

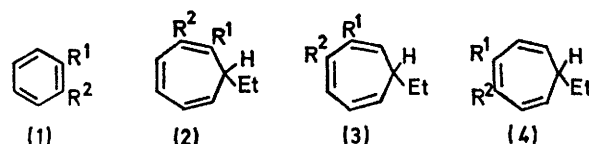
Ring-expansion of Alkylbenzenes by the Zinc-carbenoid Reaction with Diethylzinc and Iodoform

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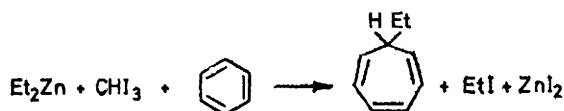
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Summary Alkyl-substituted 7-ethylcyclohepta-1,3,5-trienes were obtained by the ring-expansion of alkylbenzenes with the iodocarbenoid reagent formed from diethylzinc and iodoform.

TABLE. Formation of alkyl-substituted 7-ethylcyclohepta-1,3,5-trienes from alkylbenzenes, Et_2Zn , and CHI_3^a



THE iodocarbenoid reagent formed from Et_2Zn and CHI_3 transfers the iodomethylene group to cyclohexene to give 7-iodonorcarane.¹ We report here that 7-ethylcyclohepta-1,3,5-triene was obtained by the treatment of Et_2Zn and CHI_3 with benzene (Scheme 1).

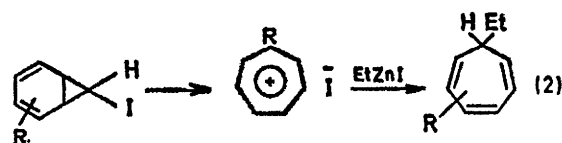


SCHEME 1

Though ring-expansion of aromatic compounds by carbene or the carbenoid reagent is well known,² the above procedure gives a novel route for the synthesis of alkyl-substituted 7-ethylcyclohepta-1,3,5-trienes from alkylbenzenes (Table). Distillation of the reaction mixture gave the cycloheptatrienes as mixtures of isomers, confirmed by elemental analysis, and n.m.r.³ and i.r. spectra. The isomer distribution of the cycloheptatrienes derived from toluene by this iodocarbenoid reagent is somewhat different from those obtained by the $\text{MeCHI}_2\text{-Et}_2\text{Zn}^4$ or the $\text{CH}_2\text{N}_2\text{-CuBr}^5$ system, but is consistent with that obtained by the chlorocarbenoid reagent formed from MeLi and

R ¹	(1) R ²	Yield (%) ^b	Isomer distribution (%) ^c		
			(2)	(3)	(4)
H	H	48			
Me	H	60	57	22	21
Et	H	45	44	27	29
Pr ^t	H	41	26	39	35
Bu ^t	H	35	3-4	37	60
Me	Me	52	66	10	24

^a Alkylbenzene (100 ml), Et_2Zn (0.1 mol), CHI_3 (0.1 mol); 50°C, 6 h. ^b Based on the CHI_3 . ^c Estimated from g.l.c.⁴ and n.m.r.³ data.



SCHEME 2²

CH_2Cl_2 .⁶ This suggests that the intermediate alkyl tropylium ions, formed from the adduct of the iodocarbenoid of zinc to alkylbenzenes, react to form the 7-ethylcycloheptatrienes (Scheme 2).

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