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A NEW SOURCE OF DIBROMOKETENE

Takehiro Okada and Rokuro Okawara
Department of Applied Chemistry, Osaka University
Yamadakami, Suita, Osaka, Japan

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Haloketenes have been prepared by treating acid halides with zinc-copper couple or trialkylamine[1)]. However, the yield of dibromoketene trapped in cyclopentadiene (58 %)[1a)] was lower than that of dichloroketene (75 %)[2)]. In this paper we show a result obtained in the course of our study on the reaction between organometal haloacetates and triphenylphosphine[3)] that the reaction of trimethylsilyl tribromoacetate with triphenylphosphine is remarkably effective for the source of dibromoketene.

The reaction of trimethylsilyl tribromoacetate* with triphenylphosphine in molar ratio 1:1 was carried out in the presence of excess cyclopentadiene at 0°C in toluene. The solvent, trimethylsilyl bromide and unreacted cyclopentadiene was removed in vacuo, followed by distillation under reduced pressure giving the cycloaddition product (77-78°C/0.5 mmHg) in 89 % yield and

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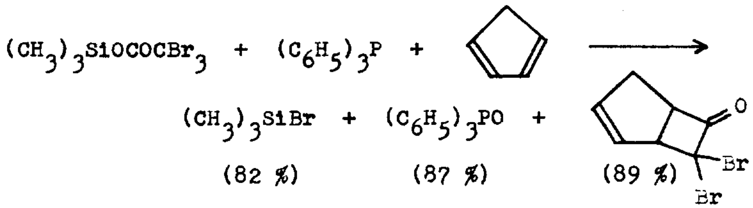
* Trimethylsilyl tribromoacetate was prepared in a yield of 75 %, from hexamethyldisilazane and tribromoacetic acid in a manner similar to the method reported[4)]. This compound is very easily hydrolysed and sublime at ca. 45°C. Found Br 64.87, Calcd. Br 64.98 %; IR (Nujol mull), $\nu_{C=O}$ 1720 cm^{-1}(s); PMR in CCl_4, $\delta(Si\text{-}CH_3)$ 0.42 ppm (from TMS as an internal standard).

triphenylphosphine oxide. This adduct is identified as 7,7-dibromobicyclo-[3.2.0]hept-2-ene-6-one by elemental analysis (Found C 31.50, H 2.23; Calcd. C 31.61, H 2.27 %), mass spectrum (parent peak m/e 266; molecular weight 266) and IR and PMR spectra[1a].



This type of reaction was also carried out in the presence of diethyl-(trimethylsilyl)amine to have an insertion product similar to that reported[5]. The hygroscopic product (m.p. 46-48°C; b.p. 90°C/0.5 mmHg), dibromo-(trimethylsilyl)acetic acid diethylamide, $(CH_3)_3SiCBr_2CON(C_2H_5)_2$ was obtained in 77 % yield with $(CH_3)_3SiBr$ (95 %) and $(C_6H_5)_3PO$ (97 %). Analysis (Found C 30.85, H 5.48, N 4.07. Calcd. C 31.32, H 5.55, N 4.06 %), mass spectrum (parent peak 345; molecular weight 345), PMR; δ(a pair of quartets at ca. 3.36, a pair of triplets at ca. 1.10 and a singlet at 0.29 ppm, in the ratio of 4:6:9) and IR ($\nu_{C=O}$1624 cm^{-1}(s)).

These results obviously indicate that dibromoketene itself or its precursor exists as a reactive species in these reactions.

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