FORMATION OF DIESTERS OF 1,2-DISUBSTITUTED CYCLOPROPENE-3,3-DICARBOXYLIC ACIDS AND SILYLALKYNYLMALONIC ACIDS IN THE REACTION OF DIMETHYL DIAZOMALONATE WITH SILYLACETYLENES IN THE PRESENCE OF $CuSO_4$*

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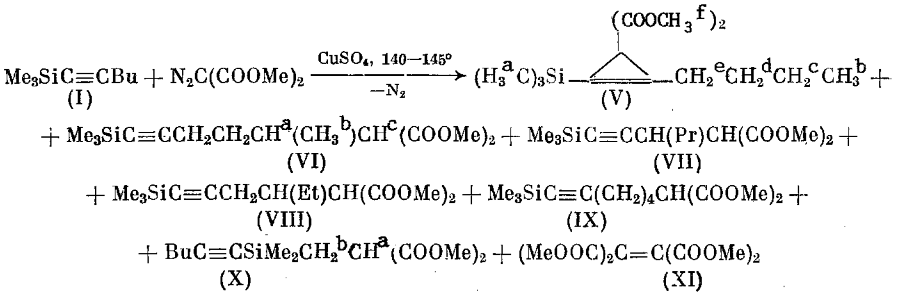
The reaction of dimethyl diazomalonate (DMM) with acetylenic hydrocarbons has been studied in the case of diphenylacetylene upon the decomposition of DMM by copper powder [2] and of 1- and 2-alkynes [3, 4] upon the photolytic generation of bis(methoxycarbonyl)carbene (BMC) from DMM. In the former case, the reaction product is the diester of 1, 2-diphenylcyclopropene-3,3-dicarboxylic acid, while in the latter cases, the formation of isomeric furans and small amounts of the products of the insertion of BMC into the C—H bond of the starting acetylenes were noted in addition to diesters of alkylcyclopropene-3,3-dicarboxylic acids.

In order to determine the feasibility of using this reaction for the preparation of esters of silyl-substituted cyclopropene-3,3-dicarboxylic acids, we studied the reaction of DMM with butyl(trimethylsilyl)acetylene (I), propyl(trimethylsilyl)acetylene (II), bis(trimethylsilyl)acetylene (III) and, for purposes of comparison, 4-octyne (IV) in the presence of $CuSO_4$ at 140-145°C in the case of a five- to sixfold molar excess of the acetylenic hydrocarbon.

Although the isomerization of the cyclopropene derivatives to the furan isomers was not observed in the reactions of DMM with acetylenes in the presence of $CuSO_4$ [3], we used 0.016 g $CuSO_4$ in order to decrease tar formation. Under these conditions, the products of the cycloaddition of BMC to (I)-(IV) are the dimethyl esters of 1-trimethylsilyl-2-cyclopropene-3,3-dicarboxylic (V), 1-trimethylsilyl-2-propylcyclopropene-3,3-dicarboxylic (XII), 1,2-bis(trimethylsilylcyclopropene-3,3-dicarboxylic (XV), and 1,2-dipropylcyclopropene-3,3-dicarboxylic acids (XVII), respectively, which are obtained in addition to the products of the insertion of MBC into the C—H bond of the acetylenic hydrocarbons, viz., the dimethyl esters of alkynylmalonic acids (VI)-(X), (XIII), (XIV), and (XVIII) [reactions (1)-(4)]. In the case of (I) and (II), the yields of the dimethyl esters of cyclopropene-3,3-dicarboxylic acids (VI) and (XII) are 20-30% and are comparable to the yields of the diesters of trimethylsilylalkynylmalonic (VI)-(IX), (XIII) and alkyldimethylsilylmethylmalonic acids (X) and (XIV) (up to 18%).



$$\underset{(I)}{Me_3SiC{\equiv}CBu} + N_2C(COOMe)_2 \xrightarrow[-N_2]{CuSO_4,\ 140-145^\circ} \underset{(V)}{(H_3^{a}C)_3Si-\overset{(COOCH_3^{f})_2}{\triangle}-CH_2^{e}CH_2^{d}CH_2^{c}CH_3^{b}} +$$
$$+ \underset{(VI)}{Me_3SiC{\equiv}CCH_2CH_2CH^{a}(CH_3^{b})CH^{c}(COOMe)_2} + \underset{(VII)}{Me_3SiC{\equiv}CCH(Pr)CH(COOMe)_2} +$$
$$+ \underset{(VIII)}{Me_3SiC{\equiv}CCH_2CH(Et)CH(COOMe)_2} + \underset{(IX)}{Me_3SiC{\equiv}C(CH_2)_4CH(COOMe)_2} +$$
$$+ \underset{(X)}{BuC{\equiv}CSiMe_2CH_2^{b}CH^{a}(COOMe)_2} + \underset{(XI)}{(MeOOC)_2C{=}C(COOMe)_2} \qquad (1)$$

The reaction of DMM with (I) gives an 18% yield of a mixture of the insertion products of BMC, which, as indicated by gas—liquid chromatography, consists largely of five isomeric diesters (VI)-(X). The PMR spectrum at 250 MHz indicates the predominance of diesters (VI)

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*For a preliminary communication, see [1].

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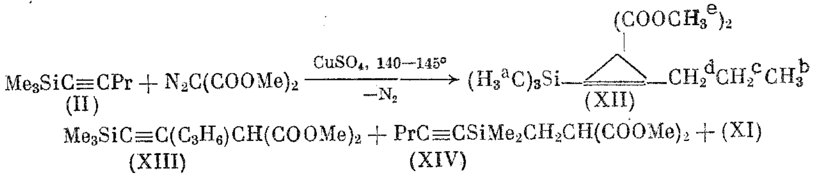
arising due to the insertion of BMC into the C–H bond of the γ-methylene group and (X), which is the product of the insertion of BMC into the C–H bond of the trimethylsilyl substituent [the fraction of (VI) and (X) is about 70 mole % of the total (VI)-(X) with (VI):(X) = 1:1.3]. Evidence for the structure of (VI) is found in the doublets at 3.35 ppm with $J_{H^aH^c} = 7$ Hz and at 1.10 ppm with $J_{H^aH^b} = 7.2$ Hz. The ratio of the intensities of these doublets is 1:3. The total amount of (VII)-(IX), which are the products of the insertion of BMC into other C–H bonds of the butyl substituent in (I), is equal to the amount of (VI). Evidence for (VII)-(IX) is found in the low-intensity signals at 3.40-3.60 ppm and the somewhat reduced value of the integral intensity of the signal for the methyl protons in the C_2H_5 group at 0.93 ppm. The singlet at 3.75 ppm corresponds to the ester CH_3 groups, while the singlet at 0.15 ppm corresponds to the Me_3Si group. The multiplets at 2.20-2.40 ppm correspond to the protons of the α-CH_2 groups, while the complex overlapping multiplets at 1.30-1.80 ppm correspond to the remaining protons.

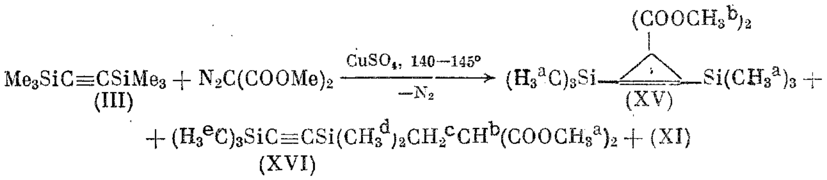
A significant portion of the BMC insertion products in the reaction of DMM with (I) is found for diester (X). The triplet at 3.55 ppm (H^a) and doublet at 1.25 ppm ($2H^b$) with intensity ratio 1:2 and J = 7.8 Hz correspond to this product. Comparison of the integral intensities of this signals and the MeO_2C and Me_3Si proton signals indicates that the fraction of (X) among the other insertion products is about 40 mole %.

When the reaction of DMM with (I) is carried out under thermolysis conditions at 140-145°C in a quartz reactor, the yield of (V) is increased to 39% but insertion products (VI)-(X) are formed in 19% yield. Analogously, the reaction of DMM with (II) gives roughly equal amounts of diesters (XII)-(XIV):



(2)

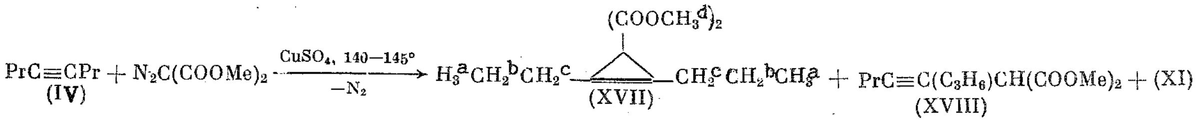
The reaction of DMM with bis(trimethylsilyl)acetylene (III) [reaction (3)] gives the product of the insertion of BMC into the C–H group of the Me_3Si group [diester (XVI)] in 5.4% yield in addition to the cycloadduct (XV) obtained in 25% yield:



(3)

The formation of (X), (XIV), and (XVI) is the first example of the detection of the products of the formal insertion of a carbene into the C–H bond of an alkyl substituent at a silicon atom. Since the Si–C and C–H bonds in $Si{-}CH_3$ fragments have approximately equal tendency to undergo homolysis [5], we might have expected the insertion of BMC into the C–H and Si–C bonds of the trimethylsilyl groups in reactions (1)-(3), i.e., the generation of both diester (VI)-(X), (XIII), (XIV), and (XVI) as well as $RC{\equiv}CCH(CO_2Me)SiMe_3$ and $RC{\equiv}CSiMe_2CH^aMe(CO_2Me)_2$ compounds. However, the PMR spectra indicate that if such products are indeed formed, they are obtained in extremely small amounts. Thus, the weak quartet at 1.95 ppm (H^a) is evidence for the formation of such compounds.

The reaction of DMM with 4-octyne in the presence of $CuSO_4$ [reaction (4)] gives diester (XVII) in 45% yield, which is 1.5-2 times greater than in the case of trimethylsilylacetylenes and is in accord with the behavior of acetylenic hydrocarbons and their silyl homologs in reactions with alkyl diazoacetates [6]. In the case of (IV), the products of BMC insertion, viz., diesters (XVIII), are also formed; the yield of these products (24%) is one-half the yield of (XVII):



(4)

The insertion of BMC into C–H bonds is characteristic for thermocatalytic reactions of DMM independently of the type of copper catalyst employed [7, 8] and is evidence for the triplet nature of the BMC ground state. However, in a previous study of the reaction of DMM with olefins in the presence of various copper salts, Wulfman et al. [9] noted a greater than 10-fold predominance of the cyclopropane adducts over the products of BMC insertion [9]. The significant fraction of insertion products found in reactions (1)-(4) is apparently a consequence of the reduced reactivity of the multiple bonds in acetylenic hydrocarbons upon their reaction with DMM.

The product of the formal dimerization of BMC, viz., the tetramethyl ester of ethylenetetracarboxylic acid (XI), is formed in about 1% yield in all the reactions studied. We should note that the detection of diesters of silylalkynylmalonic acids such as (VI)-(X), (XIII), (XIV), and (XVI) holds independent interest since the synthesis of such compounds by other methods is extremely difficult.

EXPERIMENTAL

The products were analyzed by gas—liquid chromatography on an LKhM-8MD chromatograph with a katharometer detector, 300 × 0.3 cm column packed with 5% SE-30,and a helium carrier gas flow rate of 30 ml/min. Preparative separation was carried out on plates with unattached Chemapol L40/100 silica gel using 3:1:1 hexane—benzene—ether as the eluent. The PMR spectra were taken on Tesla BS-497 and Bruker WP-250 spectrometers.

A sample of dimethyl diazomalonate was obtained according to Wulfman et al. [10]. A sample of butyl(trimethylsilyl)acetylene (I) was obtained in 37% yield, and a sample of propyl(trimethylsilyl)acetylene (II) was obtained in 68% yield according to Petrov et al. [11], while a sample of bis(trimethylsilyl)acetylene (III) was obtained in 76% according to Petrov and Shchukovskaya [12].

Dimethyl Esters of 1-Butyl-2-(trimethylsilyl)cyclopropene-3,3-dicarboxylic Acid (V). A solution of 7.68 g (0.05 mole) DMM in 7.7 g (0.05 mole) (I) was added over 10 h to a mixture of 37.4 g (0.24 mole) butyl(trimethylsilyl)acetylene (I) and 0.016 g (0.1 mmole) anhydrous $CuSO_4$ heated to 140-145°C. The mixture was heated until no further nitrogen was liberated, and the (I) was distilled off at 25 mm. Distillation of the residue gave 4.1 g (29% relative to DMM) of a fraction with bp 96-103°C (1 mm). Thin-layer chromatography gave (V) in 99.5% purity with bp 103°C (1 mm), d_4^{20} 0.9887, n_D^{20} 1.4553. Found: C 59.20; H 8.55; Si 9.96%. Calculated for $C_{14}H_{24}O_4Si$: C 59.15; H 8.45; Si 9.95%. IR spectrum (ν, cm^{-1}): 1730 ($C=O$) and 1845 ($C=C$). PMR spectrum ($CHCl_3$, δ, ppm): 0.16 s ($9H^a$), 0.86 t ($3H^b$), 1.14-1.69 m ($2H^c + 2H^d$), 2.5 t ($2H^e$), 3.66 s ($6H^f$). The residue yielded 2.12 g (18% relative to DMM) of a mixture of (VI)-(X), mp 120-163°C (1 mm). Mol. wt. 284 (mass spectrometry). Found: C 59.08; H 8.73; Si 9.88%. Calculated for $C_{14}H_{24}O_4Si$: C 59.15; H 8.45; Si 9.85%. IR spectrum (ν, cm^{-1}): 1730-1760 ($C=O$) and 2189 ($C\equiv C$).

Dimethyl Ester of Propyl-2-(trimethylsilyl)cyclopropene-3,3-dicarboxylic Acid (XII). Analogously to (V), compound (II) and DMM in the presence of $CuSO_4$ gave (XII) in 22.5% yield with 99.5% purity, bp 91-92°C (1 mm), d_4^{20} 1.0123, n_D^{20} 1.4533. IR spectrum (ν, cm^{-1}): 1725 ($C=O$) and 1840 ($C=C$). PMR spectrum ($CHCl_3$, δ, ppm): 0.14 s ($9H^a$), 0.88 t ($3H^b$, $J_{H^bH^c}$ = 7.8 Hz), 1.56 t. q ($2H^c$), 2.44 t ($2H^d$, $J_{H^cH^d}$ = 7.8 Hz), 3.6 s ($6H^e$). In addition, we also obtained 7% of a fraction with bp 115-121°C (2 mm), from which a mixture of (XIII) was isolated. IR spectrum (ν, cm^{-1}): 1730-1770 ($C=O$) and 2185 ($C\equiv C$).

Dimethyl Ester of 1,2-Dipropylcyclopropene-3,3-dicarboxylic Acid (XVII). Compound (IV) and DMM in the presence of $CuSO_4$ gave (XVII) in 27% yield, bp 82-87°C (1 mm), d_4^{20} 1.0184, n_D^{20} 1.4538. IR spectrum (ν, cm^{-1}): 1730 ($C=O$). PMR spectrum (CCl_4, δ, ppm): 0.84 t ($6H^a$), 1.56 t. q ($4H^b$, $J_{H^fH^b}$ = 7 Hz), 2.38 t ($4H^c$, $J_{H^bH^c}$ = 7 Hz), 3.75 s ($6H^d$).

Dimethyl Ester of 1,2-Bis(trimethylsilyl)cyclopropene-3,3-dicarboxylic Acid (XV). Compound (III) and DMM in the presence of DMM gave (XV) in 25% yield, bp 80-82°C (1 mm), n_D^{20} 1.4555. IR spectrum (ν, cm^{-1}): 1730 ($C=O$). PMR spectrum ($CHCl_3$, δ, ppm): 0.2 s ($18H^a$), 3.65 ($6H^b$). Distillation gave (XVI) in 5.4% yield, bp 65-80°C (1 mm). IR spectrum (ν, cm^{-1}): 1740 ($C=O$) and 2140 ($C\equiv C$). PMR spectrum ($CHCl_3$, δ, ppm): 3.71 s ($6H^a$), 3.47 t ($1H^b$, J=7 Hz), 1.2 d ($2H^c$, J = 7 Hz), 0.12 s ($6H^d$), 0.1 s ($9H^e$).

CONCLUSIONS

1. The thermocatalytic reaction of dimethyl diazomalonate with trimethylsilylalkynes taken in excess in the presence of $CuSO_4$ gave approximately equal amounts of cyclopropene derivatives and the products of the formal insertion of bis(methoxycarbonyl)carbene into all the C—H bonds of the alkyl substituents of the starting acetylene.

2. The insertion of bis(methoxycarbonyl)carbene into the C–H bond of a trimethylsilyl group was observed for the first time.

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