

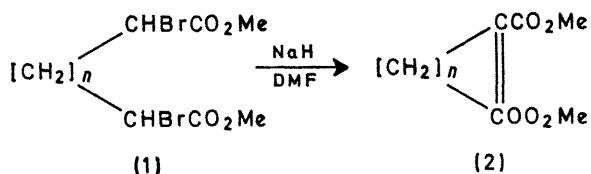
A Convenient Cyclization of Dimethyl Esters of C₆—C₉ α,α'-Dibromoalkanedioic Acids to the Corresponding Dimethyl Cycloalk-1-ene-1,2-dicarboxylates

By RICHARD N. McDONALD* and ROBERT R. REITZ†

(Department of Chemistry, Kansas State University, Manhattan, Kansas 66502)

Summary Several dimethyl α,α'-dibromoalkanedicarboxylates when treated with sodium hydride in dimethylformamide yield the corresponding dimethyl cycloalk-1-ene-1,2-dicarboxylates; evidence is presented supporting the existence of dimethyl cycloprop-1-ene-1,2-dicarboxylate as an intermediate in the reaction of dimethyl α,α'-dibromoglutarate with potassium t-butoxide.

We report a new synthesis of several dimethyl cycloalk-1-ene-1,2-dicarboxylates by a convenient and time-saving method. The dimethyl α,α'-dibromoalkanedicarboxylates (1) (C₆—C₉ acids) when treated with sodium hydride in dimethylformamide (DMF) yield the corresponding dimethyl cycloalk-1-ene-1,2-dicarboxylates (2).



The homologous dibromodiester, (1), (prepared in 90—96% yield^{1,2}) were treated with two equivalents of sodium hydride (mineral oil dispersion) in DMF at ice-bath temperatures. When hydrogen evolution had ceased the reaction was complete. The Table summarizes the results obtained in these combined cyclization-elimination reactions.³

Dibromodiester (1)	Reaction time	Cycloalkenediester ^a (2) (% yield)
n = 1 (Glutarate)	1.5 h	0 ^b
2 (Adipate)	1.0 h	48 ^a
3 (Pimelate)	1.5 h	69 ^b
4 (Suberate)	3.0 h	71 ^c
5 (Azelate)	1.5 days ^c	21
6 (Sebacate)	1.5 days ^c	0

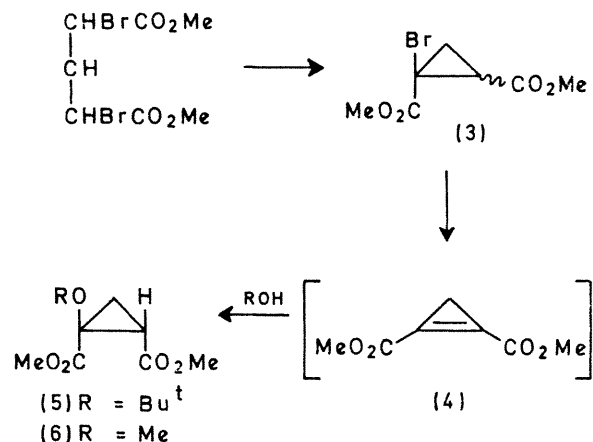
^a None of the isomeric cycloalkenedicarboxylates was observed.

^b Longer reaction times and increases in reaction temperature only gave increasing amounts of polymeric material.

^c Reaction carried out at room temperature; slow hydrogen evolution.

Reaction of dimethyl α,α'-dibromoglutarate (1; n = 1) with sodium hydride in DMF, after the initial, steady

evolution of hydrogen had ceased, gave dimethyl *cis*- and *trans*-1-bromocyclopropane-1,2-dicarboxylate (3) (77%) [g.l.p.c. showed the *cis*:*trans* ratio of (3) as 1:3; structural assignments based on n.m.r. spectra]. No cyclopropene (4) was found. Treatment of (1; n = 1) with two equivalents of potassium t-butoxide in t-butyl alcohol gave two products, dimethyl *cis*-1-t-butoxycyclopropane-1,2-dicarboxylate (5) (46%) and dimethyl *cis*-1-methoxycyclopropane-1,2-dicarboxylate (6) (9%) (structural assignments based on



their n.m.r. spectra). Repetition of this reaction with only one equivalent of potassium t-butoxide leads to the formation of *cis*- and *trans*-(3); further treatment of this mixture of *cis*- and *trans*-(3) leads to a mixture of (5) and (6).

These results rule out prior nucleophilic displacement of bromide by alkoxide followed by cyclization to (5) and (6). The possibility that (5) and (6) may be formed from the cyclopropene (4) by elimination followed by addition of an alcohol is consistent with the addition of t-butyl alcohol to ethyl cyclopropene-1-carboxylate.⁷

The conversion (1) → (2) is a simple, one-step process with reasonably good isolated yields of (2; n = 2—4), and provides a new and easier synthesis of (2; n = 2—5).‡

We acknowledge support of this research by the National Science Foundation.

(Received, September 28th, 1970; Com. 1663.)

† National Defense Education Act Trainee, 1968—1970.

‡ Satisfactory analyses were obtained for all new compounds.

¹ P. C. Guha and D. K. Sankaran, *Org. Synth. Coll. Vol.*, 1955, **3**, 623.

² E. Buchman, A. Reims, T. Skei, and M. Schlatter, *J. Amer. Chem. Soc.*, 1942, **64**, 2697.

³ Small amounts of the diacids of (2; n = 2, 3) and (4) have been obtained from base hydrolyses of the corresponding esters of (1); see A. Hassell and C. K. Ingold, *J. Chem. Soc.*, 1926, 1465, and F. R. Goss and C. K. Ingold, *ibid.*, p. 1471.

⁴ W. H. Perkins, *J. Chem. Soc.*, 1894, **65**, 950; F. B. Kipping and J. J. Wren, *ibid.*, 1957, 1733. See R. C. Fuson and T. Y. Kao, *J. Amer. Chem. Soc.*, 1929, **51**, 1537 for the preparation of cyclobutane-1,2-dicarboxylic acid.

⁵ E. Hayworth and W. H. Perkin, *J. Chem. Soc.*, 1894, **65**, 978.

⁶ A. Baeyer, *Annalen*, 1890, **258**, 203; G. Kon and B. Nandi, *J. Chem. Soc.*, 1933, 1633.

⁷ K. B. Wiberg, R. K. Barnes, and J. Albin, *J. Amer. Chem. Soc.*, 1957, **79**, 4994.