μ (N_3); uv (C_2H_5OH) λ_{max} 289–290 nm (ϵ 18); nmr δ 1.03 (9), 1.30 (6), 1.49 (2).

Registry No.—Triflyl azide, 3855-45-6; *n*-hexyl azide, 6926-45-0; 2,4,4-trimethyl-2-pentyl azide, 35426-97-2.

Acknowledgment.—This research was supported in part by Grant AT(11-1)-1008 from the United States Atomic Energy Commission (Document No. COO-1008-20). Fellowship support from the Meade Johnson Company for Carol Cavender is also gratefully acknowledged.

A Convenient Synthesis of Homocubane-4-carboxylic Acid

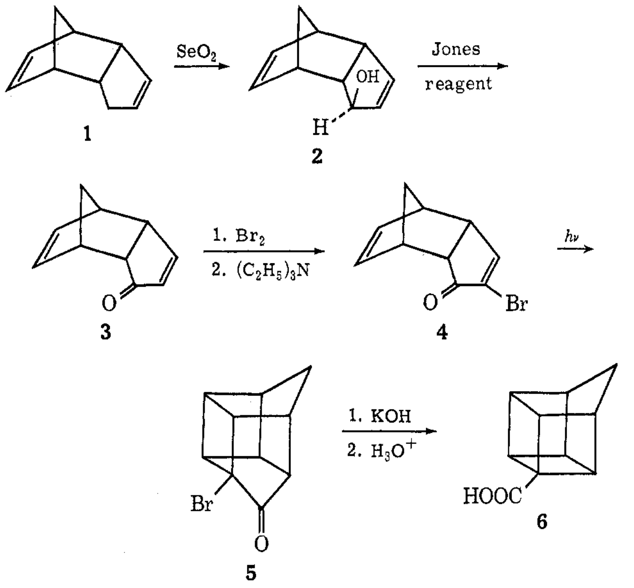
Leo A. Paquette* and John S. Ward[1]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Received May 12, 1972

In connection with studies concerning mechanistic aspects of the Ag^+-catalyzed rearrangement of cubyl systems,[2] a number of various 4-substituted homocubanes (pentacyclo[$4.3.0.0^{2,5}.0^{3,8}.0^{4,7}$]nonanes) were required.[3] Since all of the desired compounds could be derived readily from that member of the series at the highest oxidation level, attention was given to the preparation of suitable quantities of homocubane-4-carboxylic acid (**6**). The original route to this compound reported in 1968 by Dunn, DiPasquo, and Hoover[4] began with relatively expensive 2-cyclopentenone and afforded **6** in less than 10% yield. We describe now a procedure which comprises only five readily executable steps, utilizes inexpensive dicyclopentadiene (**1**) as starting material, and results in at least 27% overall conversion to **6**.

Selenium dioxide oxidation of freshly distilled **1** according to the procedure of Woodward and Katz[5] led to the formation of allylic alcohol **2** in 63% yield. Efficient oxidation (75% yield) of this compound was achieved by treatment with Jones reagent.[6] Further studies indicated that **3** could be selectively brominated α to the carbonyl group by direct addition of elemental bromine in carbon tetrachloride solution and subsequently dehydrobrominated with triethylamine. The halogenated ketone obtained in this manner (75% yield) was identical with an authentic sample of **4** prepared in unequivocal fashion.[4] Photocyclization of **4** and Favorskii-type ring contraction of **5**[4] complete the sequence.



Experimental Section

endo-**3a,4,7,7a-Tetrahydro-4,7-methanoinden-1-one (3)**.—A solution of 40 g (0.27 mol) of **2**[5] in 500 ml of acetone was cooled in an ice bath and titrated with a total of 170 ml of Jones reagent (*ca.* 0.2 *M*) prepared according to the method of Meinwald, *et al.*[7] The reaction mixture was added to 1 l. of brine and extracted with ether. The combined organic extracts were washed with water and dried. Evaporation of the solvent left an oily residue which solidified on standing. Recrystallization of the white solid from pentane gave 30 g (75%) of crystalline ketone, mp 80° (lit.[6] mp 80°).

endo-**2-Bromo-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one (4)**.—A solution of bromine (20.1 g, 0.126 mol) in 200 ml of carbon tetrachloride was added rapidly to a vigorously stirred solution of ketone **3** (18.3 g, 0.126 mol) in 500 ml of the same solvent. This was quickly followed by the addition of triethylamine (25 g, 0.25 mol) in 100 ml of carbon tetrachloride. The reaction mixture was warmed on a steam bath for 30 min and then stirred for a final 1.5 hr. The precipitate was separated by filtration and the filtrate was washed with water. The aqueous washings were extracted with ether and the combined organic layers were dried and evaporated. Short-path distillation of the residue afforded 21.5 g (75%) of **4** as a pale yellow oil, bp 95–100° (0.1 mm), which crystallized subsequently, mp 55–57° (lit.[4] mp 56–57°). The nmr spectrum of this material conformed to the reported spectrum of **4**.

Registry No.—**3**, 5530-96-1; **4**, 10481-35-3; **6**, 15844-05-0.

---

[1] Postdoctoral Fellow of the National Institutes of Health, 1972.

[2] L. A. Paquette, R. S. Beckley, and T. McCreadie, *Tetrahedron Lett.*, 775 (1971); L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, **93**, 2459 (1971); **92**, 4295 (1970); L. A. Paquette, *ibid.*, **92**, 5765 (1970).

[3] L. A. Paquette and J. S. Ward, unpublished results.

[4] G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Org. Chem.*, **33**, 1455 (1968).

[5] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[6] A somewhat less efficient synthesis of **3** has been described previously: K. Alder and F. H. Flock, *Chem. Ber.*, **87**, 1916 (1954).

[7] J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Syn.*, **45**, 77 (1965).