Synthesis of Tricyclo[4.4.1.$1^{2,5}$]dodec-3-en-11-one

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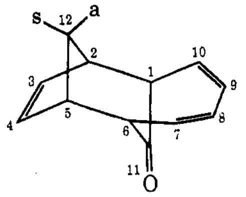
To convert tricyclo[4.4.1.$1^{2,5}$]dodeca-3,7,9-trien-11-one (**1**) into tricyclo[4.4.1.$1^{2,5}$]dodec-3-en-11-one (**4**), it was necessary to protect the isolated double bond while hydrogenation of the conjugated diene was accomplished. Both *m*-chloroperbenzoic acid and chlorine react selectively with the isolated double bond to give, respectively, an exo epoxide and a trans dichloride which are retained during hydrogenation of the remaining diene unit, and from which the isolated double bond can be regenerated. Regeneration from the epoxide fails with reagents which attack the sterically hindered carbon atom of the heterocycle (sodium iodide, zinc and acetic acid, and triphenylphosphine) but is facile with reagents which attack the unhindered epoxide oxygen atom (chromous ion and zinc-copper couple). Regeneration of the olefin from the dichloride is readily effected with zinc in refluxing ethanol. In the present example, which is one of the first employing protecting groups for this purpose, it is clear that the conversion *via* the dichloride is the superior route. Some of the spectral properties (nmr, ir, and uv) of the various compounds prepared are presented and discussed and some of the nmr parameters of the tricyclo-[4.4.1.$1^{2,5}$]dodecyl and norbornyl ring systems compared.

A frequently encountered and often vexing synthetic problem is that of protecting one functional group while reactions are carried out on another. Although the literature abounds with examples of protecting groups, there are relatively few examples of ones which protect specifically one double bond in the presence of another.[1] We would like to report the use of two groups that we have used to protect an isolated double bond while a reaction is carried out on a distant diene unit.

As part of our general interest in the use of rigid polycyclic molecules as stereochemical models, it became necessary to synthesize tricyclo[4.4.1.$1^{2,5}$]dodec-3-en-11-one (**4**), the most promising precursor of which is the well-known tricyclo[4.4.1.$1^{2,5}$]dodeca-3,7,9-trien-11-one (**1**),[2] formed from tropone and cyclopentadiene. We initially considered reducing the activity of the isolated double bond of **1** (it is hydrogenated more readily than is the diene unit[2a]) by chlorine substitution in the cyclopentadiene starting material, but the direction taken by this cycloaddition can be greatly altered by substitution in the addends;[3] in particular neither 1,2,3,4-tetrachlorocyclopentadiene[3a] nor hexachlorocyclopentadiene add to tropone to give derivatives of **1**. It was thus necessary to protect the isolated double bond of **1**.

Reaction of **1** with 1 equiv of *m*-chloroperbenzoic acid[4,5] afforded *exo*-3,4-epoxytricyclo[4.4.1.$1^{2,5}$]dodeca-7,9-dien-11-one (**2**) in addition to some unidentified minor products. The ir spectrum of **2** shows all the bands typical of epoxides.[6] The uv spectrum is almost identical with that reported for **5**[2a] and eliminates other conceivable, symmetrical but unconjugated structures such as **6**; in fact the uv parameters of this diene chromophore have proven to be very diagnostic in **1**, in a variety of its derivatives (Table I) and in related compounds.[7] The nmr spectrum, discussed more fully below, establishes that **2** has a plane of symmetry, the same ring structure as **1**, and the exo stereochemistry as shown.



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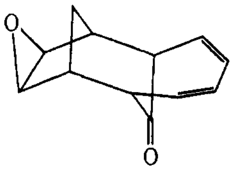

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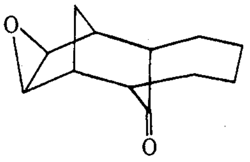

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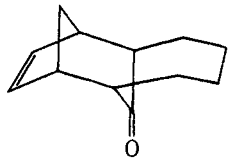

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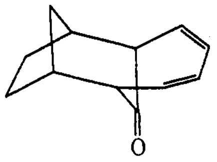

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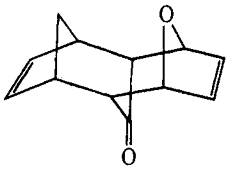

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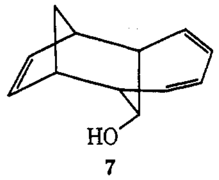

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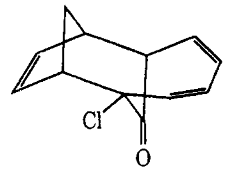

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[1] *Cf.* J. F. W. McOmie, *Advan. Org. Chem.*, **3**, 191 (1963).

[2] (a) R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Commun.*, 15 (1966); (b) S. Itô, Y. Fujise, T. Okuda, and Y. Inoue, *Bull. Chem. Soc. Jap.*, **39**, 1351 (1966); S. Itô, K. Sakan, and Y. Fujise, *Tetrahedron Lett.*, 2873 (1970).

[3] (a) Y. Kitahara, I. Murata, M. Funamizu, and T. Asano, *Bull. Chem. Soc. Jap.*, **37**, 1399 (1964); (b) S. Itô, K. Sakan and Y. Fujise, *Tetrahedron Lett.*, 775 (1969).

[4] (a) It was expected that the more electron-rich isolated double bond of **1** would react preferentially with peracids. *Cf.* H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 304–306; J. March, "Advanced Organic Chemistry: Reactions, Mechanisms and Structure," McGraw-Hill, New York, N. Y., 1968, pp 575, 620. (b) A referee has pointed out that experimental justification of the above expectation is lacking. We are unaware of any good, pertinent kinetic data for diene epoxidation, although conjugation to a phenyl group enhances the epoxidation rate of a double bond by a factor of *ca.* 2 (compare the rates for styrene and simple terminal olefins in ref 4c). Since electron-withdrawing groups retard epoxidation (ref 4a, 4c, and 4d) and since the value of σ^* for vinyl groups indicates electron withdrawal [*Cf.* a recent tabulation: C. Laurence and B. Wojtkowiak, *Ann. Chim. (Paris)*, **5**, 163 (1970)], the expectation seems quite reasonable. (c) *Cf.* D. Swern in "Organic Peroxides," Vol. II, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1971, Chapter V, and references cited therein. (d) *Cf.* P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," C. Eaborn, Ed., Elsevier, Amsterdam, 1966, pp 155–159.

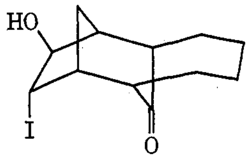
[5] *m*-Chloroperbenzoic acid is the reagent of choice for selective epoxidations. *Cf.* L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis, Vol. 1, Wiley, New York, N. Y., 1968, pp 135–139.

[6] J. Bomstein, *Anal. Chem.*, **30**, 544 (1958).

[7] S. Itô, H. Ohtani, S. Narita, and H. Honma, *Tetrahedron Lett.*, 2223 (1972).

Catalytic hydrogenation of **2** gave the saturated epoxide *exo*-3,4-epoxytricyclo[4.4.1.1^{2,5}]dodecan-11-one (**3**). Retention of the epoxide ring was shown spectroscopically, in particular by the ir bands,[6] and by the nmr singlet at τ 6.73.

Several procedures are commonly used for the regeneration of olefins from epoxides.[8] Treatment of **3** with sodium iodide, zinc and acetic acid,[9] or triphenylphosphine and hydroquinone[10] according to the published procedures gave only recovered **3**. Both of these reagents attack epoxide rings stereospecifically from the back side of one of the carbon atoms to give, respectively, a trans iodohydrin,[9] *e.g.*, **9**, and a trans betaine,[11] *e.g.*, **10**, which then undergo elimination to give an olefin, *e.g.*, **4**. We feel that the deoxygenation fails with both reagents at the ring opening rather than at the elimination step. Cornforth, Cornforth, and Mathew treated epoxides with iodide ion and isolated iodohydrins which were subsequently converted to olefins with zinc;[9] however, **3** failed to react with iodide ion with or without zinc present. Although direct elimination of triphenylphosphine oxide from **10** is untenable because it requires rotation about the C-3–C-4 bond to eclipse the phosphorus and oxygen atoms and leads to the highly strained trans olefin **11**, it is expected[12] that **10** will equilibrate *via* ylide intermediates with either of its cis epimers, from which elimination should be facile. We thus conclude that neither **9** nor **10** is formed because the required attack by the bulky nucleophiles from the endo side of **3** is too sterically hindered.



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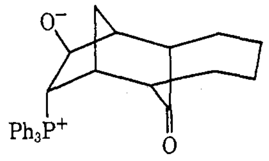

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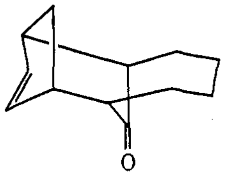

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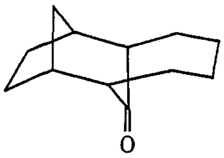
An alternative mode of epoxide ring opening, attack by the phosphorus at the oxygen atom (unhindered in **3**), is the predominant, if not the exclusive, route in the closely related desulfurization of episulfides.[13] It is not the commonly found pathway for deoxygenation, however, and one considered unlikely on theoretical grounds.[14] Our results are the first experimental evidence that epoxide deoxygenation by a trivalent phosphorus compound will not occur by this route should the preferred attack at carbon be impossible.

In contrast to the two reagents discussed above, both zinc–copper couple[15] and chromous ion[15,16] deoxygenate **3** readily, giving **4** as the sole product (overall yield from **1**, *ca.* 30%). The structure of **4** followed from its method of preparation, its conversion upon mild catalytic hydrogenation into the known ketone **12**,[2a] and its nmr spectrum. These two reagents effect the desired deoxygenation because they attack the unhindered epoxide oxygen atom of **3**[15,16] rather than one of the hindered carbon atoms.



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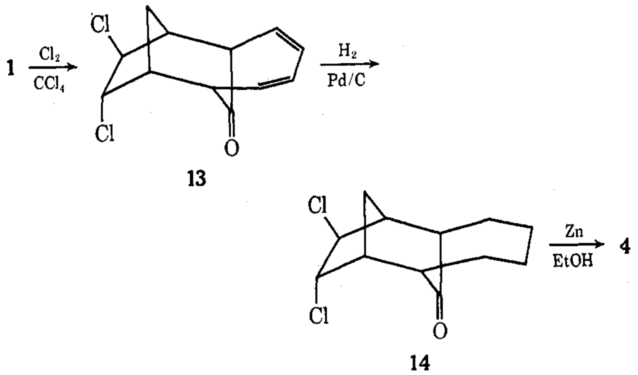
We have also found that the isolated double bond in **1** can be protected as its dichloride. Trienone **1** reacted with chlorine to give *trans*-3,4-dichlorotricyclo[4.4.1.1^{2,5}]dodeca-7,9-dien-11-one (**13**) as the predominant product. As with **2**, structural assignment of **13** rested on spectral evidence which clearly showed the presence of the diene chromophore and the trans relationship of the chlorine atoms.

Catalytic hydrogenation of **13** gave *trans*-3,4-dichlorotricyclo[4.4.1.1^{2,5}]dodecan-11-one (**14**), whose structure was assigned by nmr. Treatment of **14** with zinc in refluxing ethanol effected removal of the blocking group to give the desired ketone **4** (overall yield from **1**, *ca.* 35%).



It is apparent from this work that both epoxidation and chlorination occur selectively at the isolated double bond of **1** and therefore usefully protect that function in the presence of the conjugated diene unit. Chlorination appears to be more selective than epoxidation in agreement with its larger value of ρ[4d] and the unlikelihood of competing reactions at the carbonyl group. The generality of these two protecting procedures awaits additional work, however, since it is not yet certain that diene units react more slowly with electrophiles than do nonconjugated olefins, or if the present example of selectivity has some other origin, for example, an exceptionally reactive C-3–C-4 bond or diene

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(8) *Cf.* C. A. Buehler and D. E. Pearson, "Survey of Organic Syntheses," Wiley-Interscience, New York, N. Y., 1970, pp 84, 97; L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, Wiley, New York, N. Y., 1968, pp 147–151, 1238–1247; I. T. Harrison and S. Harrison, "Compendium of Organic Synthetic Methods," Wiley-Interscience, New York, N. Y., 1971, pp 502–504.

(9) J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 112 (1959).

(10) G. Wittig and W. Haag, *Chem. Ber.*, **88**, 1654 (1955).

(11) M. J. Boskin and D. B. Denney, *Chem. Ind. (London)*, 330 (1959); A. J. Speziale and D. E. Bissing, *J. Amer. Chem. Soc.*, **85**, 1888, 3878 (1963).

(12) D. E. Bissing and A. J. Speziale, *ibid.*, **87**, 2683 (1965).

(13) N. P. Neureiter and F. G. Bordwell, *ibid.*, **81**, 578 (1959); R. D. Schuetz and R. L. Jacobs, *J. Org. Chem.*, **23**, 1799 (1958).

(14) F. G. Bordwell, H. M. Andersen, and B. M. Pitt, *J. Amer. Chem. Soc.*, **76**, 1082 (1954).

(15) S. M. Kupchan and M. Maruyama, *J. Org. Chem.*, **36**, 1187 (1971).

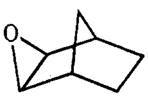
(16) J. K. Kochi and D. M. Singleton, *J. Amer. Chem. Soc.*, **90**, 1582 (1968); J. K. Kochi, D. M. Singleton, and L. J. Andrews, *Tetrahedron*, **24**, 3503 (1968).

deactivation by the nearby carbonyl group.[4] Extensions of our studies on the spectroscopic and chemical properties of **4** and some of its derivatives are currently in progress.

Nmr Spectra.—The nmr spectra of the tricyclo[4.4.1.1^{2,5}]dodecane derivatives prepared in this study have proven to be very useful for stereochemical and structural assignments and to demonstrate that this ring system has much in common with the norbornyl one.

The epoxide ring protons in **2** appear as a sharp singlet at almost the same postion as the sharp signals exhibited by the exo epoxides **15**,[17] **16**,[18] and **17**;[19] the endo epoxides **18**[18] and **19**[18] give signals which are broader and at somewhat lower field than those of their exo counterparts.[20] Although it is tempting to assign the exo stereochemistry to **2** on the basis of this chemical shift data alone, we do not feel that such an argument is justified at this time because the anisotropic effects of the bonds in **1** on protons at C-3 and C-4 are as yet unknown, because the chemical shift differences between the known exo–endo pairs of epoxides is relatively small, and because only one isomer of **2** is yet available. The stereochemistry of **2** can be assigned from the observed coupling, however.

Each of the four exo epoxides **2**, **15**, **16**, and **17** displays a very sharp signal for the epoxide ring protons, owing to a very small coupling to the adjacent bridgehead protons, whereas the endo epoxides **18** and **19** show a broader, more strongly coupled signal. This coupling pattern is typical of *exo*- and *endo*-norbornyl[21] and more pertinently of *exo*- and *endo*-tricyclo[3.2.1.0^{2,4}]octyl[22] derivatives. The implied similarly between the norbornyl and the tricyclo[4.4.1.1^{2,5}]dodecyl systems is supported by molecular models which indicate little geometric change upon removal of the C-1–C-6 bond, the dihedral angles between H-2 and H-3 being about 75° in **2** (small coupling) and about 5° in the as yet unknown **20** (larger coupling).[23] The corresponding angles measured for **15** and **18** are 60 and 20°, respectively, so that the coupling difference between *exo*- and *endo*-norbornyl derivatives should be enhanced in the tricyclo[4.4.1.1^{2,5}]dodecyl system.



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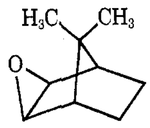

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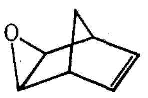

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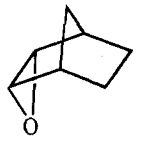

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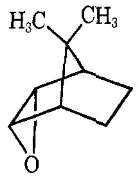

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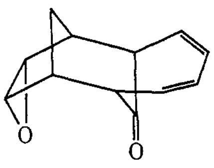

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Corroborative evidence for both the similarity between the two ring systems and the assigned stereochemistry of **2** comes from a consideration of the bridge protons. It has finally been established that the H-7a proton of norbornene absorbs at higher field than H-7s.[24] The assignment of the bridge proton signals in **1** and its derivatives rests on the examination of molecular models, which indicate that the complex, highest field signal is due to H-12s (dihedral angle about 40°) whereas the simple, lower field doublet is due to H-12a (dihedral angle about 80°). Although the relative positions of the syn and anti protons in **1** and norbornene are opposite, epoxidation to **2** and **15** is accompanied by identical behavior: an upfield shift of about 0.3 ppm of the anti proton, the syn proton being relatively ununaffected. This parallel behavior of the bridge protons strengthens the arguments for an exo stereochemistry in **2** and emphasizes the geometric similarity between the norbornyl and tricyclo[4.4.1.1^{2,5}]dodecyl ring systems.

The two dichlorides **13** and **14** have also provided interesting nmr spectra. The assignment of the two protons H-3 and H-4 was based on the relative chemical shifts of *trans*-2,3-dichloronorbornene,[21] in which H-2$_{exo}$ is at lower field, and on the larger coupling to the adjacent bridgehead expected for the exo proton. A more rigorous analysis is required to more firmly assign the chemical shifts and coupling constants in these rather complex molecules.

Experimental Section

Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. The nmr spectra were obtained on a Varian A-60A spectrometer in deuteriochloroform solution. Peak positions are given in units of τ relative to internal tetramethylsilane at τ 10.00; in all cases the relative peak areas are consistent with assigned structure. Infrared spectra were recorded as Nujol mulls or as neat liquids on a Unicam SP200 spectrometer; the peak positions are recorded in wavenumbers. Ultraviolet spectra (Table I) were recorded on a Unicam SP800 recording uv spectrophotometer using ethanol as the solvent. Gas–liquid chromatograms (glc) were obtained on a Varian-Aerograph A90P3 instrument using a single column of Carbowax 20M (25%) packed on acid-washed Chromosorb W. Combustion microanalyses were obtained from Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

TABLE I

ULTRAVIOLET SPECTRA OF SOME TRICYCLO[4.4.1.1^{2,5}]DODEC-7,9-DIENES

Compd	Band positions (ϵ)[a]					Ref
1[b]	267 (4935)	258 (4600)	249 (3375)	240 (2730)	216 (3510)	
1[c]	267 (7870)	257 (7680)				2a
1[b,d]	266 (4630)	257 (4520)	248 (3370)	238 (2840)		2b
5[c]	269 (4620)	258 (4720)				2a
2[b]	266 (6075)	256 (6000)	248 (4100)	239 (2800sh)	222 (3500)	
13[b]	270 (4080)	260 (4280)	252 (3075)	243 (2100sh)	223 (2440)	
7[d]	273 (3173)	262 (5568)	252 (5720)	243 (4552sh)		2b
8	270 (4040)	261 (4100)	252 (3070)			3b

[a] λ_{max} in nm obtained in ethanol unless otherwise stated. [b] In addition a broad weak peak (ϵ *ca.* 500) was noted at *ca.* 300 nm. [c] Solvent not specified. [d] Methanol as solvent.

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(18) H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Amer. Chem. Soc.*, **92**, 6914 (1970); H. C. Brown and S. Krishnamurthy, private communication.

(19) J. Meinwald, S. S. Labana, L. L. Labana, and G. H. Wahl, *Tetrahedron Lett.*, 1789 (1965).

(20) *endo*-Norbornadiene oxide, the endo analog of **17**, has been reported but no nmr data were given. See J. T. Lumb and G. H. Whitham, *J. Chem. Soc.*, 1189 (1964), and ref 19.

(21) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

(22) R. E. Pincock and J. Haywood-Farmer, *Tetrahedron Lett.*, 4759 (1967); J. Haywood-Farmer, Ph.D. Thesis, University of British Columbia, 1967.

(23) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

(24) B. Franzus, W. C. Baird, N. F. Chamberlain, T. Hines, and E. I. Snyder, *ibid.*, **90**, 3721 (1968); A. P. Marchand and J. E. Rose, *ibid.*, **90**, 3724 (1968).

Reaction of Tropone and Hexachlorocyclopentadiene.—An nmr tube containing a mixture of 230 mg of freshly distilled tropone, 600 μl of acetone, and 655 mg of freshly distilled hexachlorocyclopentadiene was heated at 60°. After 21 hr the tube contents had turned black with the deposition of black particles but the nmr had not changed. The reaction was discontinued.

Tricyclo[4.4.1.$1^{2,5}$]dodeca-3,7,9-trien-11-one (1).—This ketone, mp 69.5–70.0° (lit.[2] mp 70–71.5°), was prepared in 65% yield by a modification of the published route. It was found advantageous to monitor the reaction by nmr, to distill off the volatile components at the completion of the reaction, and to purify the product by column chromatography followed by recrystallization. The nmr spectrum showed peaks at τ 3.8–4.6 (m, H-3, H-4, H-7–H-10), 6.7–6.9 (m, H-1, H-6), 6.9–7.05 (m, H-2, H-5), 7.68 (d, H-12a, J = 11 Hz), 8.50 (dt, H-12s, J = 11, 5.5 Hz).

***exo*-3,4-Epoxytricyclo[4.4.1.$1^{2,5}$]dodeca-7,9-dien-11-one** (2).—A mixture of 1.00 g of 1 and 1.24 g of 85% *m*-chloroperbenzoic acid in 15 ml of chloroform was stirred at room temperature until a positive test with starch iodide paper was no longer obtained (*ca.* 2–5 hr). Additional chloroform was added to dissolve a white precipitate and the organic solution was washed with 10% aqueous sodium carbonate solution and water and then dried over magnesium sulfate. The drying agent was filtered off and the solvent was evaporated to give a yellow oil which deposited sticky crystals on standing. The product was chromatographed on a column of alumina eluting unreacted **1** (benzene), mixtures of **1** and **2** (benzene), and mixtures of **2** and an as yet unidentified third component (benzene and ether).

Unreacted **1** could be separated from **2** by virtue of its greater solubility in ether to leave an analytically pure sample of **2**, mp 141.5–142°, sublimation of which [115° (0.2 mm)] depressed the melting point somewhat (139.5–142°). The ir spectrum showed characteristic peaks at 3050, 1710, 1280, 1260, 900, and 840 cm^{-1}. The nmr spectrum showed peaks at τ 3.80–4.65 (m, H-7–H-10), 6.65 (s, H-3, H-4), 6.68–6.95 (m, H-1, H-6), 7.26–7.48 (m, H-2, H-5), 7.95 (d, H-12a, J = 13 Hz), 8.63 (dt, H-12s, J = 13, 5.5 Hz).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.76; H, 6.40.

The yield of **2** was very difficult to determine because of the difficulty of separating it from the unidentified product.

***exo*-3,4-Epoxytricyclo[4.4.1.$1^{2,5}$]dodecan-11-one** (3).—The crude product from the epoxidation of 1.10 g of **1** (*vide supra*) was dissolved in 75 ml of 95% ethanol and exposed to hydrogen gas in the presence of 400 mg of 10% palladium on charcoal. After the hydrogen uptake ceased (400 ml) the catalyst was removed by filtration and the solvent was evaporated to give a yellow oil which was purified by chromatography on alumina. Benzene elution afforded 0.16 g of tricyclo[4.4.1.$1^{2,5}$]dodecan-11-one (**12**) from hydrogenation of unreacted **1**,[25] followed closely by 0.39 g (32% from **1**) of pure **3**, sublimation of which [100° (1.0 mm)] gave an analytical sample, mp 88.5–89.5°. The ir spectrum showed characteristic peaks at 1690, 1265, 1250, 890, and 850 cm^{-1}. The nmr spectrum showed peaks at τ 6.73 (s, H-3, H-4), 7.10–7.50 (m, H-1, H-6), 7.50–7.70 (t, H-2, H-5, J = 4 Hz), 7.75–8.85 (m, H-7–H-12).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.08; H, 8.51.

An additional 0.64 g of a yellow oil, as yet unidentified, was obtained by further elution with methanol. The only volatile component of this oil had a shorter retention time (glc) than **3** and was present in smaller amounts (ratio *ca.* 1:2.5).

Treatment of 3 with Zinc–Copper Couple.—The method of Kupchan and Maruyama[15] was followed. Zinc–copper couple was prepared from 900 mg of zinc as usual[26] except that the ether wash and drying were omitted. A mixture of this couple, 3 ml of ethanol, and 102 mg of **3** was sealed in a thick-walled glass tube, which had been flushed out with nitrogen, and heated at 140° for 24 hr. The mixture was cooled to room temperature and filtered and the solvent was evaporated to give 93 mg (99%) of glc homogeneous, white, crystalline **4**. Sublimation [110° (10 mm)] gave an analytical sample, mp 60.5–61.5°. The ir spectrum showed peaks at 3020 and 1710 cm^{-1}; the nmr spectrum showed peaks at τ 3.89 (s, H-3, H-4), 7.3–7.5 (m, H-1, H-2, H-5, H-6), 7.56 (d, H-12a, J = 12 Hz), and 7.9–8.7 (m, H-7–H-10, H-12s).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.62; H, 9.18.

Longer reaction times caused further reduction to **18**; milder conditions (reflux for 70 hr) gave only 2% reaction.

Treatment of 3 with Cr(II).—A solution of $Cr(ClO_4)_2$ was prepared according to the method of Kupchan and Maruyama.[15] To a thoroughly degassed (argon) solution of 40 mg of **3** in 12 ml of *N*,*N*-dimethylformamide was added 1.2 ml of the Cr(II) solution and 60 μl of ethylenediamine. This solution was stirred and heated at 90° for 5 hr under a slow stream of argon. The mixture was cooled to room temperature, poured into 20 ml of 2 *N* aqueous hydrochloric acid, and extracted three times with ether. The ether was washed with 10% aqueous sodium carbonate and dried over magnesium sulfate. The drying agent was filtered off and the solvent was evaporated to give a yellow oil. The product was purified by chromatography on alumina. Benzene eluted 25 mg (68%) of pure **4** identical with that prepared above.

Treatment of 3 with Triphenylphosphine.—The procedure of Wittig and Haag[10] was followed. A mixture of 100 mg of **3**, 138 mg of triphenylphosphine, and 21 mg of hydroquinone was heated to 180° over a period of 1 hr and kept at that temperature for an additional 2.5 hr. The black reaction mixture was cooled to room temperature and chromatographed on a 10-g column of alumina. Benzene (25 ml) eluted triphenylphosphine (80 mg) and unreacted **3** (100 mg) cleanly separated from it. The nmr spectrum of the recovered **3** was identical with that of authentic material and showed no trace of the expected product **4**.

Treatment of 3 with Sodium Iodide.—This experiment was based on the published procedure.[9] A mixture of 100 mg of **3**, 164 mg of sodium iodide, 17 mg of sodium acetate, 0.3 ml of acetic acid, and 0.6 ml of propionic acid was heated at 100° for 18 hr. The mixture was diluted with ether, washed with 10% aqueous sodium bicarbonate solution, sodium bisulfite solution, and water, and dried over magnesium sulfate. The drying agent was filtered off and the solvent was evaporated to give a yellow solid. The nmr spectrum showed that it was unreacted **3**.

Treatment of 3 with Sodium Iodide and Zinc.—The method used was that described by Cornforth, Cornforth, and Mathew.[9] An ice-cooled solution of 134 mg of sodium iodide and 45 mg of sodium acetate in 0.27 ml of acetic acid and 0.02 ml of water was prepared and 134 mg of zinc powder was added to it. To this magnetically stirred mixture was added 100 mg of **3**, which caused the suspension to turn brown and then gray and very pasty. After standing at 0° for about 75 min the mixture was filtered and the residues were washed well with ether. The organic solution was washed with 10% aqueous sodium carbonate solution and water and dried over magnesium sulfate. The drying agent was filtered off and the solvent was evaporated to give 60 mg of a yellow solid shown to be unreacted **3** by comparison of its nmr spectrum with that of an authentic sample.

***trans*-3,4-Dichlorotricyclo[4.4.1.$1^{2,5}$]dodeca-7,9-dien-11-one** (13).—A solution of 1.64 g of chlorine in 25 ml of carbon tetrachloride was added to a solution of 4.05 g of trienone **1** in 115 ml of carbon tetrachloride at room temperature. After about 0.5 hr of stirring the initial green color had disappeared and an additional 1.64 g of chlorine in 25 ml of carbon tetrachloride was added. After a total reaction time of 1 hr the solvent was evaporated to give a viscous green oil which was decolorized by elution with ether through a short alumina column followed by treatment with charcoal in ethanol. Evaporation gave yellow crystals which were rechromatographed on alumina using ether as the eluent giving 4.7 g of crude white product, the nmr of which clearly showed **13** to be the predominant component. Recrystallization (ether) afforded 2.15 g (37%) of pure **13**. Additional material was present in the mother liquors. Sublimation [125° (0.4 mm)] gave an analytical sample, mp 156–156.5°. The ir spectrum showed peaks at 1720, 800, and 700 cm^{-1}. The nmr spectrum showed peaks at τ 3.80–4.70 (m, H-7–H-10), 5.45–5.70 (m, H-4_{exo}, J = 4.2, 6.4 Hz), 6.00 (dd, H-3_{endo}, J = 4.2, 2.4 Hz), 6.27–6.85 (m, H-1, H-6), 7.15–7.55 (m, H-2, H-5, H-12a), 8.02 (ddt, H-12s, J = 13.7, 4.6, 1.0 Hz).

Anal. Calcd for $C_{12}H_{12}Cl_2O$: C, 59.28; H, 4.98; Cl, 29.16. Found: C, 59.23; H, 4.91; Cl, 29.08.

***trans*-3,4-Dichlorotricyclo[4.4.1.$1^{2,5}$]dodecan-11-one** (14).—A solution of 4.09 g of **13** in 300 ml of 95% ethanol was exposed to hydrogen gas in the presence of 1.72 g of 10% palladium on charcoal. After the hydrogen uptake ceased (940 ml) the catalyst was removed by filtration and the solvent was evaporated to give 3.90 g (94%) of pure **14**. Sublimation [125°

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[25] This ketone was identified by a spectral and chromatographic comparison with an authentic sample of **12** prepared by hydrogenation of **1**.[2]

[26] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, Wiley, New York, N. Y., 1968, p 1292.

(0.4 mm)] gave an analytical sample, mp 139–140°. The ir spectrum showed peaks at 1710 and 800 cm^{-1}. The nmr spectrum showed peaks at τ 5.50–5.80 (m, H-4$_{exo}$, J = 4.2, 6.4 Hz), 6.18 (dd, H-3$_{endo}$, J = 4.0, 2.4 Hz), 6.70–7.70 (m, H-1, H-2, H-5, H-6, H-12a), 7.80–8.20 (m, H-7–H-10, H-12s).

Anal. Calcd for $C_{12}H_{16}Cl_2O$: C, 58.31; H, 6.53; Cl, 28.69. Found: C, 58.55; H, 6.50; Cl, 28.50.

Tricyclo[4.4.1.1^{2,5}]dodec-3-en-11-one (4).—A mixture of 3.90 g of **14**, 2.0 g of zinc chloride, and 21.3 g of zinc dust in 215 ml of 95% ethanol was refluxed at 100° for 25 hr. The mixture was allowed to cool to room temperature, the gray solid was filtered off, and the ethanol solution was diluted with ether. The ether was washed twice with water and the water was back extracted twice with ether. The combined ether fractions were dried over magnesium sulfate, the drying agent was filtered off, and the ether was evaporated. Purification of the resulting crystals by sublimation [100° (12 mm)] yielded 2.52 g (91%) of pure **4** identical in all respects with a sample prepared from deoxygenation of **3** (*vide supra*).

Catalytic Hydrogenation of Tricyclo[4.4.1.1^{2,5}]dodec-3-en-11-one (4).—A solution of 48 mg of **4** in 3 ml of 95% ethanol was exposed to hydrogen gas in the presence of 35 mg of 10% palladium on charcoal. After 25 min the uptake ceased; no additional hydrogen was taken up over the next 15 min. The solution was filtered and the solvent was evaporated to give 48 mg (98%) of pure colorless **12**.[25] The nmr spectrum showed only a complex multiplet between τ 7.2 and 8.9.

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The Isomerization of Tri-*tert*-butylcyclopropenyl Azide[1]

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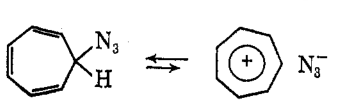
Tri-*tert*-butylcyclopropenyl azide has been synthesized by the reaction of tri-*tert*-butylcyclopropenyl perchlorate or fluoroborate with sodium azide. The nmr spectra exhibited both solvent and temperature dependence as the result of chemical exchange of the azide function between three equivalent annular sites. Total line shape analyses of the spectra provided activation parameters in six widely different solvents. The sensitivity of the degenerate isomerization rate to the nature of the solvent suggests that the process proceeds *via* an ionization–recombination (ion-pair) mechanism.

In recent years much interest has been devoted to the problem of structure and reactivity of organic azides.[2] The rates of rearrangement of allylic azides (eq 1) have been shown to be relatively insensitive to

(1)

alkyl substitution and changes in solvent polarity.[3] These results are consistent with a concerted mechanism involving a [3,3] sigmatropic shift. On the other hand, Wulfman, *et al.*,[4] have suggested that the temperature and solvent dependence of the nmr spectrum of tropyl azide (**1**) can be rationalized on the basis of a mechanism involving ionization to the tropylium ion–azide ion pair (**1a**). Upon warming a



1 **1a**

solution of **1** in acetone-d_6 at −35 to −15°, all nmr (60 MHz) spin–spin splitting disappears, whereas, at 30°, all chemical shifts are indistinguishable and the spectrum exhibits a single broad maximum. The position of the center of gravity of the spectrum at −35°, namely δ 5.85, is identical with the corresponding position at 52° but is much further upfield than the tropylium ion resonance (δ 10.0). The independence of the spectra of concentration provided evidence that the protons in tropyl azide approach equivalency *via* an intramolecular degenerate isomerization process. However, it was shown that **1** in the presence of added tropylium perchlorate exhibits spectra ranging from those showing a single sharp line between tropylium ion and exchanging azide peaks, through those showing broad absorption in the same region, to those showing separate peaks. Furthermore, it was reported that under certain conditions these spectra show extreme concentration dependence attributed to an intermolecular exchange process between tropyl azide and tropylium perchlorate *via* an ion triplet **2**.

$$C_7H_7^+\quad N_3^-\quad C_7H_7^+$$

2

Since cyclopropenyl azides are $(4n + 2)$ vinylogs of tropyl azide (**1**), it was of interest to establish whether they revealed in their nmr spectra any of the unusual features exhibited by **1**. However, it has been reported that the reaction of triphenylcyclopropenyl bromide with sodium azide in DMF gives the unstable covalent triphenylcyclopropenyl azide (**3**) which undergoes facile rearrangement to the *v*-triazine **4**.[5,6]

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(1) A preliminary communication of this work has appeared in which a different total line shape analysis (TLS) program was employed: R. Curci, V. Lucchini, P. J. Kocienski, G. T. Evans, and J. Ciabattoni, *Tetrahedron Lett.*, 3293 (1972).

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