separated as described in the previous section and chromatographed over alumina. Elution with hexane afforded 3 mg of a less polar blue azulene, mp of TNB adduct 141–145°; with TNB adduct of guaiazulene mmp 141–145°. The visible spectrum of azulene was superimposable on that of guaiazulene. Further elution of the alumina column with benzene–hexane (1:1) afforded an azulene mixture. Elution with benzene yielded 2 mg of a more polar azulene; TNB adduct mp 151°; with authentic linderazulene adduct mmp 149–152°. The visible spectrum of the azulene liberated from the TNB adduct was superimposable on that of linderazulene.

## A Convenient Synthesis of *cis*- and *trans*-Cyclodecene

JAMES G. TRAYNHAM, DEWITT B. STONE,[1] AND JOHN L. COUVILLION

*Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana 70803*

*Received October 28, 1966*

Although both *cis*- and *trans*-cyclodecene have been prepared by several different routes, none of the published routes is truly convenient in the sense of requiring few steps from cheap starting materials.[2] Cyclodecane is now available,[3] it is easily chlorinated, and the chlorocyclodecane can be dehydrochlorinated by potassium *t*-butoxide in dimethyl sulfoxide to 97% *cis*-cyclodecene and by lithium dicyclohexylamide in hexane to 96% *trans*-cyclodecene.[4]

Because of the ease with which these preparations can be carried out, and because the isomeric cyclodecenes may be used for the preparation of numerous cyclodecane derivatives otherwise difficult or expensive to obtain, these procedures promise to be particularly useful.

(1) National Aeronautics and Space Administration Trainee, 1964–1966.

(2) Illustrative examples are (a) 87% *cis* and 85–94% *trans* from bromocyclodecane [A. C. Cope, M. Brown, and G. L. Woo, *J. Am. Chem. Soc.*, **87**, 3107 (1965)]; (b) *cis* only from 10,10-dibromobicyclo[7.1.0]decane [J. G. Traynham and P. M. Greene, *ibid.*, **86**, 2657 (1964)]; (c) 83% *trans* from cyclodecyl tosylate [V. Prelog, W. Küng, and T. Tomljenović, *Helv. Chim. Acta*, **45**, 1352 (1962)]; (d) 98% *trans* from cyclodecyltrimethylammonium hydroxide [A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **82**, 1744 (1960)]; (e) 98% *trans* from cyclodecyldimethylamine oxide [A. C. Cope, D. C. McLean, and N. A. Nelson, *ibid.*, **77**, 1628 (1955)]; (f) *cis* only from *cis,trans*-1,5-cyclodecadiene [G. A. Knesel, Ph.D. Dissertation, Louisiana State University, 1966].

(3) From Columbian Carbon Co., Lake Charles, La. We gratefully acknowledge the gift of a generous sample of cyclodecane from this company.

(4) Other reagents tried gave mixtures containing more of the minor component; for example, silver nitrate in DMSO gave a mixture consisting of 92% *cis*- and 8% *trans*-cyclodecene.

### Experimental Section

**Chlorocyclodecane.**—A 1-l., three-neck Pyrex flask equipped with a condenser, stirrer, and gas dispersion tube was charged with cyclodecane (420 g, 3.0 moles) and irradiated with a 150-w light bulb in a reflector about 4 in. from the flask. Chlorine gas (71 g, 1.0 mole) was passed through a trap containing concentrated sulfuric acid, through an empty trap, and into the stirred cyclodecane during 4 hr. Irradiation was continued for 35 min longer, and air was then bubbled through the mixture for 30 min to sweep out chlorine and hydrogen chloride. Distillation of the mixture at reduced pressure gave the following three well-separated fractions.

**Recovered cyclodecane** amounted to 286 g (2.04 moles), bp 72–73.5° (12 mm), $n^{25}D$ 1.4697.

**Chlorocyclodecane** was obtained in 64% yield (based on $Cl_2$) (111.4 g), bp 109–110.5° (12 mm), $n^{25}D$ 1.4923. *Anal.* Calcd for $C_{10}H_{19}Cl$: C, 68.74; H, 10.96. Found: C, 68.55; H, 10.75.

**Dichlorocyclodecane** was formed in small amount (14.1 g, 13.5%), bp 135–137° (12 mm), $n^{25}D$ 1.5078. *Anal.* Calcd for $C_{10}H_{18}Cl_2$: C, 57.42; H, 8.67. Found: C, 58.00; H, 8.92.

**Dehydrochlorination. A. *cis*-Cyclodecene.**—A solution of chlorocyclodecane (105 g, 0.60 mole), dimethyl sulfoxide (500 ml), and potassium *t*-butoxide (100.8 g, 0.90 mole) was stirred for 3 hr. The mixture was diluted with water (750 ml) and extracted with four 200-ml portions of petroleum ether (bp 60–70°). The combined organic material was dried with Drierite and concentrated by rotary evaporation. Distillation of the residue gave *cis*-cyclodecene (66.0 g, 80%), bp 44–45° (2 mm). Analysis by gas chromatography on a 1/8 in. × 15 ft Ucon column at 110° indicated that the sample contained 97% *cis*- and 3% *trans*-cyclodecene.

**B. *trans*-Cyclodecene.**[5]—A solution of butyllithium in hexane (400 ml, 1.6 *M*) was added to a solution of dicyclohexylamine (124 g, 0.68 mole) in anhydrous ethyl ether (200 ml) contained in a 2-l. flask fitted with a condenser, magnetic stirrer, and nitrogen atmosphere. To the resulting mixture was added a solution of chlorocyclodecane (105 g, 0.60 mole) in hexane (200 ml). The mixture was refluxed for 24 hr, allowed to cool, washed with four 50-ml portions of water, and dried with Drierite. Removal of solvent by rotary evaporation and distillation of the residue gave *trans*-cyclodecene (58.0 g, 70%), bp 53–55° (4 mm). Analysis by gas chromatography on a 1/8 in. × 15 ft Ucon column at 110° indicated that the sample contained 96% *trans*- and 4% *cis*-cyclodecene. Dicyclohexylamine was recovered in good yield by continuing the distillation.[6]

(5) This procedure parallels that for dehydrobromination of bromocyclodecane with lithium di-*sec*-butylamide.[2a]

(6) Dicyclohexylammonium chloride is sparingly soluble in water. When attempts were made to remove the amine (as its salt) from the organic layer by washing with aqueous acid, a heavy, white precipitate formed and made subsequent work-up difficult.