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of Organic Compounds

Working with Hazardous Chemicals

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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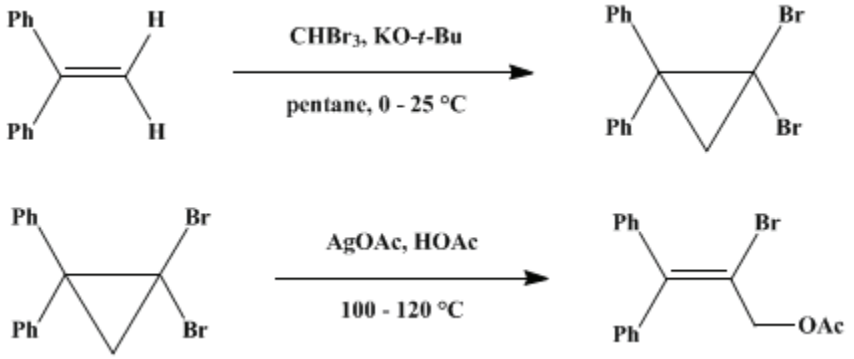
CHAIN ELONGATION OF ALKENES *via gem*-DIHALOCYCLOPROPANES: 2-BROMO-3,3-DIPHENYL-2-PROPEN-1-YL ACETATE

[2-Propen-1-ol, 2-bromo-3,3-diphenyl-, acetate]



Submitted by Stanely R. Sandler[1]
Checked by D. W. Brooks and S. Masamune.

1. Procedure

A. 1,1-*Dibromo*-2,2-*diphenylcyclopropane*. A 500-ml., three-necked, round-bottomed flask equipped with a mechanical stirrer, a dropping funnel, and a condenser fitted with a drying tube is flushed with dry nitrogen, then charged with 25.0 g. (0.139 mole) of 1,1-diphenylethylene (Note 1), 100 ml. of pentane, and 28 g. (0.25 mole) of potassium *tert*-butoxide (Note 2). The mixture is stirred and cooled to 0° before 66.0 g. (0.261 mole) of bromoform (Note 3) is added dropwise over 30–45 minutes. Stirring is continued for an additional 2–3 hours at room temperature, and 200 ml. of water is added. The yellowish insoluble product is filtered, dried, and digested with 300 ml. of refluxing 2-propanol for 30 minutes. After cooling, the product is filtered and washed with 100 ml. of 2-propanol, yielding 31–38 g. (63–78%) of colorless crystals, m.p. 151–152°.

B. 2-*Bromo*-3,3-*diphenyl*-2-*propen*-1-*yl acetate*. A 250-ml. flask equipped with a condenser is charged with 17.6 g. (0.0500 mole) of 1,1-dibromo-2,2-diphenylcyclopropane, 12.5 g. (0.0748 mole) of silver acetate (Note 4), and 50 ml. of glacial acetic acid, then immersed in an oil bath at 100–120° for 24 hours (Note 5). After cooling, the mixture is diluted with 200 ml. of diethyl ether and filtered. The ethereal filtrate is washed with two 100-ml. portions of water, two 100-ml. portions of aqueous saturated sodium carbonate, and finally with two 100-ml. portions of water. After drying over anhydrous sodium sulfate, the ether is removed on a rotary evaporator. Distillation of the resulting residue under reduced pressure yields 12.0 g. (72%) of the product, b.p. 142–145° (0.15 mm.), n_D^{22} 1.6020–1.6023 (Note 6).

2. Notes

1. 1,1-Diphenylethylene was purchased from Eastman Organic Chemicals.
2. Potassium *tert*-butoxide was supplied by Mine Safety Appliances (MSA) Research Corporation. See end of Discussion section below.
3. Bromoform was supplied by the Dow Chemical Company and used without further purification.
4. The silver acetate can be replaced by a mixture of sodium acetate and silver nitrate.
5. A 24-hour period may not be required but was found to be convenient.
6. UV (CH_3OH) nm. max. (log ε): 260 (3.94); ^1H NMR ($CDCl_3$), δ (multiplicity, number of protons): 2.08 (s, 3H), 4.87 (s, 2H), 7.3 (m, 10H).

3. Discussion

The present procedure is that of the submitter[2] and illustrates a general method for the chain extension of alkenes *via gem*-dihalocyclopropanes, earlier described by Skell and Sandler.[3] The reaction of dihalocyclopropanes with electrophilic reagents yields haloallylic derivatives,[2] the thermal reaction yields haloallylic halides or halodienes, and the reaction with magnesium, sodium, or lithium alkyl reagents yields allenes.[2] These reactions are summarized in Figure 1, and examples are given in Table I.

Figure 1.

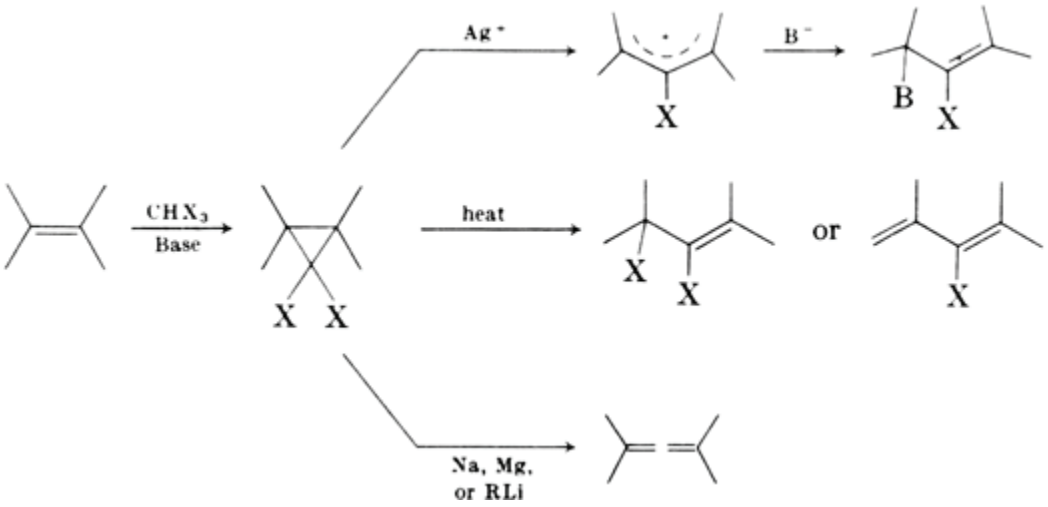
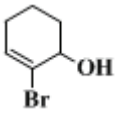
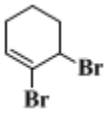
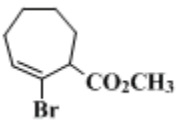
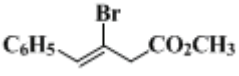
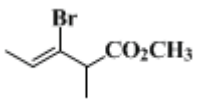
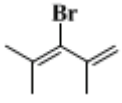
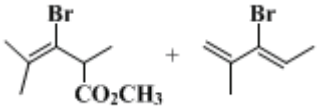


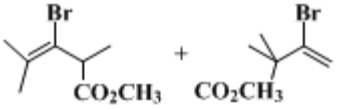
TABLE I
CHAIN ELONGATION OF ALKENES *via gem*-DIBROMOCYCLOPROPANES

Alkene	Conditions for Dibromocyclopropane Opening	Product
	$AgNO_3$, H_2O	
	Heat	
	CH_3CO_2Ag, CH_3CO_2H	
	CH_3CO_2Ag, CH_3CO_2H	
	CH_3CO_2Ag, CH_3CO_2H	
	Heat or CH_3CO_2Ag, CH_3CO_2H	

CH_3CO_2Ag, CH_3CO_2H



CH_3CO_2Ag, CH_3CO_2H



This general method has been used by Parham and co-workers[4] to transform indenes into β-halonaphthalenes. The method is also useful for the conversion of pyrroles to β-substituted pyridines and of indoles to β-haloquinolines.[3] More recently, phase transfer agents have been used to aid the preparation of *gem*-dihalocyclopropanes by the reaction of olefins with haloforms, using aqueous sodium hydroxide.[5,6,7]

References and Notes

1. Borden, Inc., Chemical Division, Central Research Laboratory, Philadelphia, Pennsylvania 19124 [Present address: Pennwalt Corp., King of Prussia, Pennsylvania 19406].
2. S. R. Sandler, *J. Org. Chem.*, **32**, 3876 (1967) and references cited therein.
3. P. S. Skell and S. R. Sandler, *J. Am. Chem. Soc.*, **80**, 2024 (1958).
4. W. E. Parham and H. E. Reiff, *J. Am. Chem. Soc.*, **77**, 1177 (1955) and subsequent papers on the reaction of indenes with dihalocarbenes to yield β-halonaphthalenes.
5. E. V. Dehmlow, *Angew. Chem. Int. Ed. Engl.*, **13**, 170 (1974).
6. E. V. Dehmlow, *Chem. Tech.*, 210 (April 1975).
7. I. Crossland, *Org. Synth.*, **60**, 6 (1981).

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

H_2O

acetic acid (64-19-7)

ether,
diethyl ether (60-29-7)

sodium acetate (127-09-3)

sodium hydroxide (1310-73-2)

silver nitrate (7761-88-8)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

2-propanol (67-63-0)

1,1-Diphenylethylene (530-48-3)

Pentane (109-66-0)

bromoform (75-25-2)

silver acetate (563-63-3)

2-BROMO-3,3-DIPHENYL-2-PROPEN-1-YL ACETATE,
2-Propen-1-ol, 2-bromo-3,3-diphenyl-, acetate (14310-15-7)

1,1-Dibromo-2,2-diphenylcyclopropane (17343-74-7)

potassium tert-butoxide (865-47-4)