Cyclopropylcarbinyl Radical Reactions in the Cycloprop[2,3]indene System

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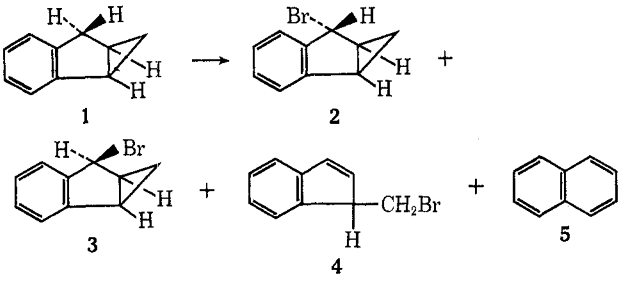
An investigation of the use of different brominating agents and reaction conditions in free-radical α bromination of cycloprop[2,3]indene (**1**) is reported. Room temperature light-initiated brominations with either *N*-bromosuccinimide or molecular bromine in carbon tetrachloride solution give both higher conversions of the starting material and higher yields of cyclopropylcarbinyl bromide products than are obtained at 77° using either light or chemical initiation. Light-initiated bromination with bromotrichloromethane, however, is unsatisfactory even at low temperatures because of extensive side-product formation. Tri-*n*-butyltin and triphenyltin hydride reductions of a mixture of *exo*- and *endo*-1-bromocycloprop[2,3]indenes (**2** and **3**) and of a pure sample of 1-bromomethylindene (**4**) were also carried out to obtain detailed information regarding the nature of the cyclopropylcarbinyl–allylcarbinyl radical rearrangement processes in the cycloprop[2,3]indene system. Evidence was obtained for the intermediacy of the 1,2-dihydronaphthyl radical in the formation of at least part of the naphthalene produced in the free-radical bromination of cycloprop[2,3]indene (**1**). Also, the formation of **1** from the tin hydride reductions of **4** demonstrated the reversibility of the cyclopropylcarbinyl–allylcarbinyl rearrangement of the cycloprop[2,3]indenyl radical to the 1-methylindenyl radical.

A preliminary investigation of the possibility of carrying out free-radical α brominations of cyclopropyl hydrocarbons by *N*-bromosuccinimide (NBS) was reported[1] recently from these laboratories. One of the compounds investigated briefly in the preliminary study was cycloprop[2,3]indene (**1**). Because of its ready availability[2] and because of the relative ease of handling and identifying its bromination products (**2**, **3**, **4**, and **5**),[1] this compound was chosen for use in the present study for investigation of the effects of different brominating agents and reaction conditions in free-radical cyclopropane α brominations. Also, we wished to carry out a detailed examination of the free-radical rearrangement processes occurring in this system.



Results and Discussion

Bromination Studies.—In the present study of the free-radical α bromination of **1**, ultraviolet light initiation was used in each case. Bromination using 1 equiv of NBS in CCl_4 solvent was carried out both at 77 and 28°, and bromination using 1 equiv of molecular bromine in CCl_4 solvent under a nitrogen sweep to remove HBr[3] was done at 28°. Finally light-initiated bromination using 5 equiv of bromotrichloromethane[4] in the absence of a solvent was examined at 28°. The results of these studies are shown in Table I along with those obtained earlier[1] for NBS bromination at 77° using azobisisobutyronitrile (AIBN) initiation.

Table I

Free-Radical Bromination of Cycloprop[2,3]indene (1)

Reaction conditions	% conversion[a] of **1**	Product composition,[b] % **2**	**3**	**4**	**5**	Unknown
1 equiv NBS, CCl_4, AIBN, 77°, 10 min	65	37	25	27	5	6[c]
1 equiv NBS, CCl_4, $h\nu$, 77°, 1 hr	67	43	27	14	8	8[c]
1 equiv NBS, CCl_4, $h\nu$, 28°, 2 hr	87	56	32	0	4	8[c]
1 equiv Br_2, CCl_4, $h\nu$, 28°, 20 min	82	53	30	0	3	14[c]
5 equiv $BrCCl_3$, neat, $h\nu$, 28°, 4 hr	54	44	23	0	2	31

[a] Brominations with NBS and Br_2 were carried to complete reaction of the brominating agent. [b] Average values, based on reacted **1**, of runs carried out in duplicate or triplicate. The per cent yields shown in each case are reproducible to *ca.* ±2%. [c] High boiling, presumed di- or tribrominated materials.

In the brominations with NBS at 77° using either light or AIBN initiation, the same four products are obtained. However, in the light-initiated process less of the cyclopropylcarbinyl–allylcarbinyl radical rearrangement product 1-bromomethylindene (**4**) is formed. This is not due to subsequent ion-pair rearrangement of the cyclopropylcarbinyl bromides **2** and **3** in the AIBN-initiated reaction since the products were shown to be stable under the reaction conditions.[1] Moreover, the reaction conditions for the AIBN-initiated reaction were less vigorous than those using light initiation. A possible, although unsupported, explanation which can be offered for this behavior is that in the light-initiated reaction the steady state concentration of molecular bromine is higher than in the AIBN-initiated reaction. Thus, the initially formed cyclopropylcarbinyl radical intermediate would be more likely to react with the bromine to form the cyclopropylcarbinyl bromides **2** and **3** in competition with rearrangement to the radical precursor of **4**.

In the light-initiated free-radical brominations at 28°, significant differences in product composition were

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[1] E. C. Friedrich, *J. Org. Chem.*, **34**, 528 (1969).

[2] A. L. Goodman and R. H. Eastman, *J. Amer. Chem. Soc.*, **86**, 908 (1964).

[3] B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc., London*, 80 (1961).

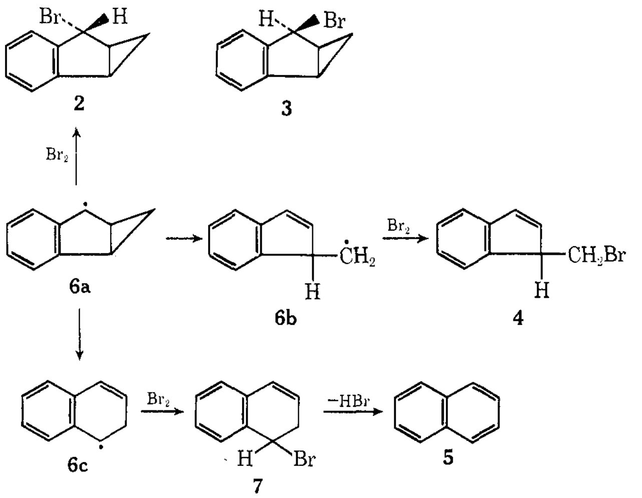
[4] (a) G. J. Gleicher, *J. Org. Chem.*, **33**, 332 (1968); (b) B. B. Jarvis, *ibid.*, **35**, 924 (1970).

observed from those obtained at 77°. Both Br_2 and NBS bromination gave essentially identical product mixtures consisting almost entirely of the unrearranged cyclopropylcarbinyl bromides **2** and **3**.[5] Also, considerably greater conversions of the cycloprop[2,3]indene were obtained.[6] These variations are most likely due to differences in the activation energies for the various processes which can take place during the bromination reactions. In practice, the light-initiated room temperature bromination of **1** with molecular bromine has proved to be a highly satisfactory procedure for preparation of a mixture of the *exo*- and *endo*-bromides **2** and **3** which we needed for the tin hydride reduction studies to be discussed later.

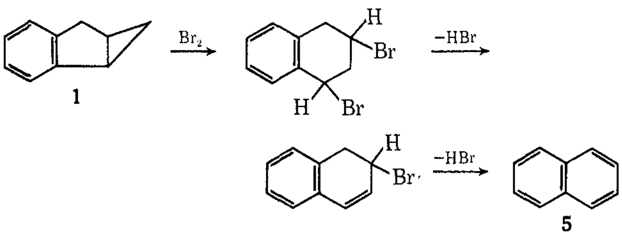
The final method for cyclopropane α bromination which was investigated in the present study involved the use of bromotrichloromethane as the source of bromine. Although light-initiated bromination of **1** at 28° with the bromotrichloromethane did proceed readily, it was unsatisfactory due to the formation of large amounts of side products (see Table I). The nature of these side products was not investigated; however, it is presumed that they result from addition of the chain carrying trichloromethyl radicals to the cyclopropane ring of **1**.[4b]

Free-Radical Rearrangement Studies.—A possible mechanistic scheme for the formation of each of the products obtained from the free-radical bromination of cycloprop[2,3]indene (**1**) is given in Scheme I. The *exo*- and *endo*-1-bromocycloprop[2,3]indenes (**2** and **3**) are formed *via* the cyclopropylcarbinyl radical intermediate **6a**, resulting from initial abstraction of a hydrogen atom from the 1 position of cycloprop[2,3]indene. 1-Bromomethylindene (**4**) results *via* bromine attack on the rearranged allylcarbinyl radical **6b**. Finally, a probable pathway for the formation of naphthalene is *via* reaction of the allylcarbinyl radical **6c** with bromine to give 1-bromo-1,2-dihydronaphthalene (**7**). This material would be expected to immediately eliminate HBr under the reaction conditions by an ionic mechanism to give naphthalene (**5**).

Scheme I

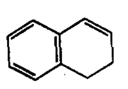


To test the validity of this free-radical bromination mechanism, it was necessary to carry out an investigation in which certain of the postulated radical intermediates were generated by independent processes. For example, besides the scheme shown earlier for the formation of naphthalene, another pathway might be *via* the process shown below. It was also of considerable theoretical interest to determine whether the proposed cyclopropylcarbinyl–allylcarbinyl radical rearrangement of **6a** to **6b** is reversible. Furthermore, we wished to obtain additional information regarding the observation that, in the free-radical bromination of **1**, rearrangement of the initially formed cyclopropylcarbinyl radical **6a** to the primary homoallyl radical **6b** apparently proceeds in preference to rearrangement to the benzylic radical **6c**.



Since tin hydride reductions of organic halides are known to proceed by free-radical mechanisms,[7] and have also been used in a number of cases for studying cyclopropylcarbinyl–allylcarbinyl radical rearrangements,[8] this process was chosen as the alternative to free-radical bromination for use in obtaining further information regarding the problems posed above. Reductions of a 65:35 mixture[9] of the *exo*- and *endo*-1-bromocycloprop[2,3]indenes (**2** and **3**) and of a pure sample of 1-bromomethylindene (**4**) were carried out using equimolar amounts of tri-*n*-butyltin hydride or triphenyltin hydride and the bromide in the absence of a solvent. Controls showed that a maximum of 7% rearrangement of the bromides **2** and **3** to bromide **4** occurred on irradiation at 26° for 4 hr in the presence of tri-*n*-butyltin bromide.

The products observed from the tin hydride reduction studies were cycloprop[2,3]indene (**1**), 1,2-dihydronaphthalene (**8**), 1-methylindene (**9**), and 3-methylindene (**10**). These were identified by isolation and comparison with known samples, and the yields were determined using a combination of nmr and glpc techniques as are described in the Experimental Section. In all cases studied the total yields of hydrocarbon products accounted for amounted to greater than 95%.



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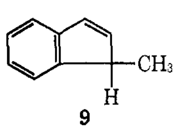

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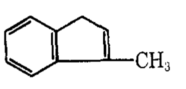

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[5] A similar temperature dependence of product composition was observed in free-radical chlorination of methylcyclopropane: C. Walling and P. S. Fredricks, *J. Amer. Chem. Soc.*, **84**, 3326 (1962).

[6] It was shown in the previous study[1] that the low conversion of **1** in the AIBN-initiated reaction with NBS at 77° was due predominately to a side rearrangement of a portion of the NBS to β-bromopropionyl isocyanate.

[7] H. G. Kuivila, "Advances in Organometallic Chemistry," Vol. 1, Academic Press, New York, N. Y., 1964, p 47.

[8] For example, see C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.* **31**, 3381 (1966).

[9] It was necessary to use the mixture of bromides **2** and **3** obtained from free-radical bromination of **1** for this study because they were too unstable for separation into the individual isomers. However, both **2** and **3** were observed to be reduced at identical rates, and for the purposes of this study starting with the mixture or with one pure isomer does not affect the conclusions which are drawn from the results.

The results obtained are summarized in Table II and are the averages of duplicate runs.

Table II

Tin Hydride Reductions[a,b]

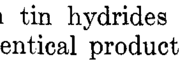
Bromide	Hydride	Relative yields of products, % 1	8	9	10
2 + 3[c]	$(n\text{-Bu})_3SnH$	35	3	62	0
2 + 3[c]	$(C_6H_5)_3SnH$	64	4	32	0
4	$(n\text{-Bu})_3SnH$	15	3	73	9
4	$(C_6H_5)_3SnH$	18	2	72	8

[a] Reductions were carried in the absence of a solvent using 1 mmol each of the tin hydride and the bromide. [b] $(n\text{-Bu})_3SnH$ reductions were carried out at 26 ± 1° using light initiation. In the $(C_6H_5)_3SnH$ reductions of **2** and **3**, the reactants were mixed at room temperature and the moderately exothermic reactions did not require light initiation. Reduction of **4** with $(C_6H_5)_3SnH$, however, required light initiation. [c] A 65% exo and 35% endo mixture.

1,2-Dihydronaphthalene (**8**) is obtained from the tin hydride reductions of both the isomeric 1-bromocycloprop[2,3]indenes (**2** and **3**) and the 1-bromomethylindene (**4**). Thus, the formation of this material supports the proposed intermediacy of the 1,2-dihydronaphthyl radical **6c**, as the source of at least part of the naphthalene in the free-radical bromination of cycloprop[2,3]indene (**1**). Also, the formation of **1** from the tin hydride reductions of 1-bromomethylindene (**4**) demonstrates the reversibility of the cyclopropylcarbinyl–allylcarbinyl radical rearrangement of **6a** to **6c**.[10]

In the reduction of the cyclopropylcarbinyl bromides **2** and **3** with triphenyltin hydride, much higher yields of the unrearranged product cycloprop[2,3]indene (**1**) were obtained than in the case using the tri-*n*-butyltin hydride. This must be due to the greater ability of the triphenyltin hydride to capture the initially formed cyclopropylcarbinyl radical **6a** before it undergoes rearrangement to the homoallyl radicals **6b** or **6c**.[7] In the case of the reduction of the homoallyl bromide (**4**), however, both tin hydrides gave within experimental error an identical product composition. It is likely that the product composition obtained here reflects the equilibrium composition of the radical intermediates **6a–c**, and thus allowing the radicals a longer lifetime would not change the final product composition.

The formation of 3-methylindene (**10**) from the reductions of 1-bromomethylindene (**4**) must be *via* reaction between the 1-methylindenyl radical **6b** and 1-methylindene (**9**) to give the allylic radical **11**. Upon reduction of **11** a mixture of **9** and **10** would be expected.



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Finally, it is interesting to note that in the tin hydride reduction studies, as well as in the free-radical bromination studies, rearrangement of the cyclopropylcarbinyl radical **6a** to the primary homoallyl radical **6b** apparently proceeds in preference to rearrangement to the benzylic radical **6c**. Based on the stabilities expected for the radical products, the opposite behavior would have been anticipated. For example, in the free-radical NBS bromination of *trans*-1-benzyl-2-methylcyclopropane,[1] the secondary and primary homoallylic bromide products were obtained in the ratio of 5:1. Also, Cristol and Barbour[11] observed that the reaction of 3,5-cyclocholestan-6-yl chloride with triphenyltin hydride or with sodium biphenyl radical anion leads exclusively to 5-cholestene, resulting from rearrangement to the secondary homoallylic radical. However, Freeman and coworkers[12] observed that free-radical chloroformylation of bicyclo[3.1.0]hexane with oxalyl chloride leads to approximately equivalent amounts of Δ^2-cyclopentenylmethylacetyl chloride and 3-cyclohexenylacetyl chloride along with other products. Also, Slaugh[13] found that the generation of the Δ^2-cyclopentenylmethyl radical by thermal decomposition of *tert*-butyl Δ^2-cyclopentenyl peracetate in the presence of *p*-cymene or benzotrichloride resulted in rearrangement, probably *via* a bicyclo[3.1.0.]hexyl radical, to produce the 4-cyclohexenyl radical.

An attempt was made to generate the dihydronaphthyl radical **6c** by an independent process to determine whether it might be involved in an equilibrium which is strongly directed toward the cyclopropylcarbinyl radical **6a**. This was done by means of light-initiated NBS bromination of 1,2-dihydronaphthalene (**8**) at 26° in CCl_4 solution. However, nmr examination of the product mixture showed the absence of any cyclopropyl products.

A possible explanation for the unexpected direction of rearrangement of the cyclopropylcarbinyl radical **6a** in the cycloprop[2,3]indene system is that the phenyl substituent on carbon 3 in the activated complex for rearrangement of **6a** to **6c** is providing a destabilizing electron-withdrawing inductive effect rather than a stabilizing electron-releasing resonance effect. We plan to test this explanation by means of cyclopropylcarbinyl radical rearrangement studies in the benzobicyclo[4.1.0.]heptyl homolog of the cycloprop[2,3]indene system.

Experimental Section

Boiling points are uncorrected. Mass spectra were run on a CEC Model 21-104 single focusing instrument by Mr. J. Voth.

Nuclear Magnetic Resonance Spectra.—All nmr spectra were obtained using a Varian Associates Model A-60A instrument. They were run either directly on the crude or distilled reaction mixtures or, in the case of pure compounds, as 5–10% solutions in carbon tetrachloride. Tetramethylsilane (TMS) was used as an internal standard, and chemical shift values are reported in parts per million (δ) downfield from the TMS. For quantitative nmr analyses, at least four integrations were obtained for the peak areas of each different proton absorption. Integral amplitudes were maximized so as to obtain the highest possible accuracy. Average values of the integrations were used for calculation of the product compositions.

Gas–Liquid Partition Chromatography.—Both analytical and preparative scale gas–liquid partition chromatography were carried out using an Aerograph A90-P3 instrument equipped with a Pyrex injector insert. Analyses of the bromination products were done as described previously.[1] Analyses of the hydrocarbon products obtained from the tin hydride reduction studies were done using a 3.5 m × 0.25 in. copper column with a 20% 3-nitro-3-methylpimelonitrile (NMPN) on 60–80 mesh Chromosorb W

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(10) Similar behavior has been observed in the simple Δ^2-cyclopentenylmethyl system: L. H. Slaugh, *J. Amer. Chem. Soc.*, **87**, 1522 (1965).

(11) S. J. Cristol and R. V. Barbour, *ibid.*, **90**, 2832 (1968).

(12) P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, *J. Org. Chem.*, **33**, 1448 (1968).

(13) L. H. Slaugh, *J. Amer. Chem. Soc.*, **87**, 1522 (1965).

packing. Helium (60 ml/min) was employed as the carrier gas. The retention times in minutes, using a column operating temperature of 112°, of certain of the compounds encountered in this work are as follows: 1-methylindene, 27; cycloprop[2,3]indene, 33; 3-methylindene, 45; and 1,2-dihydronaphthalene, 47.

Photolysis Equipment.—Light-initiated brominations and tin hydride reductions were carried out using a 275-W General Electric sun lamp placed approximately 10 cm from the object being irradiated. All glassware employed was Pyrex.

Cycloprop[2,3]indene (1).—This material was prepared using the Le Goff modification[14] of the procedure employed by Goodman and Eastman.[2] The reaction of a zinc–copper couple, prepared from 58.8 g (0.9 mol) of 30-mesh zinc granules, with 121.8 g (0.7 mol) of dibromomethane and 58 g (0.5 mol) of freshly distilled indene in 300 ml of anhydrous ether at reflux for 68 hr gave, after work-up and distillation through a 60-cm spinning-band column, 14.1 g (22%) of pure cycloprop[2,3]indene: bp 85° (18.5 mm); $n^{23}\text{D}$ 1.5583 [lit.[2] bp 104° (40 mm); $n^{26}\text{D}$ 1.5545]; mass spectrum (70 eV) *m/e* (rel intensity) 131 (11), 130 (100), 129 (99), 128 (57), 127 (26), 115 (67), and 102 (7).

Light-Initiated Bromination of Cycloprop[2,3]indene by NBS.—Light-initiated brominations at 28° were carried out by placing 0.34 g (1.91 mmol) of NBS along with 0.237 g (1.82 mmol) of cycloprop[2,3]indene and 5 ml of carbon tetrachloride solvent in an 18 × 150 mm test tube fitted with a thermometer. The mixture was stirred magnetically and the reaction temperature was maintained by running a stream of tap water over the tube. Brominations at 77° were carried out using the same quantities of starting materials as shown above. However, a 10-ml two-necked ₸ 14/20 flask fitted with a thermometer, a reflux condenser, and a calcium chloride drying tube was used as the reaction vessel. The magnetically stirred reaction mixture was brought to reflux temperature within 2–3 min by irradiating without cooling. The temperature was maintained by blowing a stream of air over the flask. After the reactions were completed, as indicated by the absence of NBS at the bottom of the reaction vessel, the product mixtures were analyzed using a combination of nmr and glpc techniques as described earlier.[1]

Light-Initiated Bromination of Cycloprop[2,3]indene Using Br_2.—Cycloprop[2,3]indene (0.237 g, 1.82 mmol) was weighed into a 10-ml two-necked ₸ 14/20 flask containing 1 ml of carbon tetrachloride solvent. The flask was fitted with a gas inlet tube and a dropping funnel. Dry nitrogen was then slowly bubbled through the mixture while the flask was irradiated and cooled by a stream of tap water, and 3.6 ml of a 0.5 *M* solution of bromine (1.8 mmol) in carbon tetrachloride solution was added slowly in a dropwise manner. Decoloration of the bromine solution occurred immediately upon addition of each drop. HBr was evolved as evidenced by the dense white fumes, which were strongly acidic to moist pHydrion paper, emitted from the top of the dropping funnel. After addition of the bromine solution was complete, irradiation was stopped but the nitrogen bubbling was continued for 1–2 min longer. The product mixture was then analyzed in the usual manner.[1]

Light-Initiated Bromination of Cycloprop[2,3]indene with Bromotrichloromethane.—Cycloprop[2,3]indene (0.13 g, 1 mmol) and bromotrichloromethane (0.99 g, 5 mmol) were carefully weighed into a polished glass, thin-wall nmr tube. The tube was then irradiated for 4 hr while being cooled by a stream of tap water. The product mixture was analyzed in the usual manner.[1]

***exo-* and *endo*-1-Bromocycloprop[2,3]indene Mixture (2 and 3).**—The reaction of 1.5 g (11.5 mmol) of cycloprop[2,3]indene (1) in 5 ml of carbon tetrachloride solvent with 35 ml of a 0.5 *M* solution of bromine (17.5 mmol) in carbon tetrachloride was carried out at 28° over a period of 15 min by a procedure similar to that described above. The carbon tetrachloride was then removed on a rotary vacuum evaporator and the resulting light yellow product was distilled, using an oil bath which was preheated to 95°, through a small short-path microdistillation apparatus. The 1-bromocycloprop[2,3]indene (1.92 g, 80%) was collected from 75 to 80° (0.5 mm): $n^{22.5}\text{D}$ 1.6097; nmr analysis[1] showed that the material consisted of a 65:35 mixture of **2** and **3**; mass spectrum (70 eV) *m/e* (rel intensity) 210 (5), 208 (6), 130 (11), 129 (100), 128 (57), and 127 (19).

1-Hydroxymethylindene.—The procedure used for preparation of this material, the precursor for 1-bromomethylindene (4), essentially followed that described by Courtot[15] involving the reaction of indenylmagnesium bromide with paraformaldehyde. 1-Hydroxymethylindene was obtained in a 62% yield based on reacted indene: bp 95–96° (1.0 mm); $n^{23}\text{D}$ 1.5865 [lit.[14] bp 134° (10 mm)]; nmr (CCl_4) δ 3.55 (m, 3 H), 6.4 (d, 1 H, J = 5 Hz, vinyl), 6.65 (d, 1 H, J = 5 Hz, vinyl), and 7.1 ppm (m, 4 H, aromatic).

1-Bromomethylindene (4).—The procedure used essentially followed that of Smith.[16] The reaction of 5.6 g (20.7 mmol) of phosphorus tribromide and 10.0 g (62.4 mmol) of 1-hydroxymethylindene in 4 ml of anhydrous benzene and 2 g of dry pyridine gave, after work-up and distillation, 4.0 g (31%) of **4**: bp 72–82° (0.5 mm); $n^{22}\text{D}$ 1.6016 (lit.[1] $n^{25}\text{D}$ 1.6003). The nmr spectrum of this material was identical with that reported earlier[1] for a sample of **4** obtained *via* free-radical NBS bromination of cycloprop[2,3]indene (**1**).

Tri-*n*-butyltin Hydride.—This was prepared in 90% yield by the reduction of tri-*n*-butyltin chloride with lithium aluminum hydride following the procedure of Kuivila:[17] bp 68–74° (0.3 mm) [lit.[17] bp 68–74° (0.3 mm)]; nmr (neat) δ 1.2 (m, 27 H) and 4.7 ppm (m, 1 H, SnH).

Triphenyltin Hydride.—This was prepared in 65% yield by the reduction of triphenyltin chloride with lithium aluminum hydride following the procedure of Kuivila:[17] bp 162–168° (0.5 mm) [lit.[17] bp 162–168° (0.5 mm)]; nmr (neat) δ *ca.* 6.9 (m, 9 H, aromatic), *ca.* 7.1 (m, 6 H, aromatic), and *ca.* 7.4 ppm (m, 1 H, SnH).

1,2-Dihydronaphthalene (8).—An impure sample of **8** was prepared *via* NBS bromination of tetralin to give 1-bromo-1,2,3,4-tetrahydronaphthalene, which upon distillation spontaneously eliminated HBr. Isolation of a pure sample of 1,2-dihydronaphthalene was accomplished by glpc techniques at 130° using a 1 m × $^3/_8$ in. column with a 20% NMPN on 80–100 mesh Chromosorb W packing: bp 65° (3.5 mm); $n^{23}\text{D}$ 1.5802 [lit.[18] bp 83–83.5° (12 mm); $n^{20}\text{D}$ 1.5817]; nmr (neat) δ 2.1 (m, 2 H), 2.65 (m, 2 H), 5.8 (sextet, 1 H, J = 10 and 4 Hz), 6.3 (sextet, 1 H, J = 10 and 1.5 Hz), and 6.9 ppm (m, 4 H).

Reductions with Tri-*n*-butyltin Hydride.—A typical reduction procedure is outlined as follows. Into a polished glass, thin-wall nmr tube was carefully weighed 0.209 g (1 mmol) of the bromide and 0.290 g (1 mmol) of tri-*n*-butyltin hydride. The mixture was then irradiated, while maintaining the temperature at 26 ± 1° by running a stream of tap water over the tube, until nmr analysis showed the complete disappearance of the tin hydride absorption (*ca.* 3–5 hr). The resulting mixture was then distilled through a short-path microdistillation apparatus to separate the hydrocarbon products from the high boiling tri-*n*-butyltin bromide. Analysis by nmr both before and after distillation showed that the relative ratios of the hydrocarbon products remained constant. The distilled hydrocarbon product was then analyzed by a combination of the glpc and nmr techniques described below.

Reductions with Triphenyltin Hydride.—The bromide (0.209 g, 1 mmol) and 0.350 g (1 mmol) of triphenyltin hydride were weighed into a 10 × 75 mm Pyrex test tube. In the case of the reductions of the *exo-* and *endo*-1-bromocycloprop[2,3]indene mixture, reaction occurred spontaneously and after about 10 min was complete. To initiate the reductions of 1-bromomethylindene, however, it was necessary to irradiate the tube at 26 ± 1° for 10–15 min. The product mixture was then extracted with three 2-ml portions of cold *n*-pentane to separate the hydrocarbon products from the triphenyltin bromide. The hydrocarbon extract was then concentrated using a stream of dry nitrogen and analyzed by a combination of the glpc and nmr techniques described below.

Hydrocarbon Analyses.—Pure samples of the various hydrocarbon products obtained from the tin hydride reductions were isolated by preparative scale glpc techniques. 1-Methylindene (**9**) and 3-methylindene (**10**) were identified by comparison of their nmr spectra with those reported by Wiedler and Bergson.[19] Cycloprop[2,3]indene (**1**) and 1,2-dihydronaphthalene (**8**) were identified by comparison of their glpc retention times and pmr spectra with those of known samples. Determination of the per cent yields of the various hydrocarbon products was done in the following manner. The yield of cycloprop[2,3]indene was obtained from the nmr spectrum of the hydrocarbon product

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[14] E. Le Goff, *J. Org. Chem.*, **29**, 2048 (1964).

[15] C. Courtot, *Ann. Chim. (Paris)*, **4**, 76, 94 (1915).

[16] L. H. Smith, "Organic Syntheses," Collect. Vol III, Wiley, New York, N. Y., 1955, p 793.

[17] H. G. Kuivila and O. F. Beumel, *J. Amer. Chem. Soc.*, **83**, 1246 (1961).

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mixture by integration of its quartet at δ 0.00 ppm (1 H) using the entire aromatic region (4 H) as an internal standard. The relative per cent yields of cycloprop[2,3]indene, 1,2-dihydronaphthalene, 1-methylindene, and 3-methylindene were then determined from glpc data. The actual yields of these materials were calculated by reference to the yield of cycloprop[2,3]indene obtained by nmr examination of the product mixture.

Registry No.—**1**, 15677-15-3; NBS, 128-08-5; Br_2, 7726-95-6; bromotrichloromethane, 75-62-7; tri-*n*-butyltin hydride, 688-73-3; triphenyltin hydride, 892-20-6.

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Azo Compounds. 1. The Synthesis and Decomposition of 3,3'-Diphenyl-5,5'-bi-1-pyrazoline[1,2]

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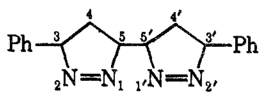
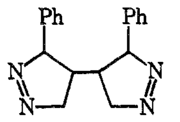
The only product isolated from the reaction of phenyldiazomethane with 1,3-butadiene was a mixture of three stereoisomers of 3,3'-diphenyl-5,5'-bi-1-pyrazoline (I). The thermal and photochemical decompositions of I and of one of the stereoisomers isolated in tlc homogeneous form are described.

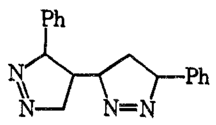
Despite a number of investigations[4-9] on the pyrolysis and photolysis of 1-pyrazolines, it has not been possible to completely generalize the mechanism of these decompositions. We report herein the formation and the decomposition of 3,3'-diphenyl-5,5'-bi-1-pyrazoline (I), obtained as a mixture of three isomers. The isolation of one of these isomers (Ia or Ib) in tlc homogeneous form, as well as its decomposition, is also described.

Results and Discussion

1. Synthesis and Assignment of Structure.—The reaction of diazoalkanes with olefins affords five-membered cyclic azo compounds in fair yields.[5-12] 3-Vinyl-1-pyrazoline has been prepared recently by this method.[11] Our attempts to prepare the 3-phenyl-5-vinyl-1-pyrazoline by the reaction of phenyldiazomethane with 1,3-butadiene resulted only in the formation of a 2:1 adduct, as shown by the elemental analysis. Three types of adducts (I, II, and III) are possible, depending on the direction of addition of phenyldiazomethane. Structure I was assigned to the product isolated on the basis of its spectral data.

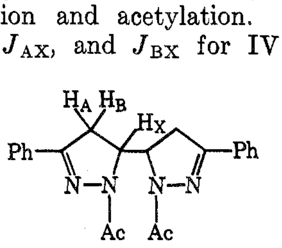

I

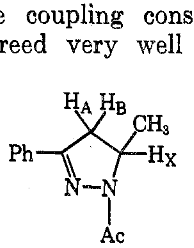

II


III

The cis-azo linkage was confirmed by its ultraviolet absorption at 328 mμ and by a sharp band at 1540 cm^{-1} in the infrared. These values are in agreement with those previously reported for monocyclic 1-pyrazolines.[4-8,10,13-17] The lack of NH absorption in the infrared spectrum also indicated the absence of isomeric hydrazone.

The presence of several complex splitting patterns in the nmr spectrum of I did not allow unambiguous distinction between structures I, II, and III. To facilitate the nmr analysis, I was converted to the 1,1'-diacetyl-bi-2-pyrazoline derivative (IV) by acid-catalyzed isomerization and acetylation. The coupling constants J_{AB}, J_{AX}, and J_{BX} for IV agreed very well with


IV


V

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(1) This is the 50th in a series of papers concerned with the preparation and decomposition of azo compounds. See previous paper in this series by C. G. Overberger and J. Stoddard, *J. Amer. Chem. Soc.*, in press.

(2) This paper comprises a portion of a dissertation submitted by R. Zangaro in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn, 1968.

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