from aqueous ethanol, m.p. 79–80°, yield (over-all) 25%. Found: C, 77.53; H, 8.85. The compound showed typical carboxylic acid infrared bands at 3300, 2560, 1703 cm.$^{-1}$. The ultraviolet spectrum showed the expected[4,5] shifts and distortion; λ_{max} 230, ϵ 7,480; λ_{should} 270 mμ, ϵ 268; λ_{max} 276 mμ, ϵ 343; λ_{max} 283, ϵ 295. The distortion of the ultraviolet absorption curve from that of a *p*-dialkylbenzene is exactly as would be predicted for the [8]paracyclophane by comparison with the spectra of the higher homologs.[4] The PMR spectrum showed a band at 9.35 τ consistent with the assigned structure.[9]

A detailed Pariser-Parr treatment of the ultraviolet spectrum will be reported in the full publication.

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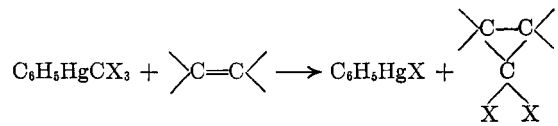
A New Preparation of Dihalocarbenes by an Organometallic Route

Sir:

The usual preparatively useful procedures for the generation of dihalocarbenes involve treatment of chloroform,[1] ethyl trichloroacetate,[2] or hexachloroacetone[3] with an alkali metal alkoxide in an inert solvent, or of bromotrichloromethane with organolithium reagents.[4] An alternative method which avoids basic conditions uses the slow thermal decomposition of sodium trichloroacetate in refluxing 1,2-dimethoxyethane to generate dichlorocarbene.[5] The yield of the carbene, as indicated by the isolated yield of its olefin adduct, did not exceed 65% in the latter procedure.

We report here a new, simply effected synthesis of dichloro- and dibromocarbene which may be carried out under very mild conditions, and which gives excellent yields of the dihalocarbenes. Russian workers[6,7] have reported recently two different syntheses of compounds of the types $RHgCCl_3$ and $RHgCBr_3$. Furthermore, it was reported that heating phenyl(trichloromethyl)mercury either alone at 150°[6] or in ethanol solution[7] produces phenylmercuric chloride in high yield. The recent work of Haszeldine and co-workers,[8] in which the pyrolysis of trichloromethyltrichlorosilane at 250° was shown to proceed *via* a dichlorocarbene intermediate, suggested to us that the decomposition of the trichloromethyl- and tribromomethyl-substituted mercurials also might involve formation of the respective dihalocarbenes. We have found this to be the case. When a benzene solution of either phenyl(trihalomethyl)mercury compound (easily prepared by the method described by Reutov and Lovtsova[7]) was refluxed with an olefin (the latter preferably in excess), phenylmercuric halide slowly precipitated from solution, and the dihalocarbene formed reacted with the olefin.



The yields of the dihalocyclopropane derivative in general were excellent, and the preparation of 7,7-dibromobicyclo[4.1.0]heptane is described to illustrate the very simple procedure used.

A suspension of 0.105 mole of phenyl(tribromomethyl)mercury in 50 ml. of benzene and 0.315 mole of cyclohexene was heated with stirring under reflux for 2 hr. During this time the starting mercurial dissolved and phenylmercuric bromide precipitated. The latter, m.p. 285–286°, was isolated in quantitative yield. Fractional distillation of the filtrate resulted in 22.5 g. (88%) of 7,7-dibromobicyclo[4.1.0]heptane, b.p. 60–63° at 0.5–0.7 mm. The product was identified by comparison of its infrared spectrum with that of an authentic sample,[1] and by its refractive index (n^{25}D 1.5582; lit.,[1] n^{22}D 1.5578). Phenyl(trichloromethyl)mercury is much more stable, and reaction times of *ca.* 36–48 hr. were required to realize comparable yields of dichlorocyclopropane compounds under the same conditions.

The procedure described above has the advantage that basic conditions are avoided and that very high yields are attainable, in contrast to the sodium trichloroacetate route. The phenylmercuric halide formed in this reaction is of good purity and can easily be reconverted[7] to new starting material in good yield. We report our initial findings at this

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time in consideration of the continued activity in the dihalocarbene area, particularly the interesting studies concerning the use of dihalocyclopropane compounds in the synthesis of allenes[9] and highly strained tricyclic systems.[10] Our studies, directed in particular at the preparation of other carbenes by the polyhalomethylmercurial route, are continuing, and details will be reported at a later date.

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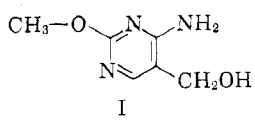
Synthesis of Bacimethrin[1]

Sir:

Tanaka and co-workers[2] have recently isolated a new antibiotic, bacimethrin, produced by *Bacillus megatherium* from a soil sample collected in Japan. This antibiotic is active against various yeasts and some bacteria.[2] Its biological activity is markedly decreased by the presence of vitamins B_1 and B_6.

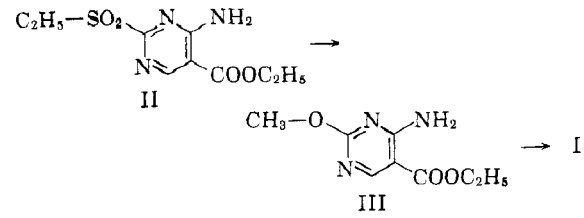
Based on degradation studies, the structure of this antibiotic has been proposed as 2-methoxy-4-amino-5-hydroxymethylpyrimidine (I).[2] This type



I

of 2-methoxypyrimidine has not been reported previously in the literature.

We now wish to report that, in connection with our current investigation on 2-methoxypyrimidines for antimetabolite and antivitamin studies, we have synthesized I *via* the following sequence of reactions: 2-Ethylsulfonyl-4-amino-5-carbethoxypyrimidine (II), prepared by the method of Sprague and Johnson,[3] was treated with sodium methoxide in absolute methanol at 5° to give 2-methoxy-4-amino-5-carbethoxypyrimidine (III), m.p. 151–153° (from benzene) in 76% yield (Calcd. for $C_8H_{11}N_3O_3$: C, 48.7; H, 5.6; N, 21.3. Found: C, 48.8; H, 5.8; N, 21.6). Compound III was then reduced by lithium aluminum hydride in anhydrous ether to give, after recrystallization from methanol, a 60% yield of 2-methoxy-4-amino-5-hydroxymethylpyrimidine (I) which melted between 173–174° to a yellow liquid (Calcd. for $C_6H_9N_3O_2$: C, 46.4; H, 5.9; N, 27.1. Found: C, 46.5; H, 6.2; N, 27.1).



II III

The synthetic product I exhibited the following ultraviolet absorption: $\lambda_{max}^{H_2O}$ 227 mμ (ε 7600), 271 mμ (ε 7300); $\lambda_{max}^{0.1\ N\ HCl}$ 229 mμ (ε 8400), 261 mμ (ε 9500); $\lambda_{max}^{0.1\ N\ NaOH}$ 231 mμ (ε 6200), 271 mμ (ε 7600). Its infrared absorption spectrum in Nujol possesses identical bands with that of the antibiotic reported in the literature.[2] Furthermore, the R_f values (at 25°, descending) of bacimethrin[4] and our synthetic compound in 3% ammonium chloride are 0.86 and 0.86, respectively; and in butanol (saturated with ammonia) are 0.62 and 0.61, respectively. Thus, we confirmed the previous assigned structure I for that antibiotic.

The striking structural similarity of bacimethrin to the known biologically active HMC (5-hydroxymethylcytosine),[5] toxopyrimidine (2-methyl-4-amino-5-hydroxymethylpyrimidine),[6,7] methioprim (2-methylthio-4-amino-5-hydroxymethylpyrimidine)[6d,7] as well as Bayer DG-428 (2-[*o*-chlorobenzylthio]-4-dimethylamino-5-methylpyrimidine)[8] suggests that compound I merits further study in various biological systems.

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