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HALOMETHYL—METAL COMPOUNDS

LXXIX*. THE GENERATION OF ISOPROPYLIDENE CARBENE BY THE ORGANOMERCURY ROUTE

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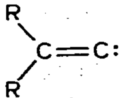
Summary

Bis(1-bromo-2-methylpropenyl)mercury, prepared via $Me_2C{=}C(Br)Li$, was treated with mercuric bromide to give $Me_2C{=}C(Br)HgBr$. The latter transferred $Me_2C{=}C$: to olefins, giving isopropylidenecyclopropanes, in sealed tube reactions carried out at 150°C in the presence of an equimolar quantity of diphenylmercury. The $Me_2C{=}C(Br)HgBr/Ph_2Hg$ reagent also reacted with triethylsilane at 150°C to give $Et_3SiCH{=}CMe_2$ in nearly quantitative yield.

Introduction

Alkylidenecarbenes, I, have been of considerable interest to organic chemists [2], and a variety of procedures has served in their generation. The action of strong base on primary vinyl halides [3] and primary vinyl triflates, II [4], of organolithium reagents on vinylidene dibromides [5], the base-induced decomposition of 5,5-disubstituted *N*-nitrosooxazolidones, III [6], the phase transfer catalyzed, base-induced decomposition of *N*-nitrosoacetylamino alcohols, IV [7], the deamination of vinylamines [8], and photofragmentation [9] have



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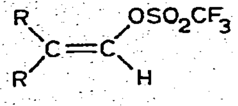

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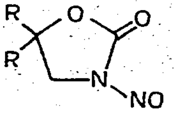

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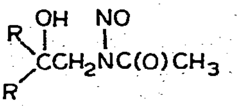


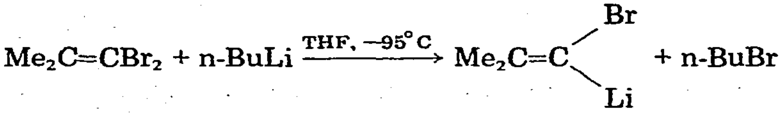
(IV)

been reported to yield alkylidenecarbenes. These intermediates have shown typical carbene reactivity, undergoing addition to C=C bonds to form alkylidenecyclopropanes and insertion into Si—H bonds to produce vinylsilanes [2]. All of the known methods of generating alkylidenecarbenes suffer from synthetic limitations and difficulties. For some procedures the use of a highly basic reaction medium is required. In some reactions the formation of intermediates other than the carbene introduces complications. As a result, the yields of carbene-derived products often are low. A cleaner, simpler method of $R_2C=C$: generation which is applicable in neutral organic medium thus would be welcome.

We report here concerning our attempts to develop a useful organomercury-based route to a simple unsaturated carbene, $Me_2C=C$:. Such an approach seemed worthwhile in view of our previous success in developing organomercury reagents for the generation of various halogenated carbenes, as described in previous papers of this series.

Results and discussion

The organolithium route served well in the preparation of the required organomercury reagent for isopropylidenecarbene generation. In a previous study [10] it had been found that 1,1-dibromo-2-methylpropene could be converted to 1-bromo-2-methylpropenyllithium in good yield (eq. 1). This reagent reacted with mercuric chloride to give bis(1-bromo-2-methylpropenyl)mercury



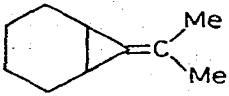
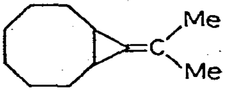
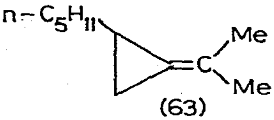
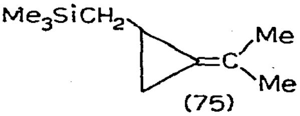
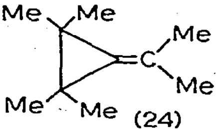
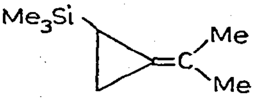
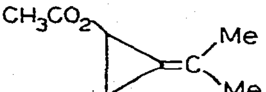
$$Me_2C=CBr_2 + \text{n-BuLi} \xrightarrow{\text{THF, }-95^\circ\text{C}} Me_2C=C\begin{matrix} \diagup Br \\ \diagdown Li \end{matrix} + \text{n-BuBr} \qquad (1)$$

in good yield. The latter was converted to 1-bromo-2-methylpropenylmercuric bromide in high yield by reaction with an equimolar amount of mercuric bromide. The 1:1 mixtures of these organomercury compounds with diphenylmercury should be effective isopropylidenecarbene transfer systems, in analogy to our previously developed $(BrCH_2)_2Hg/Ph_2Hg$, $BrCH_2HgBr/Ph_2Hg$ and ICH_2HgI/Ph_2Hg reagent systems for the transfer of CH_2 to diverse substrates [11].

Our initial investigations showed the $(Me_2C=CBr)_2Hg/Ph_2Hg$ system to be a source of isopropylidenecarbene. When such a mixture was heated in cyclooctene for 6 h at 140°C, phenylmercuric bromide was formed in 79% yield and 9-isopropylidenebicylco[6.1.0]nonane in 41% yield, based on available $Me_2C=CBr$ groups. A similar experiment carried out at 80°C in refluxing cyclohexene gave no phenylmercuric bromide during a 6 day reflux period at ca. 80°C. However, in a sealed tube reaction of this mercurial pair with cyclohexene (with benzene dilu-

TABLE 1

DIVALENT CARBON TRANSFER REACTIONS OF THE $Me_2C{=}CBrHgBr/Ph_2Hg$ SYSTEM [a]

Carbenophile	Reaction time (h)	Product (% yield)	PhHgBr (% yield)
Cyclohexene [b]	4	 (87)	95
Cyclooctene [c]	4	 (64)	92
n-$C_5H_{11}CH{=}CH_2$	18	 (63)	95
$Me_3SiCH_2CH{=}CH_2$	16	 (75)	91
$Me_2C{=}CMe_2$	23	 (24)	95
$Me_3SiCH{=}CH_2$ [d]	8	 (24)	96
$CH_3CO_2CH{=}CH_2$	16	 (52)	90
Et_3SiH	20	$Et_3SiCH{=}CMe_2$ (97)	94

[a] All reactions were carried out at 150°C in a sealed tube with vigorous shaking; 5 mmol each of the mercury reagents and 50 mmol of carbenophile in 10 ml of benzene, unless otherwise noted. [b] 65 mmol. [c] 37 mmol. [d] 9 mmol each of the mercury reagents, 90 mmol of olefin in 15 ml of pentane.

ent) carried out at 160°C for 6 h, phenylmercuric bromide was obtained in 61% yield and 7-isopropylidenenorcarane in 48% yield. A longer reaction time of 18 h under these conditions resulted in marginally increased yields of 75% and 58%, respectively.

The reaction of $Me_2C{=}CBrHgBr$ with diphenylmercury in benzene at 80°C was rapid and essentially irreversible, with phenylmercuric bromide precipitating in quantitative yield. The unsymmetrical mercurial which was formed symmetrized under the reaction conditions (eq. 2, 3). When carried out in the presence

$$Me_2C{=}CBrHgBr + Ph_2Hg \rightleftharpoons PhHgCBr{=}CMe_2 + PhHgBr(s) \tag{2}$$

$$PhHgCBr{=}CMe_2 \rightleftharpoons \tfrac{1}{2}\, Ph_2Hg + \tfrac{1}{2}\, Hg(CBr{=}CMe_2)_2 \tag{3}$$

of cyclohexene in benzene at 80°C, the reaction followed the same course and no divalent carbon transfer occurred. The synthesis of isopropylidenecyclopropanes using the $Me_2C{=}CBrHgBr/Ph_2Hg$ reagent was successful when the reactions were carried out at 150°C in a sealed tube. Good agitation was required in order to obtain good yields of cyclopropane product. The required reaction time appeared to be substrate-dependent. Thus a reaction of the mercurial reagent pair with cyclohexene in benzene gave phenylmercuric bromide in 95% yield and 7-isopropylidenenorcarane in 87% yield after 4 h reaction time at 150°C. An analogous reaction of the poorer carbenophile 1-heptene resulted in a phenylmercuric bromide yield of only 50% after 5 h, but an 18 h reaction period at 150°C gave phenylmercuric bromide in 95% yield and the expected cyclopropane in 63% yield.

The results of our limited studies are given in Table 1. Although in all reactions the phenylmercuric bromide yields were nearly quantitative, the cyclopropane yields were low in the case of tetramethylethylene and vinyltrimethylsilane. This is not surprising in view of the experience of previous workers (e.g., ref. 6c) that steric effects are much more pronounced with isopropylidenecarbene than with sterically less demanding carbenes such as CCl_2 and $Me_2C{=}C{=}C{:}$ In the case of vinyltrimethylsilane both steric and electronic effects combine to make it a rather poor carbenophile [12], but tetramethylethylene is the most reactive of all methylated ethylenes toward CCl_2 [13], so the poor reactivity toward $Me_2C{=}C{:}$ must be ascribed to the operation of steric factors. In any case, the product yields obtained with the $Me_2C{=}CBrHgBr/Ph_2Hg$ reagent are higher than the yields obtained in other methods of $Me_2C{=}C{:}$ transfer.

No information concerning the mechanism of these $Me_2C{=}C{:}$ transfer reactions is available, so we do not know if a free carbene intermediate is involved. Any mechanistic studies would be complicated by the fact that $Me_2C{=}C{:}$ transfer should in principle be possible from all three $Me_2C{=}CBr$-containing compounds which are involved in the equilibria shown in eq. 2 and 3, albeit at different rates.

Experimental

General comments

High temperature reactions were carried out in thick-walled Pyrex bomb tubes. The contents of the bomb tube (mercurial, olefin and solvent) were degassed by means of one freeze—thaw cycle and the tube was sealed under vacuum. It then was cushioned inside an electrically heated, thick-walled metal bomb cylinder which was mounted on a Burrell "wrist-action" mechanical shaker. Reaction temperatures were monitored using a calibrated thermocouple.

Infrared spectra were measured using a Perkin—Elmer 457A infrared spectrophotometer, NMR spectra using a Varian Associates T60 spectrometer. Carbon tetrachloride was the solvent used in NMR spectral measurements unless otherwise specified. Chemical shifts are given in δ units, ppm downfield from internal tetramethylsilane. Gas chromatography (GLC) was used in the analysis of product mixtures, in yield determinations (internal standard method) and in product isolation.

Preparation of 1,1-dibromo-2-methylpropene

The general procedure of Corey and Fuchs [14] for the preparation of $R_2C{=}CBr_2$ compounds was used.

A solution of 118 g (0.355 mol) of CBr_4 (sublimed at 50°C/0.07 mmHg) in 200 ml of dichloromethane was added to a suspension of 93 g (0.355 mol) of triphenylphosphine and 23.2 g (0.355 mol) of zinc dust in 300 ml of dichloromethane over a period of 1 h, with water-bath cooling. The resulting mixture was stirred at 20°C for 23 h and then was treated with 11.7 g (0.20 mol) of dry acetone. The addition resulted in a moderately exothermic reaction. The mixture was stirred for 2 h, filtered and the filtrate was concentrated under reduced pressure. The residue was extracted with pentane. The pentane-insoluble residue was redissolved in dichloromethane and this procedure of concentration and pentane extraction was repeated several times. The combined pentane extracts were dried and distilled to give 25.5 g (0.119 mol, 67%) of the desired product, b.p. 29-34°C/42 mmHg.

Preparation of bis(1-bromo-2-methylpropenyl)mercury

A solution of 32.0 g (150 mmol) of 1,1-dibromo-2-methylpropene in 300 ml of dry THF in a one-liter Morton flask equipped with a mechanical stirrer, addition funnel and a nitrogen inlet tube was cooled to —92°C and treated, with stirring under nitrogen, with 85 ml of 1.89 *N* n-butyllithium (161 mmol) in hexane. The colorless reaction mixture was stirred at —95°C for 45 min and then a solution of 19.5 g (72 mmol) of mercuric chloride in 60 ml of THF was added slowly with stirring. The resulting greyish reaction mixture was stirred at —92°C for 90 min and then was allowed to warm slowly to room temperature. Suction filtration through Celite removed the fine grey solid phase. The filtrate was concentrated at reduced pressure and the residue was extracted with dichloromethane. Evaporation of the extracts left a white, crystalline solid. Recrystallization from hexane/dichloromethane gave 25.4 g (75%) of the title mercurial, white needles, m.p. 154-155°C. An additional recrystallization gave an analytical sample, m.p. 155.5-156°C (Found: C, 20.53; H, 2.63; Br, 34.23. $C_8H_{12}Br_2Hg$ calcd.: C, 20.50; H, 2.58; Br, 34.11%). NMR (in CCl_4): δ 2.00 and 2.07 ppm (singlets); (in benzene-d_6): δ 1.51 and 1.83 ppm (singlets). IR (KBr pellet): ν(C=C), 1608 cm^{-1}.

Preparation of 1-bromo-2-methylpropenylmercuric bromide

Five mmol each of bis(1-bromo-2-methylpropenyl)mercury and mercuric bromide were dissolved in 10 ml of dry THF at room temperature. Ten ml of hexane was added and the solution was placed in the freezer. The white solid which formed overnight was filtered to give 3.85 g (93%) of the title mercurial, white needles, m.p. 130-131°C. Recrystallization from methanol raised the m.p. to 132-133°C. (Found: C, 11.67; H, 1.56; Br, 38.46. $C_4H_6Br_2Hg$ calcd.: C, 11.59; H, 1.46; Br, 38.56%). NMR (in $CDCl_3$): δ 2.03 and 2.09 ppm (singlets); (in benzene-d_6): δ 1.19 and 1.59 ppm (singlets). IR (KBr): ν(C=C), 1610 cm^{-1}.

Reaction of (Me_2C=CBr)$_2$Hg/Ph_2Hg with cyclooctene

A 50 ml round-bottomed flask equipped with a reflux condenser, a magnetic stirring unit and a nitrogen inlet tube was charged with 7 ml of cyclooctene and a mixture of 7.2 mmol of $(Me_2C{=}CBr)_2Hg$ and 5.4 mmol of diphenylmercury. The reaction mixture was stirred and heated at 140°C for 6 h, cooled and filtered to remove 3.05 g of phenylmercuric bromide (79%), m.p. 283-285°C. The filtrate was trap-to-trap distilled at 0.1 mmHg and the distillate was examined by GLC (10% UC-W98 at 130°C). It was established that 9-isopropylidenebicyclo[6.1.0]nonane was present in 41% yield, based on available Me_2C=C groups. A sample isolated by GLC had n_D^{25} 1.4862 and its IR and NMR spectra were in agreement with published data [6c].

Sealed tube reactions of Me_2C=CBrHgBr/Ph_2Hg with olefins and triethylsilane

The reaction with cyclohexene is described to illustrate the procedure used. See also "General comments".

A sealed tube containing 2.08 g of Me_2C=CBrHgBr (5.0 mmol), 1.78 g of diphenylmercury (5.0 mmol), 5.3 g of cyclohexene (65 mmol) and 10 ml of dry benzene was maintained at 150°C with continuous shaking for 4 h. The tube was cooled and opened and the contents were filtered to remove the solid which had been formed (3.43 g, 96%, of phenylmercuric bromide). The filtrate was trap-to-trap distilled at 0.1 mmHg and the distillate was analyzed by GLC. 7-Isopropylidenenorcarane, n_D^{25} 1.4752 (lit. [3c] n_D^{24} 1.4753), was present in 87% yield. Its IR and NMR spectra were in agreement with literature data [3c, 5a, 6c]. A minor product (2.5% yield) was identified as 3,3'-bicyclohexenyl. Its IR, NMR and 70 eV mass spectra were in agreement with previously reported data [15]. An authentic sample was prepared by coupling of the Grignard reagent derived from 3-bromocyclohexene [16] and was found to have identical spectroscopic properties and GLC retention time.

Analytical and spectroscopic data for the other products listed in Table 1 follow below.

1-Isopropylidene-2-n-amylcyclopropane. n_D^{25} 1.4440. NMR: δ 0.3-1.6 (m, with maxima at 0.92 and 1.38 ppm, 14H) and 1.80 ppm (broad s, 6H). Found: C, 86.40; H, 13.59. $C_{11}H_{20}$ calcd.: C, 86.76; H, 13.24%.

1,1,2,2-Tetramethyl-3-isopropylidenecyclopropane. n_D^{25} 1.4339, a known compound [6c]. NMR: δ 1.67 (s, 6H) and 1.11 ppm (s, 12H). Found: C, 86.68; H, 13.26. $C_{10}H_{18}$ calcd.: C, 86.88; H, 13.12%.

1-Isopropylidene-2-trimethylsilylmethylcyclopropane. n_D^{25} 1.4472. NMR: δ 0.07 (s, 9H, Me_3Si), 0.17-1.4 (m, 5H, $SiCH_2$ and ring protons) and 1.79 ppm (m, 6H). Found: C, 71.24; H, 11.95. $C_{10}H_{20}Si$ calcd.: C, 71.34; H, 11.97%.

1-Isopropylidene-2-trimethylsilylcyclopropane. n_D^{25} 1.4448. NMR: δ 0.01

(s, 9H, Me_3Si), 0.4-1.4 (m, 3H) and 1.82 ppm (m, 6H). Found: C, 70.17; H, 11.84. $C_9H_{18}Si$ calcd.: C, 70.04; H, 11.75%.

2-Isopropylidenecyclopropyl acetate. n_D^{25} 1.4488. NMR: δ 0.93-1.5 (m, 2H, ring CH_2), 1.86 (m, 6H, CMe_2), 1.97 (s, 3H, CH_3CO_2) and 4.42 ppm (broad m, 1H, AcOCH).

2-Methylpropen-1-yltriethylsilane. n_D^{25} 1.4508 (lit. [17] n_D^{20} 1.4538). The IR and NMR spectra were in good agreement with those reported for this compound by previous workers [6e].

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