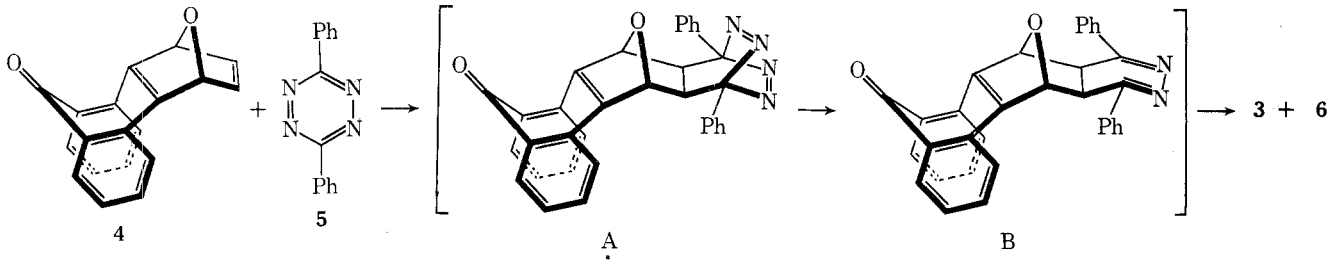
2

3

Results and Discussion

Preparation of Dibenzo[4,5-*c*]furotropone. Reaction of 3,6-epoxy-3,6-dihydrotribenzocycloheptatrienone (**4**)[6] with 3,6-diphenyltetrazine (**5**) under reflux in benzene afforded dibenzo[4,5-*c*]furotropone (**3**) in a high yield together with 3,6-diphenylpyridazine (**6**) as evidenced by the immediate disappearance of the purple color of the solution. Presumably the formation of **3** might proceed via initially

Scheme I



4 **5** **A** **B** → **3** + **6**