

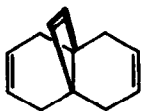
NEW CONVENIENT SYNTHESIS OF SUBSTITUTED CYCLOBUTENES¹

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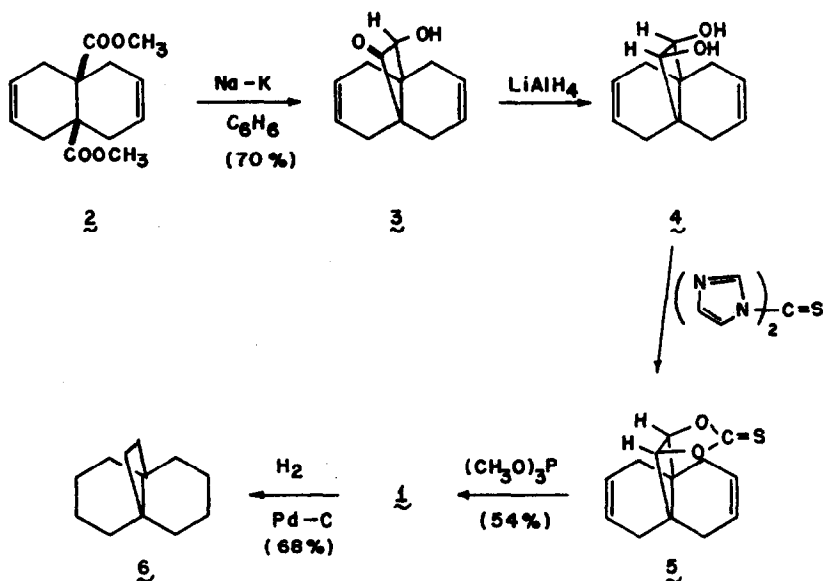
In the course of other studies, we required a quantity of 1, a hydrocarbon which possesses the unusual structural feature of a cyclobutene ring fused to the 9,10-bond of a hexahydronaphthalene unit. In this communication, we wish to describe two syntheses of



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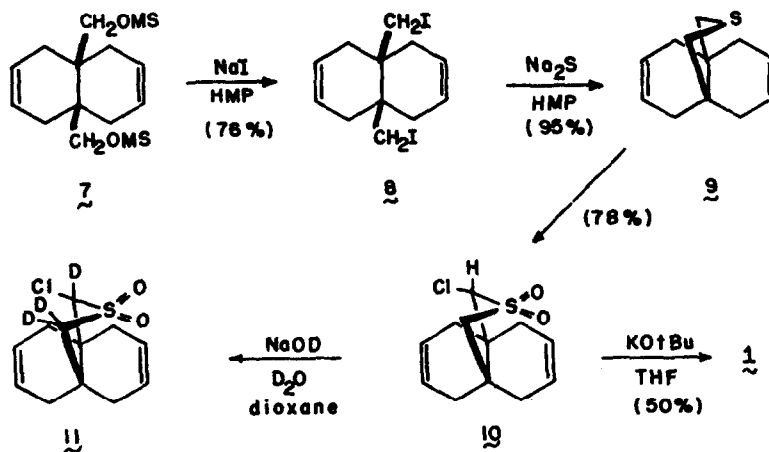
1 by methods which can be expected to have further utility in the preparation of cyclobutenes from acyclic precursors.

In the first approach, dimethyl $\Delta^{2,6}$ -hexalin-9,10-dicarboxylate (2) was cyclized to the four-membered acyloin 3, mp 81.5-82^o, with 1:1 sodium-potassium alloy in refluxing benzene according to the procedure of Bloomfield and Ireland.⁴ Lithium aluminum hydride reduction of 3 afforded a mixture of cis (4) and trans 1,2-diols (84% yield) which without purification was treated with N,N-thiocarbonyldiimidazole.⁵ The cis diol was thereby readily transformed (47% yield) to the cis thiocarbonate ester (5), mp 122.5-123^o.⁶ When a solution of 5 in trimethylphosphite was refluxed for 96 hrs.,⁷ the desired hydrocarbon (1) was obtained in good yield and a high state of purity after one distillation. The structure of 1 was assigned on the basis of its nmr spectrum [$\delta_{\text{TMS}}^{\text{CDCl}_3}$ 2.02 (multiplet, 8H,



allylic protons) and ca. 5.75 (multiplet, 6H, vinyl protons)] and its catalytic hydrogenation to the known⁸ saturated hydrocarbon 6.

Because of the tedious nature of the conversion of 2 to 3, an alternative, more convenient, route to 1 was sought. The second synthesis, which has proven to be operationally simpler, comprises a new application of the Ramberg-Bäcklund reaction.⁹ Thus, treatment of the highly hindered (dineopentyl) dimesylate 7¹⁰ with sodium iodide in hexamethylphosphoramide (HMP) gave rise to the diiodide 8, mp 97-98^o,^{8a} in 76% yield. Reaction of 8 with anhydrous sodium sulfide in HMP led in near quantitative yield to the cyclic sulfide 9, mp 55.5-56.5^o, which was further characterized as its sulfone, mp 115.5-116.5^o. In contrast to a wide variety of other solvents, the utilization of HMP in the conversion of 7 to 9 permitted efficient displacement of the neopentyl leaving groups and led to the expected products in excellent yields, and with essentially complete conversion.¹¹ When the sulfide was exposed to one equivalent of N-chlorosuccinimide¹² and the resulting crude α -chlorosulfide was directly oxidized with m-chloroperbenzoic acid in ether solution,



the α -chlorosulfone 10 could be readily isolated.

Treatment of 10 with 2N sodium hydroxide in aqueous dioxane at reflux for 4 days led to the almost complete recovery of starting material. The formation of α -sulfonylcarbanions under these conditions was established definitively by conducting the reaction in deuterium oxide (with NaOD) for 40 hrs.; the trideuterated chlorosulfone 11 was obtained in high yield.¹³ The failure of the α -halosulfone rearrangement under these conditions may be attributed to the fact that strong aqueous solvation of the carbanionic centers prevents the attainment of a geometry favorable to the requisite intramolecular S_N2 process.¹⁴ In order to minimize such solvation factors, 10 was treated with powdered potassium t-butoxide in dry tetrahydrofuran solution (reflux, 13 hrs.). Using this procedure, the α -chlorosulfone is smoothly converted to 1 in 50% yield.¹⁵ It is apparent therefore that both base and solvent play central positions in the practical applications of the Ramberg-Bäcklund reaction. Now that the first synthesis of a cyclobutene derivative by this procedure has been achieved,¹⁵ its use in many synthetic problems may be endowed with definite advantages, as in the present instance.

REFERENCES AND FOOTNOTES

- (1) α -Halosulfones. VIII. For previous paper in this series, see L. A. Paquette, L. S. Wittenbrook, and V. V. Kane, J. Am. Chem. Soc., in press.
- (2) Alfred P. Sloan Foundation Research Fellow, 1965-1967.
- (3) National Institutes of Health Predoctoral Fellow, 1966-present.
- (4) J. J. Bloomfield and J. R. S. Irelan, J. Org. Chem., 31, 2017 (1966).
- (5) H. A. Staab and G. Walther, Ann., 657, 98 (1962).
- (6) Satisfactory elemental analyses and spectra were obtained for all new compounds reported herein.
- (7) E. J. Corey and R. A. E. Winter, J. Am. Chem. Soc., 85, 2677 (1963); E. J. Corey, F. A. Carey, and R. A. E. Winter, ibid., 87, 934 (1965).
- (8) (a) E. Vogel, W. Maier, and J. Eimer, Tetrahedron Letters, 655 (1966); (b) J. J. Bloomfield and J. R. S. Irelan, ibid., 2971 (1966); (c) J. Altman, E. Bascad, J. Itzhaki, and D. Ginsburg, Tetrahedron, Suppl., 2, 279 (1967).
- (9) For a review, see L. A. Paquette in B. S. Thyagarajan (ed.), "Mechanisms of Molecular Migrations," Vol. I, in press.
- (10) G. Snetzke and G. Zanati, Ann., 684, 62 (1965).
- (11) The advantages of utilizing HMP to achieve rapid and efficient displacement of a neopentyl bromide has also recently been noted; R. G. Lewis, D. H. Gustafson, and W. R. Erman, Tetrahedron Letters, 401 (1967).
- (12) D. L. Tuleen and T. B. Stephens, Chem. Ind. (London), 1555 (1966).
- (13) Deuterium analysis (falling drop method) was performed by Josef Nemeth, Urbana, Illinois.
- (14) L. A. Paquette, J. Am. Chem. Soc., 86, 4085 (1964).
- (15) The yield in this reaction is probably not yet maximized.
- (16) The synthesis of cyclopentenes and cyclohexenes has been documented earlier.⁹