

## Ring-Opening Reactions of Triphenylcyclopropyllithium Compounds

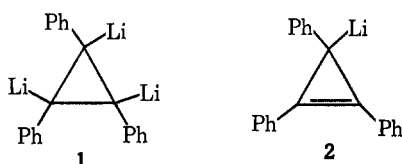
J. E. MULVANEY\* AND DENNIS SAVAGE<sup>1</sup>*Department of Chemistry, The University of Arizona, Tucson, Arizona 85721*

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*trans*-1,2,3-Triphenylcyclopropane undergoes ring opening with *n*-BuLi to give, after treatment with D<sub>2</sub>O, a mixture of *cis*- and *trans*-stilbenes **4** and **5** in which the *trans* isomer prevails. The use of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) did not effect polymetalation of the cyclopropyl ring. Although attempts to trap a cyclopropyl anion in the above experiment were unsuccessful, the 1,2,3-triphenylcyclopropyl anion can form without immediately undergoing ring opening. This was demonstrated by hydrogen-deuterium exchange of the cyclopropyl hydrogens in both *cis*- and *trans*-1,2,3-triphenylcyclopropane, accompanied by isomerization of the *cis* isomer to the *trans*, using potassium *tert*-butoxide in dimethyl sulfoxide-*d*<sub>6</sub>. Treatment of triphenylcyclopropane with *n*-butyl- or *tert*-butyllithium-TMEDA resulted in addition to the cyclopropenyl double bond followed by ring opening to give a mixture of stilbenes **13**–**16**. Attempts to prepare the anti aromatic triphenylcyclopropyllithium with triptycylithium TMEDA and triphenylcyclopropane were unsuccessful.

Since 1965 a number of remarkable polyolithiated compounds have been prepared by treatment of acetylenes with excess alkylolithium compounds. From propyne one obtains C<sub>3</sub>Li<sub>4</sub>;<sup>2</sup> 1-butyne yields CH<sub>3</sub>-CHLi≡CLi<sup>3</sup> or CH<sub>3</sub>Li<sub>3</sub>;<sup>4</sup> 1-phenylpropyne was first shown to yield C<sub>6</sub>H<sub>5</sub>C<sub>3</sub>Li<sub>3</sub>,<sup>5</sup> but, later, using 50 mol of *n*-butyllithium per mole of alkyne the principal products were shown to contain five or six lithium atoms per molecule as well as a trace of the perolithiated compound C<sub>9</sub>Li<sub>6</sub>.<sup>6</sup> Polyolithiation is not a phenomenon restricted to alkynes. In the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA), a reagent which highly activates organolithium compounds,<sup>7,8</sup> toluene and *n*-butyllithium produce trilithiated toluene as the principal product.<sup>9</sup>

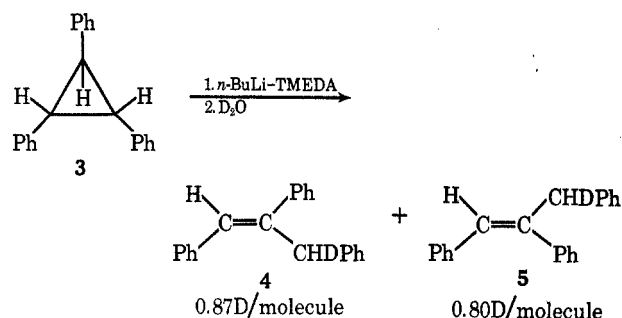
Because of the powerful metalating capacity of RLi-TMEDA, we investigated the possibility of preparing **1**



and **2**. To the extent that these lithiated compounds behave as carbanions, they would be examples of a three-membered ring containing a Hückel number of electrons (**1**) and an anti aromatic<sup>10</sup> cyclopropenyl anion **2**. Although compounds **1** and **2** were not prepared, we wish to report some of the reactions of anionic derivatives of triphenylcyclopropane.

Treatment of *trans*-1,2,3-triphenylcyclopropane (**3**) with 3 mol of *n*-butyllithium-TMEDA in hexane for 6 hr at room temperature followed by treatment of the purple solution with excess D<sub>2</sub>O gave 90% *trans*- (**4**) and 10% *cis*-3-deuterio-1,2,3-triphenylpropene (**5**). No starting material remained nor were other compounds detected by glpc. Furthermore it was shown

that compounds **3**, **4**, and **5** did not react under the work-up conditions.



The structure of the products was confirmed by spectroscopic methods as well as independent synthesis (see Experimental Section). Stereochemical assignments of **4** and **5** (without the deuterium) have previously been made on the basis of solubility and melting point<sup>11</sup> as well as ultraviolet spectra.<sup>12</sup> The nmr spectra confirm these earlier reports in that the vinyl proton of **5** appears at a higher field than the corresponding proton in **4**. Such observations have previously been used to determine the stereochemistry of substituted stilbenes.<sup>13</sup>

Two attempts were made to trap a lithio derivative of **3**. In the first experiment 1.0 mol of **3** in hexane was slowly added to 3.0 mol of *n*-butyllithium containing 0.75 mol of TMEDA (this ratio having been reported to be most effective in the metalation of toluene<sup>9</sup>). The deep orange reaction mixture was worked up with deuterium oxide after a considerably shorter time (30 min) at room temperature to yield 83% of pure **3** containing no deuterium.

Bey and Weyenberg<sup>14</sup> have previously shown that *tert*-butyllithium and trimethylchlorosilane do not react. Accordingly, **3** (1.0 mol) was treated with *tert*-butyllithium (3.0 mol) in the presence of trimethylchlorosilane (1.4 mol) in THF-hexane at -80°. The reaction could not be carried out in the presence of TMEDA because the latter reacts with the silane. After quenching with deuterium oxide and work-up,

(1) Research supported in part by AFOSR(SRC)-OAR, USAF Grant No. 720-67; from the Ph.D. Thesis of D. S., 1970.

(2) R. West, P. A. Carney, and I. C. Mineo, *J. Amer. Chem. Soc.*, **87**, 3788 (1965).

(3) K. C. Eberly and H. E. Adams, *J. Organometal. Chem.*, **3**, 165 (1965).

(4) R. West and P. C. Jones, *J. Amer. Chem. Soc.*, **91**, 6156 (1969).

(5) J. E. Mulvaney, T. L. Folk, and D. J. Newton, *J. Org. Chem.*, **32**, 1647 (1967).

(6) Private communication from Professor West.

(7) G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, **29**, 2928 (1964);

G. G. Eberhardt and W. R. Davis, *J. Polym. Sci., Part A*, **3**, 3753 (1965).

(8) A. W. Langer, *Trans. N. Y. Acad. Sci.*, **27**, 741 (1965).

(9) R. West and P. C. Jones, *J. Amer. Chem. Soc.*, **90**, 2656 (1968).

(10) R. Breslow, *Angew. Chem., Int. Ed. Engl.*, **7**, 565 (1968).

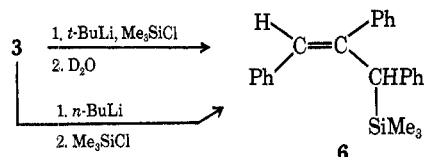
(11) M. S. Evantova and N. I. Shapchenko, *Vestn. Mosk. Univ., Khim.*, **16**, 71 (1961); *Chem. Abstr.*, **57**, 7143f (1962).

(12) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965).

(13) D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind. (London)*, 1205 (1958); J. E. Mulvaney, Z. G. Gardlund, and S. L. Gardlund, *J. Amer. Chem. Soc.*, **85**, 3897 (1963); J. E. Mulvaney and L. J. Carr, *J. Org. Chem.*, **33**, 3286 (1968).

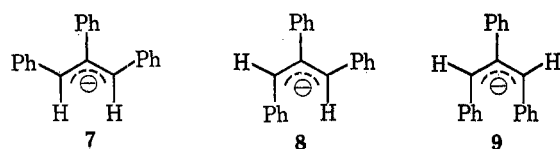
(14) A. E. Bey and D. R. Weyenberg, *ibid.*, **30**, 2436 (1965).

there was obtained a 70% yield of **3** containing no deuterium. The glpc of the remaining oil revealed the presence of 4.5% of **6** plus a smaller amount of the *cis* isomer. Pure **6** was isolated and its structure was confirmed by spectroscopy and independent synthesis involving treatment of **3** with *n*-butyllithium followed by trimethylchlorosilane. The failure to trap the cyclo-



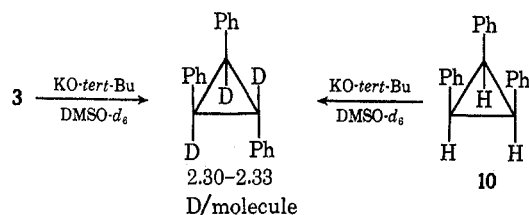
propyllithium derivative in this experiment cannot be regarded as proof that it is *not* an intermediate and that ring opening occurs in a concerted manner. The lithio derivative of **3** is also a hindered species and reaction with the silane could well be slow relative to ring opening.

The similarity of the nmr spectrum of the 1,2,3-triphenylallyllithium intermediate in TMEDA-hexane to that of the ionic species 1,3-diphenylallyllithium<sup>15</sup> leads us to conclude that we are dealing with one or more of three delocalized carbanions (**7-9**). Just as in



the case of the 1,3-diphenyl compound the aromatic protons show a pronounced upfield shift to  $\tau$  3.4 indicating delocalization of charge into the benzene rings and hence over the allylic carbons. In addition, the signal at  $\tau$  7.60 (cyclopropyl protons) gradually disappears and a poorly resolved doublet appears centered at  $\tau$  5.30 which increases with time for at least 25 min with one component apparently increasing at the expense of the other. Inasmuch as deuterolysis of the anion yields 90% *trans*-**4** and 10% *cis*-**5**, we can conclude that **7** which would give only *cis*-**4** is a minor, or absent, component of the mixture. Compound **8** could give a *cis*-*trans* mixture whereas compound **9** would yield only *trans*-**4**. It is reasonable then that **9** is the principal component of the reaction mixture.

It was of interest to examine the triphenylcyclopropanes in a more acidic medium in which the triphenylcyclopropyl anion intermediate could capture a proton prior to ring opening. Accordingly, **3** as well as *cis*-1,2,3-triphenylcyclopropane (**10**) were treated with

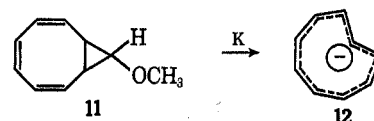


potassium *tert*-butoxide in dimethyl sulfoxide-*d*<sub>6</sub> for 18 hr at room temperature. Neither nmr nor glpc re-

vealed the presence of any ring-opened products. Deuterium was incorporated to the extent shown below and glpc revealed that the *cis* isomer had been completely converted to the *trans*. These results show that the 1,2,3-triphenylcyclopropyl anion is capable of existing for a finite period of time as an intermediate without undergoing ring opening. It is likely, therefore, that the 1,2,3-triphenylcyclopropyl anion is an intermediate in the above discussed work with organolithium reagents in aprotic media. A concerted E2-like elimination in the organolithium case would involve a leaving group which could not be *trans* coplanar with the proton.

The fact that inversion accompanies exchange in the case of **10** is of interest because of the tendency of cyclopropyl anions to maintain configuration even when adjacent to a nitrile or carbonyl group.<sup>16</sup> Although the data from this experiment are insufficient to allow quantitative comparison, it should be noted that steric compression in a nonplanar anion derived from **10** as well as a large gain in delocalization energy in the planar form are two potent driving forces for the isomerization.

It should be noted that ring opening of cyclopropyl anions or anion-like species is a rare phenomenon.<sup>16,17</sup> In fact, the only possible example of this reaction of which we are aware has been reported by Boche, Martens, and Danzer<sup>18</sup> who treated the bicyclic ether **11** with potassium in THF and obtained the 10  $\pi$  electron system **12**. The fact that compound **3** undergoes ring



opening may be taken as further evidence for a highly delocalized 1,2,3-triphenylallyl carbanion as the product.

In an attempt to prepare the monolithiated triphenylcyclopropenyl compound **2**, triphenylcyclopropene (1.0 mol) and TMEDA (1.6 mol) were treated with *n*-butyllithium (6.4 mol) in hexane at room temperature. After 24 hr the deep red solution was treated with excess deuterium oxide to give, after work-up, a 58% yield of an oil which was shown by nmr to contain four products, two sets of stereoisomers, resulting from addition of *n*-butyllithium to the double bond of the cyclopropene ring followed by ring opening. These results, including nmr assignments, are outlined in the following equations (p 2594).

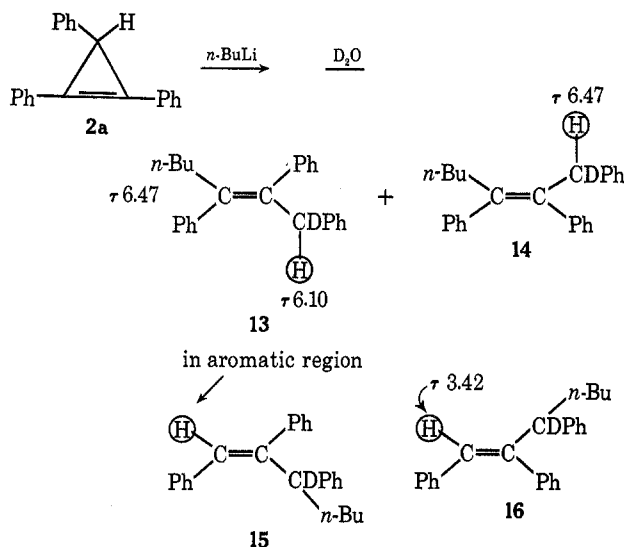
A portion of the oil crystallized to give **14**, identified by its nmr and ultraviolet spectra and elemental analysis. Stereochemical assignments for compounds **13-**

(16) H. M. Walborsky and J. M. Motes, *ibid.*, **92**, 2445 (1970); J. M. Motes and H. M. Walborsky, *ibid.*, **92**, 3697 (1970), and references cited therein.

(17) For examples of cyclopropyl anions or organometallics which do not undergo ring opening, see (a) H. M. Walborsky, A. A. Youssef, and J. M. Motes, *ibid.*, **84**, 2465 (1962); (b) D. E. Applequist and A. H. Peterson, *ibid.*, **83**, 862 (1961); (c) H. M. Walborsky and F. J. Impastato, *ibid.*, **81**, 5835 (1959); (d) H. M. Walborsky, F. J. Impastato, and A. E. Young, *ibid.*, **86**, 3283 (1964); (e) H. M. Walborsky and F. J. Impastato, *ibid.*, **84**, 4838 (1962); (f) M. J. S. Dewar and J. M. Harris, *ibid.*, **91**, 3652 (1969); (g) R. M. Magid and J. G. Welch, *ibid.*, **90**, 5211 (1968); (h) D. Seyferth and H. M. Cohen, *J. Organometal. Chem.*, **1**, 15 (1963); and (i) H. M. Cohen, *ibid.*, **9**, 375 (1967).

(18) G. Boche, D. Martens and W. Danzer, *Angew. Chem., Int. Ed. Engl.*, **8**, 984 (1969).

(15) H. H. Freedman, V. R. Sandel, and B. D. Thill, *J. Amer. Chem. Soc.*, **89**, 1762 (1967).



16 were made in analogy to the benzyl stilbenes discussed earlier in this paper.

The only other example of the addition of an organolithium compound to a cyclopropene of which we are aware is the case of phenyllithium and cyclopropene<sup>17</sup> in which a 2.5% yield of adduct is formed.

The reaction of *tert*-butyllithium-TMEDA with 2a gave results similar to those obtained with *n*-butyllithium as determined by spectroscopy.

Because even a sterically hindered base like *tert*-butyllithium would add to 2a rather than abstract the cyclopropenyl hydrogen, it was desirable to use an even more hindered organolithium reagent, such as triptycylithium.

Treatment of a solution of 2a in THF with triptycylithium in benzene-ether followed by deuterolysis of the reaction mixture gave only 2a containing no deuterium and 9-deuteriotriptycene.

It is apparent then that even extraordinary metalating agents such as RLi-TMEDA which are capable of producing perlitiated hydrocarbons are not capable of generating a cyclopropenyllithium compound.<sup>19</sup>

### Experimental Section

Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Nuclear magnetic resonance (nmr) spectra were determined on either a Varian Model A-60 spectrometer at 60 MHz or a Varian Model HA-100 spectrometer at 100 MHz using tetramethylsilane as an internal standard.

Microanalyses were performed by the Micro-Tech Laboratories, Skokie, Ill. Deuterium analyses reported as "atom per cent excess deuterium" were performed by Josef Nemeth, Urbana, Ill., using the falling drop method; those reported as "deuterium atom per molecule" were calculated from mass spectra data. Deuterium analyses reported in this manner and all other molecular weight determinations were obtained from a Hitachi Perkin-Elmer RHU-6E mass spectrometer. For analytical glpc determinations, correction factors for mole ratio/area ratio data were determined with standards containing the same compounds as in the unknown mixture.

Hexane was purified by stirring overnight with 95% sulfuric acid, washing with distilled water, drying over sodium sulfate, and refluxing over sodium metal for 24 hr prior to final distillation.

Mallinckrodt anhydrous reagent grade ether was used without further purification. Reagent grade tetrahydrofuran was purified by distillation from lithium aluminum hydride. Reagent grade

benzene was refluxed over sodium metal for 24 hr prior to final distillation.

Eastman grade *N,N,N',N'*-tetramethylethylenediamine was dried and distilled over calcium hydride. It was then stored over potassium hydroxide.

Matheson Coleman and Bell practical grade potassium *tert*-butoxide was used without further purification.

Deuterium oxide (99.8 atom % deuterium) and dimethyl sulfoxide-*d*<sub>6</sub> (99.5 atom % deuterium) were obtained from Stohler Isotope Chemicals.

Lithium wire and *tert*-butyllithium in pentane were obtained from the Lithium Corp. of America. *n*-Butyllithium, 1.6 mol in hexane, was obtained from Foote Mineral Co. All organolithium reactions were run under a nitrogen atmosphere in flame-dried apparatus protected by calcium chloride drying tubes.

*cis*- and *trans*-1,2,3-Triphenylpropane. Phenylidibenzylcarbinol.—This compound was prepared in 42% yield according to the procedure of Allen and Converse<sup>20</sup> for the synthesis of methyl-diphenylcarbinol.

Dehydration of Phenylidibenzylcarbinol.—This procedure was adopted from that of Evantova and Shapchenko.<sup>11</sup> A mixture of phenylidibenzylcarbinol (8.10 g, 0.085 mol) and anhydrous cupric sulfate (1.35 g, 0.085 mol) was distilled through a short path column under reduced pressure. The main fraction afforded 5.09 g (68%) of a clear, colorless oil, bp 168–170° (0.30 Torr), which crystallized on standing. The melting point of the crude olefin mixture was 45–50°.

The olefin mixture was separated by fractional recrystallization from 95% ethanol. The more insoluble component separated as white prisms which, after three recrystallizations from 95% ethanol, produced pure *trans*-1,2,3-triphenylpropene, mp 63–64° (lit.<sup>11</sup> mp 62–63°). The ultraviolet spectrum (95% ethanol) had  $\lambda_{\text{max}}$  275 nm ( $\epsilon$  13,300), 210 (16,900). The nmr spectrum ( $\text{CCl}_4$ ) showed peaks centered at  $\tau$  2.95 (multiplet, 16 H) assigned to the aromatic protons and the buried vinyl proton, 6.00 (singlet, 2 H) assigned to the benzyl protons.

The *cis* olefin was obtained from the filtrate of the *trans* isomer. Two recrystallizations from 95% ethanol gave long, white needles, mp 64–65° (lit.<sup>11</sup> mp 63–64°). The ultraviolet spectrum (95% ethanol) had  $\lambda_{\text{max}}$  260 nm ( $\epsilon$  4800), 225 (shoulder, 7100), 208 (12,100). The nmr spectrum ( $\text{CCl}_4$ ) showed peaks centered at  $\tau$  3.00 (multiplet) assigned to the aromatic protons, 3.65 (singlet, 1 H) assigned to the vinyl proton, 6.35 (singlet, 2 H) assigned to the benzyl protons. A mixture melting point of pure *cis* and pure *trans* olefins was 45–58°.

*trans*-1,2,3-Triphenylcyclopropane (3).—3,4,5-Triphenyl-2-pyrazoline<sup>21</sup> was pyrolyzed using a modification of a literature procedure.<sup>22</sup> 3,4,5-Triphenyl-2-pyrazoline (27.0 g, 0.090 mol) was heated for 2 hr at 220–250° with a catalytic amount of powdered potassium hydroxide. The reaction mixture was cooled, diluted with water, and extracted with ether. The ether layer was dried over sodium sulfate. Removal of solvent left an off-white solid which was shown by glpc (10-ft GE-SE-54, 250°) to contain only one component. Two recrystallizations from 95% ethanol gave 16.7 g (69%) of *trans*-1,2,3-triphenylcyclopropane as small white needles, mp 67.0–67.5° (lit.<sup>22</sup> mp 66.5–67.5°). The nmr spectrum ( $\text{CCl}_4$ ) showed peaks centered at  $\tau$  3.00 (multiplet, 15 H) assigned to the aromatic protons, 7.25 (singlet, 3 H) assigned to the cyclopropyl protons.

*n*-Butyllithium, TMEDA, and *trans*-1,2,3-Triphenylcyclopropane in Hexane.—In a typical experiment *n*-butyllithium (0.150 mol) in 94 ml of hexane was slowly added to a stirred solution of *trans*-1,2,3-triphenylcyclopropane (13.5 g, 0.050 mol) and TMEDA (16.4 g, 0.150 mol) in 250 ml of hexane. The solution was cooled in an ice bath during the *n*-butyllithium addition. After being stirred for 6 hr at room temperature, the purple reaction mixture was cooled in an ice bath and quenched by rapid addition of excess deuterium oxide. The now clear, colorless solution was stirred for an additional 45 min and allowed to stand overnight. The reaction mixture was diluted with water. The aqueous layer was extracted with ether and the combined organic layers were dried over sodium sulfate. Removal of the solvent left 12.6 g of an opaque yellow oil which contained 90% *trans*-3-deuterio-1,2,3-triphenylpropene (4) and 10% *cis*-3-deuterio-

(20) C. T. H. Allen and S. Converse, "Organic Syntheses," Collect Vol. I, 2nd ed. A. H. Blatt, Ed., Wiley, New York, N. Y., 1941, p 226.

(21) W. E. Parham and W. R. Hasek, *J. Amer. Chem. Soc.*, **76**, 799 (1954).

(22) Yu. S. Shabarov, A. A. Podterebkov, and R. Ya. Levina, *Vestn. Mosh. Univ., Khim.*, **21**, 118 (1966); *Chem. Abstr.*, **65**, 20023b (1966).

(19) The  $pK_a$  of triphenylcyclopropene is approximately 51: R. Breslow and K. Balasubramanian, *J. Amer. Chem. Soc.*, **91**, 5182 (1969).

1,2,3-triphenylpropene (5) by glpc (10-ft GE-SE-54, 225°). The oil was seeded with authentic *trans*-1,2,3-triphenylpropene. After crystallization the product was collected on a filter, washed with cold 95% ethanol, and dried in the air. This material was recrystallized from 95% ethanol to give 4.10 g of *trans*-3-deuterio-1,2,3-triphenylpropene as small white prisms, mp 63.0–63.5°. A mixture melting point with an authentic sample of undeuterated material gave no depression.

From the filtrate precipitated 2.90 g of small white needles, mp 45–50°. This material was recrystallized from 95% ethanol to give 1.20 g of *cis*-3-deuterio-1,2,3-triphenylpropene as long white needles, mp 64.5–65.0°. A mixture melting point with an authentic sample of undeuterated material was not depressed.

The deuterium content of the benzyl stilbenes was determined by mass spectrometry. The *trans*-3-deuterio-1,2,3-triphenylpropene contained 0.87 deuterium atom per molecule. The *cis*-3-deuterio-1,2,3-triphenylpropene contained 0.80 deuterium atom per molecule.

***n*-Butyllithium, TMEDA, and *trans*-1,2,3-Triphenylcyclopropane in Hexane. Inverse Addition.**—To an ice-cold solution of *n*-butyllithium (0.075 mol) and TMEDA (2.05 g, 0.019 mol) in 97 ml of hexane was added *trans*-1,2,3-triphenylcyclopropane (6.75 g, 0.025 mol) in 200 ml of hexane. The brilliant orange solution was stirred 30 min at room temperature, cooled in an ice bath, and quenched with excess deuterium oxide. The reaction mixture was allowed to stir overnight, after which it was diluted with water. The layers were separated and the aqueous layer was extracted with ether. The combined organic layers were dried over sodium sulfate. Removal of the solvent left 6.0 g of a white solid, mp 61–64°. This material was recrystallized from 95% ethanol to give 5.60 g (83%) of pure *trans*-1,2,3-triphenylcyclopropane, mp 66.5–67.0°. A mixture melting point with authentic material was not depressed. A quantitative deuterium analysis of the recovered cyclopropane by mass spectrometry showed no deuterium incorporation.

***n*-Butyllithium and *trans*-1,2,3-Triphenylcyclopropane. Termination by Silylation.**—To an ice-cold solution of *trans*-1,2,3-triphenylcyclopropane (3.37 g, 0.012 mol) in 200 ml of tetrahydrofuran was added *n*-butyllithium (0.012 mol) in 20 ml of hexane. The solution was stirred for 4 hr at 0°. Upon addition of trimethylchlorosilane (6.0 ml, 0.054 mol), the purple solution turned colorless. The reaction mixture was then diluted with water and extracted with ether. The combined organic layers were dried over sodium sulfate. After removal of the solvent there remained 3.65 g of a clear, colorless oil. The nmr (CCl<sub>4</sub>) showed peaks centered at  $\tau$  2.95 (multiplet, 148 H) assigned to the aromatic protons and the buried vinyl proton of *cis*-3-trimethylsilyl-1,2,3-triphenylpropene, 3.35 (singlet, 4 H) assigned to the vinyl proton of *trans*-3-trimethylsilyl-1,2,3-triphenylpropene, 6.75 (singlet, 4 H) assigned to the benzyl proton of *trans*-3-trimethylsilyl-1,2,3-triphenylpropene, 7.17 (singlet, 12 H) assigned to the benzyl proton of *cis*-3-trimethylsilyl-1,2,3-triphenylpropene, 9.83 (singlet, 65 H) assigned to the methyl protons of the trimethylsilyl group.

Analysis of the oil by nmr indicated *cis*-3-trimethylsilyl-1,2,3-triphenylpropene (67%) and *trans*-3-trimethylsilyl-1,2,3-triphenylpropene (33%).

The oil solidified on standing after approximately 2 weeks. Three recrystallizations from 95% ethanol gave 0.10 g of *trans*-3-trimethylsilyl-1,2,3-triphenylpropene as small white prisms, mp 82–83°. The nmr spectrum (CCl<sub>4</sub>) showed peaks centered at  $\tau$  2.80 (multiplet, 22 H) assigned to the aromatic protons, 3.25 (singlet, 1.5 H) assigned to the vinyl proton, 6.65 (singlet, 1.5 H) assigned to the benzyl proton, 9.75 (singlet, 17 H) assigned to the methyl protons of the trimethylsilyl group. The ultraviolet spectrum (95% ethanol) had  $\lambda_{\max}$  265 nm ( $\epsilon$  15,000), 230 (shoulder 25,000), 204 (70,000).

*Anal.* Calcd for C<sub>24</sub>H<sub>26</sub>Si: C, 84.20; H, 7.60; mol wt, 342. Found: C, 84.02; H, 7.72; mol wt (mass spectrum), 342.

***tert*-Butyllithium, Trimethylchlorosilane, and *trans*-1,2,3-Triphenylcyclopropane in THF-Pentane.**—To a solution of *trans*-1,2,3-triphenylcyclopropane (6.70 g, 0.025 mol) and trimethylchlorosilane (14.7 g, 0.035 mol) in 400 ml of THF at –80° was added *tert*-butyllithium (0.075 mol) in 42 ml of pentane. The lemon yellow reaction mixture was stirred for 2 hr at –80°. The solution was then allowed to reach room temperature, turning purple as it warmed. Excess deuterium oxide was then added and the reaction mixture was stirred overnight. The reaction mixture was then diluted with water and extracted with ether. The combined organic layers were dried over sodium sulfate. Re-

moval of the solvent and two recrystallizations from 95% ethanol afforded 4.65 g (70%) of pure *trans*-1,2,3-triphenylcyclopropane, mp 66.0–67.0°. Mixture melting point with an authentic sample was not depressed. Deuterium analysis of the recovered cyclopropane by mass spectrometry showed no deuterium incorporation.

Work-up also afforded 1.22 g of a yellow oil. Analysis of the oil by glpc (5-ft GE-SE-30, 200°) and nmr indicated *trans*-1,2,3-triphenylpropene (4.5%), and *cis*-3-trimethylsilyl-1,2,3-triphenylpropene (10%). The mass spectrum of the oil indicated a molecular weight of 342, the correct molecular weight for the silylated derivative. Seeding the oil with an authentic sample of *trans*-3-trimethylsilyl-1,2,3-triphenylpropene caused a portion of the oil to crystallize. About 40 mg of *trans*-3-trimethylsilyl-1,2,3-triphenylpropene was obtained as small white, needles, mp 63.0–65.5°. The ultraviolet spectrum (95% ethanol) of this compound had  $\lambda_{\max}$  265 nm ( $\epsilon$  2000), 224 (23,000), 206 (28,000).

**Triphenylcyclopropane.**—This compound was synthesized in 36% yield according to the procedure of Breslow and Dowd<sup>23</sup> with the exception that elution chromatography of the crude 1,2,3-triphenylcyclopropane was usually not necessary. The product was identified by its nmr, mass spectrum, and melting point.

***n*-Butyllithium, TMEDA, and *trans*-1,2,3-Triphenylcyclopropane.**—To an ice-cold solution of 1,2,3-triphenylcyclopropane (2.0 g, 0.0074 mol) and TMEDA (1.39 g, 0.012 mol) in 200 ml of hexane was added *n*-butyllithium (0.048 mol) in 30 ml of hexane. The deep red reaction mixture was stirred for 24 hr at room temperature, and then terminated with excess deuterium oxide. The reaction mixture was diluted with water and extracted with ether. The combined organic layers were dried over sodium sulfate. Removal of the solvent afforded 4.80 g of a slightly opaque, pale yellow oil. The oil was distilled through a short path column to give 1.40 g (58%) of a viscous, clear, light yellow oil, bp 150–155° (0.15 Torr). The nmr spectrum (CCl<sub>4</sub>) showed peaks centered at  $\tau$  3.00 (multiplet, 142 H) assigned to the aromatic protons and the buried vinyl proton of *trans*-3-deuterio-1,2,3-triphenyl-1-heptene (15), 3.42 (singlet, 1 H) assigned to the vinyl proton of *cis*-3-deuterio-1,2,3-triphenyl-1-heptene (16), 6.10 (singlet, 3 H) assigned to the benzyl proton of *trans*-1-deuterio-1,2,3-triphenyl-2-heptene (13), 6.47 (singlet, 3 H) assigned to the benzyl proton of *cis*-1-deuterio-1,2,3-triphenyl-2-heptene (14), 8.50–9.40 (multiplet, 80 H) assigned to the *n*-butyl group protons.

Upon standing for several days the oil solidified and was recrystallized from aqueous 95% ethanol to give 0.22 g of *cis*-1-deuterio-1,2,3-triphenyl-2-heptene (14) as a white crystalline solid, mp 85–86°. The nmr spectrum (CCl<sub>4</sub>) showed peaks centered at  $\tau$  2.80 (multiplet, 16.5 H) assigned to the aromatic protons, 6.50 (singlet, 1.0 H) assigned to the benzyl proton, 7.80 (multiplet, 2.0 H) assigned to the methylene protons on the *n*-butyl group, 8.80 (multiplet, 7.0 H) assigned to the *n*-propyl protons. The ultraviolet spectrum (95% ethanol) had  $\lambda_{\max}$  234 nm (shoulder,  $\epsilon$  7000), 206 (23,000).

*Anal.* Calcd for C<sub>25</sub>H<sub>25</sub>D: C, 91.74; H, 7.64; D, 3.84 atom % excess deuterium; mol wt, 327. Found: C, 91.75; H, 8.10; D, 4.30 atom % excess deuterium; mol wt (mass spectrum), 327.

**Triptycylithium.**—A solution of triptycylithium in benzene (90 ml)–ether (200 ml) was prepared according to the procedure of Dence and Roberts.<sup>24</sup>

**Triptycylithium and Triphenylcyclopropane.**—To a stirred solution of triptycylithium at –80° was added 1,2,3-triphenylcyclopropane (2.0 g, 0.0074 mol) in benzene (25 ml)–ether (25 ml). Tetrahydrofuran (50 ml) was also added and the solution was stirred for 2 hr at –80°. No color change resulted when the cyclopropane was added. The solution was allowed to warm and excess deuterium oxide was added. After work-up in the usual manner there was obtained 9-deuteriotryptycene (mol wt 255, mass spectrum) and unreacted triphenylcyclopropane containing no deuterium.

This experiment was repeated using tetrahydrofuran as the only solvent for both the triptycylithium and 1,2,3-triphenylcyclopropane. The results obtained were essentially the same as in the previous experiment.

***trans*-1,2,3-Triphenylcyclopropane and Potassium *tert*-Butoxide in Dimethyl Sulfoxide-*d*<sub>6</sub>.**—Potassium *tert*-butoxide (0.42 g, 0.0038 mol) was added to DMSO-*d*<sub>6</sub> (2 ml, 0.024 mol) with stirring under nitrogen. *trans*-1,2,3-Triphenylcyclopropane (0.37 g,

(23) R. Breslow and P. Dowd, *J. Amer. Chem. Soc.*, **85**, 2729 (1963).

(24) J. B. Dence and J. D. Roberts, *J. Org. Chem.*, **33**, 1251 (1968).

0.0014 mol) was added and the solution turned a clear violet color. The reaction mixture was stirred at room temperature for 18 hr after which time the clear orange solution was diluted with water and extracted with ether. The ether layer was dried over sodium sulfate. Removal of the solvent left a pale yellow solid which was recrystallized from 95% ethanol to give 0.24 g (65%) of *trans*-1,2,3-triphenylcyclopropane. Mixture melting point with an authentic sample was not depressed.

A deuterium analysis by mass spectrometry of the recovered cyclopropane indicated 2.30 deuterium atom per molecule. The nmr spectrum showed that the cyclopropyl hydrogens had been exchanged.

*cis*-1,2,3-Triphenylcyclopropane.—This compound was synthesized in 80% yield according to the procedure of Battiste.<sup>25</sup>

*cis*-1,2,3-Triphenylcyclopropane and Potassium *tert*-Butoxide in DMSO-*d*<sub>6</sub>.—Potassium *tert*-butoxide (0.69 g, 0.0062 mol) was added to DMSO-*d*<sub>6</sub> (3 ml, 0.036 mol) with stirring under nitrogen. Then *cis*-1,2,3-triphenylcyclopropane (0.55 g, 0.0020 mol) was added. The resulting deep blue-green solution was stirred for 18

(25) M. A. Battiste, *Tetrahedron Lett.*, 3795 (1964).

hr at room temperature. The reaction mixture was then diluted with water and extracted with ether. The ether layer was dried over sodium sulfate. Removal of the solvent left 0.50 g (91%) of a viscous clear yellow oil which was shown by glpc (5 ft SE-30, 220°) to contain only one component having the same retention time as authentic *trans*-1,2,3-triphenylcyclopropane. It should be noted that it was possible to separate an authentic mixture of *cis*-1,2,3-triphenylcyclopropane and *trans*-1,2,3-triphenylcyclopropane on the glpc column used for the crude reaction product.

A deuterium analysis by mass spectrometry of the recovered oil indicated 2.33 deuterium atom per molecule. The nmr spectrum showed that the cyclopropyl hydrogens had been exchanged.

**Registry No.**—3, 10539-10-3; 4, 30477-01-1; 5, 30409-61-1; 6, 30409-62-2; 13, 30409-63-3; 14, 30477-02-2; 15, 30409-64-4; 16, 30409-65-5; *trans*-1,2,3-triphenylpropene, 3239-33-6; *cis*-1,2,3-triphenylpropene, 3239-32-5; *cis*-3-trimethylsilyl-1,2,3-triphenylpropene, 30409-68-8.

## The Copper Chloride-Ethanolamine-Catalyzed Addition of Polyhaloalkanes to Substituted Olefins<sup>1</sup>

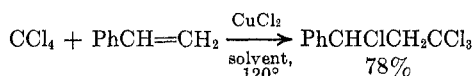
DONALD J. BURTON\* AND LAWRENCE J. KEHOE

Department of Chemistry, The University of Iowa, Iowa City, Iowa 52240

Received January 22, 1971

The copper chloride-ethanolamine redox system initiates the addition of polyhaloalkanes to a variety of olefins. The structure of the initial olefin greatly affects both the yield and the structure of the final product. Halogenated olefins showed decreased reactivity toward radical attack. The telogen CF<sub>2</sub>BrCFClBr gave good yields with simple  $\alpha$  olefins, while only the more reactive CCl<sub>3</sub>Br reacted with several halogenated olefins. This redox system of radical initiation exhibits considerable potential as a synthetic tool. The preparation and characterization of several new addition adducts are reported.

The addition of polyhalogenated alkanes to the double bond of olefins has received considerable attention in the literature.<sup>2</sup> While the usual systems for free-radical initiation give varying amounts of telomeric products, the "redox" system described by Asscher and Vofsi leads to almost exclusive formation of 1:1 adducts.<sup>3,4</sup> This system utilizes iron or copper salts to catalyze the addition of carbon tetrachloride and chloroform to olefins. Reaction conditions are quite mild



and, because telomerization reactions are minimized, the use of a large excess of alkyl polyhalide is unnecessary. Additionally, vigorous reaction conditions and the need for special apparatus can be avoided. Because of these advantages, the redox technique holds much promise for the preparation of many polyhalogenated compounds, and a study of the scope and utility of this system was of interest.

We recently reported<sup>5</sup> a study of the scope of this reaction with a series of alkyl polyhalides. 1-Octene was used as the model olefin for that reactivity survey. Our

initial study has now been expanded to include a variety of olefins, with the hope that the effect of olefin structure on the polyhalide additions could be ascertained.

### Results and Discussion

In this study, CF<sub>2</sub>BrCFClBr was used as a model halide. Our previous report<sup>5</sup> showed it to be very reactive under redox conditions, giving a good yield of stable, 1:1 addition product with 1-octene. As previously described, the additions were carried out by refluxing the olefin, alkyl polyhalide, copper chloride, ethanolamine, and *tert* butyl alcohol, with stirring, for 24 hr. If no significant reaction was noted after this time, reflux was continued for at least an additional 24 hr. The results of these addition reactions are summarized in Table I.

An examination of the data in Table I reveals that this redox method successfully initiates the addition of polyhaloalkanes to both terminal and internal olefins as well as several halogen-substituted olefins.

Vpc showed that in almost every reaction, in addition to the major product, small amounts (generally less than 5% of the total product) of isomeric compounds were formed. These by-products were not identified.

The redox-initiated additions proceed in the same manner as that described for additions initiated by ordinary techniques. We have shown<sup>5</sup> that addition to straight-chain, terminal olefins gives almost exclusively the simple, straight-chain 1:1 addition adduct.

(1) (a) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966; (b) preliminary report in *Tetrahedron Lett.*, 5163 (1966); (c) this investigation was supported in part by Public Health Service, Grant GM 11809.

(2) For extensive reviews of this work, cf. (a) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, Chapter 6. (b) G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," Macmillan, New York, N. Y., 1964, Chapter 2.

(3) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1887 (1963).

(4) M. Asscher and D. Vofsi, *ibid.*, 3921 (1963).

(5) D. J. Burton and L. J. Kehoe, *J. Org. Chem.*, **35**, 1339 (1970).