

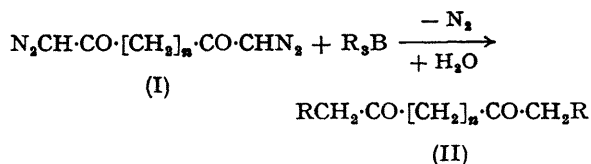
A New Diketone Synthesis *via* Alkylation of Bisdiazo-ketones with Trialkylboranes

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We have reported novel syntheses of ketones, nitriles, and esters by treatment of organoboranes with diazo-compounds.¹

Here we report the smooth alkylation of bisdiazo-ketones (I) with organoboranes to give the symmetrical diketones (II). The bisdiazoketones are prepared by treatment of diacyl chlorides with diazomethane.²



The method is illustrated (Table) for the synthesis of 1,4- and 1,5-diketones (II; $n = 2,3$).

Since 1,4- and 1,5-diketones undergo base-catalyzed

intramolecular cyclization to cyclopentenones and cyclohexenones, respectively, we have synthesized these cycloalkenones in one preparative step by employing alkaline conditions of hydrolysis. The crude mixture from reaction of bis-1,6-diazoheptane-2,5-dione (I; $n = 2$) and triethylborane, on treatment with hot aqueous potassium hydroxide afforded an 2-ethyl-3-n-propylcyclopent-2-enone (87%); similar treatment of the reaction mixture derived from (I; $n = 3$) with Et_3B gave 2-ethyl-3-n-propylcyclohex-2-enone (96%).

An attempt to prepare unsymmetrical diketones by this method was unsuccessful. Successive treatment of bis-1,7-diazoheptane-2,6-dione with triethylborane (quantitative nitrogen evolution) gave a mixture of the three possible diketones.

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*Reaction of bisdiazoketones with trialkylboranes**

R_3B^b (mol.) R	Bisdiazoketone (I) (mol.) n	Product ^c	Yield (%) ^d
Et (20)	2 (9.8)	Decane-4,7-dione	92
Bu ⁿ (20)	2 (9.7)	Tetradecane-6,9-dione	84
Et (22)	3 (10.5)	Hendecane-4,8-dione	87
Bu ⁿ (20)	3 (9.5)	Pentadecane-6,10-dione	83
n-hexyl (20)	3 (8.5)	Nonadecane-8,12-dione	52

* All reactions performed at 25° in tetrahydrofuran as solvent. Nitrogen yields were quantitative except in the case of trihexylborane (78%); ^b organoboranes were prepared by hydroboration of the corresponding alkene (H. C. Brown, "Hydroboration," W. A. Benjamin, New York, 1962), except for Et_3B which was purchased from Alfa Inorganics, Inc; ^c correct elemental analyses and compatible spectral data were obtained for all new compounds; ^d yields by g.l.p.c. analysis.

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¹ J. Hooz and S. Linke, *J. Amer. Chem. Soc.*, 1968, **90**, 5936, 6891.

² E. Fahr, *Annalen*, 1960, **638**, 1.