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Reactions of the Iodocarbenoid of Zinc. I. The Synthesis of Alkyl-substituted 7-Ethylcyclohepta-1,3,5-trienes *via* the Ring-expansion of Alkylbenzenes with Diethylzinc and Iodoform

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By treatment with diethylzinc and iodoform, benzene gave 7-ethylcyclohepta-1,3,5-triene in a yield of 58%, along with a quantitative formation of ethyl iodide. Alkylbenzenes, including methyl-, ethyl-, isopropyl-, *tert*-butyl-, and *o*-dimethylbenzene, gave the corresponding alkyl-substituted 7-ethylcyclohepta-1,3,5-trienes in yields of 60, 45, 41, 35, and 52% respectively. The tropylium iodide resulting from the adduct of the iodocarbenoid of zinc to benzene (7-iodonorcaradiene) is suggested as an intermediate in the formation of the 7-ethylcycloheptatriene.

Recently Furukawa and Nishimura reported that the halocarbenoid of zinc obtained from diethylzinc and haloforms transfer the halomethylene groups to cyclohexene to give 7-halonorcaranes.[1] When iodoform was used as the halomethylene source, 7-iodonorcarane was obtained in only a trace amount.

In the course of our investigation of the zinc-carbenoid reaction, we found that alkyl-substituted 7-ethylcyclohepta-1,3,5-trienes are obtained by the treatment of diethylzinc and iodoform in alkylbenzenes.[2] In this report, we will describe the details of the reaction, and will present evidence for the tropylium iodide intermediate in the formation of 7-ethylcyclohepta-1,3,5-triene from benzene.

TABLE 1. REACTIONS OF THE IODOCARBENOID OF ZINC FROM IODOFORM AND DIETHYLZINC WITH BENZENE[a]

Run	CHI_3 10^{-2} mol	7-Ethylcyclohepta-1,3,5-triene 10^{-2} mol	EtI 10^{-2} mol	Iodide ion 10^{-2} eq.
1	0.53	0.22	0.55	0.98
2	1.01	0.49	1.00	1.93
3	2.03	1.12	2.04	3.88
4	2.97	1.73	3.03	5.66
5	3.51	1.74	3.06	5.70
6[b]	3.03	1.54	3.28	5.72
7[c]	3.02	0.28	3.11	5.44

a) To a stirred solution of Et_2Zn (0.030 mol) in benzene (50 ml), CHI_3 was added portionwise during 1 hr period at 50°C under a nitrogen atmosphere, and the reaction was continued for another 5 hr.
b) Et_2Zn was added to a CHI_3 suspension in benzene.
c) Benzene; 10 ml, *n*-hexane; 40 ml.

Results and Discussion

Reactions of Diethylzinc and Iodoform with Benzene. Table 1 shows the results of the reactions of diethylzinc and iodoform with benzene. To a stirred diethylzinc solution in benzene, iodoform was added over a 1 hr period under a nitrogen atmosphere, after which the reaction was continued for another 5 hr. Besides 7-ethylcyclohepta-1,3,5-triene and ethyl iodide, propylene and cyclohepta-1,3,5-triene were obtained as side reaction products in yields of 28 and 3% respectively (No. 4). The amount of ethyl iodide depended on the limiting component (iodoform or diethylzinc), and the total iodides recovered were almost equal to the iodoform consumed. These facts suggest the following stoichiometry for the formation of 7-ethylcycloheptatriene and propylene (Eqs. (1) and (2) respec-

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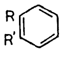
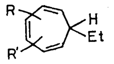
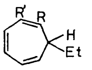
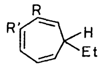
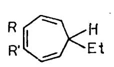
[1] J. Nishimura and J. Furukawa, *Chem. Commun.*, **1971**, 1375.
[2] S. Miyano and H. Hashimoto, *ibid.*, **1973**, 216.

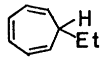
Table 2. Reactions of alkylbenzenes

			Isomer distribution (%)[c]		
R	R′	Yield (%)[b]			
H	H	48			
CH_3	H	60	57	22	21
CH_2CH_3	H	45	44	27	29
$CH(CH_3)_2$	H	41	26	39	35
$C(CH_3)_3$	H	35	3.4	37	60
CH_3	CH_3	52	66	10	24

a) Alkylbenzene; 100 ml, Et_2Zn; 0.10 mol, CHI_3; 0.10 mol, 50 °C, 6 hr.
b) Determined by glc, and based on tbe CHI_3.
c) Determined by glc and NMR spectra.

tively):

$C_6H_6 + CHI_3 + Et_2Zn \longrightarrow$

 $+ EtI + ZnI_2$ (1)

$CHI_3 + Et_2Zn \longrightarrow CH_3CH{=}CH_2 + EtI + ZnI_2$ (2)

Reactions of Alkylbenzenes. Table 2 shows that alkylbenzenes also gave the corresponding alkyl-substituted 7-ethylcyclohepta-1,3,5-trienes in fairly good yields on treatment with diethylzinc and iodoform. All the cycloheptatrienes were separated by distillation as mixtures of positional isomers and were confirmed by elemental analysis and by a study of their NMR and IR spectra. Though the ring-expansion of aromatic compounds by carbene or carbenoid reagents is well-known,[3] this iodocarbenoid reaction gives a convenient route for the synthesis of alkyl-substituted 7-ethylcycloheptatrienes from alkylbenzenes.

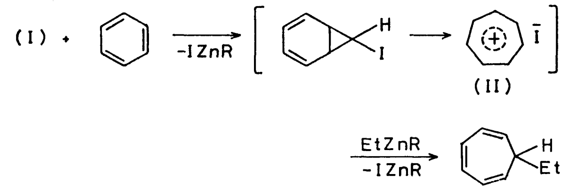
In a preliminary experiment, ethylzinc iodide[4] obtained from zinc-copper couple[5] and ethyl iodide also gave the 7-ethylcycloheptatriene when allowed to react with iodoform in benzene.

A competition study was carried out by allowing an equimolar mixture of benzene and isopropylbenzene to compete for a deficient amount of diethylzinc and iodoform. The latter gave 1.5 times more of the corresponding cycloheptatrienes than the former. This seems to show that the addition of the iodocarbenoid of zinc to the benzene nuclei is electrophilic in nature (*vide infra*).

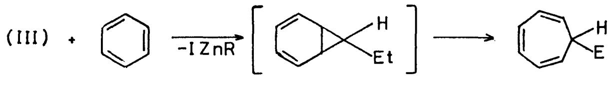
Anisole and chlorobenzene gave complex mixtures of unidentified products which contained cycloheptatriene derivatives, judging from the NMR spectra.

Addition of the Iodomethylene Group from the Iodocarbenoid of Zinc to the Benzene Ring, and the Tropylium Iodide Intermediate in the Formation of 7-Ethylcyclohepta-1,3,5-triene. The following two reaction paths are possible for the formation of 7-ethylcyclohepta-1,3,5-triene through the ring-expansion of benzene with diethylzinc and iodoform (Path (a) and Path (b))[6] (R=Et or I):

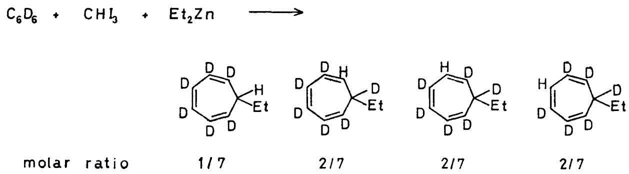
(a) $EtZnR + CHI_3 \longrightarrow EtI + \underset{(I)}{CHI_2ZnR}$



(b) $(I) + EtZnR \longrightarrow \underset{(III)}{EtCHIZnR} + IZnR$



Furukawa *et al.* reported the ring-expansion of aromatic compounds by means of the methylcarbenoid of zinc formed from diethylzinc and ethylidene iodide.[7] This might suggest the addition of propylidene from the ethylcarbenoid of zinc (III) to the benzene ring (Path (b)), but the following result shows that, in the present case, Path (a) is the reasonable one. After benzene-d_6 had been allowed to react with diethylzinc and iodoform, the 7-ethylcycloheptatriene-d_6 thus formed was analyzed by studying its NMR spectra. It was found that, in the 7-ethylcycloheptatriene-d_6, the hydrogen atom derived from iodoform was statistically distributed throughout the cycloheptatriene ring:



This fact can most reasonably be explained by the tropylium iodide intermediate (II) and the nucleophilic replacement of iodine by the ethyl group, thus forming 7-ethylcycloheptatriene.[8]

The isomer distribution of the cycloheptatrienes from toluene by this iodocarbenoid reaction is somewhat different from those obtained by the CH_3CHI_2–Et_2Zn[7a] and CH_2N_2–CuBr[10] systems, but it is consistent with that obtained by the chlorocarbenoid of lithium formed from methyllithium and methylene chloride.[11] For the latter reaction, tropylium chloride was detected as the intermediate in the formation of 7-methylcycloheptatriene from benzene.[12] There seems to be few reports dealing with the orientation of alkyltropylium

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[3] W. Kirmse, "Carbene Chemistry," 2nd ed., Academic Press, New York, London, (1971), p. 381.

[4] M. H. Abraham and P. H. Rolfe, *J. Organometal. Chem.*, **7**, 35 (1967).

[5] E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

[6] D. B. Miller, *Tetrahedron Lett.*, **1964**, 989.

[7] a) J. Nishimura, J. Furukawa, N. Kawabata, and T. Fujita, *Tetrahedron*, **26**, 2229 (1970). b) J. Nishimura, J. Furukawa, and N. Kawabata, This Bulletin, **43**, 2195 (1970).

[8] The reaction of tropylium ions with carbanions is a synthetic route for the 7-alkylcyclohepta-1,3,5-trienes.[9]

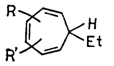
[9] For example, a) C. Jutz, *Chem. Ber.*, **97**, 2050 (1964). b) G. A. Gladkovskii, S. S. Skorokhodov, S. G. Slyvina, and A. S. Khachaturov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1963**, 1273.

[10] E. Müller, H. Kessler, H. Fricke, and W. Kiedaisch, *Ann. Chem.*, **675**, 63 (1964).

[11] O. M. Nefedov, N. N. Novitskaya, and A. D. Petrov, *Dokl. Akad. Nauk SSSR*, **158**, 411 (1964).

[12] G. L. Closs and L. E. Closs, *Tetrahedron Lett.*, **1960**, 38.

Table 3. Separated cycloheptatrienes

		Yield of separated cycloheptatrienes (%)[a]	Bp[b] (°C/mmHg)	Elemental analysis			
R	R′			C(%)	(Calcd)	H(%)	(Calcd)
H	H	27	73—73.5/43	89.79	(89.94)	10.29	(10.06)
CH_3	H	39	64/11	89.39	(89.49)	10.63	(10.51)
CH_2CH_3	H	36	63—64/6.5	89.29	(89.12)	10.96	(10.88)
$CH(CH_3)_2$	H	30	62.5—63/3	88.69	(88.82)	11.02	(11.18)
$C(CH_3)_3$	H	25	72—78/3.5	88.36	(88.56)	11.63	(11.44)
CH_3	CH_3	32	70.5—71/7	89.07	(89.12)	10.80	(10.88)

a) Based on the CHI_3.
b) For the mixture of the isomers.

ions for the nucleophilic reaction,[13] and the preferential formation of 2-methyl-7-ethylcycloheptatriene from toluene is not yet explained.[14]

Propylene seems to be formed by the facile 1,2-hydride shift of the ethylcarbenoid of zinc (III).[12] Similar olefin-forming reactions have been reported for the reaction of Grignard reagents and bromoform.[16]

Experimental

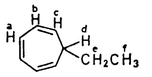
Materials. Commercial diethylzinc was distilled under reduced pressure. The iodoform was recrystallized from ethanol–acetone. The alkylbenzenes and other materials were of commercial origin and were purified as usual. Distillation or recrystallization was carried out under a nitrogen atmosphere. Materials were stored under nitrogen.

The glc analysis was carried out on a Shimadzu GC 3AF apparatus equipped with hydrogen flame detectors; four different stainless steel columns (3 m × 3 mm) were used, packed with Diasolid M coated with Silicone DC 550, Silicone DC 410, Apiezon Grease L, and PEG 2000 respectively.

Reaction of Benzene with Diethylzinc and Iodoform. The general procedure used for the reaction of diethylzinc, iodoform, and benzene was as follows. The reaction was carried out in a round-bottomed flask equipped with a magnetic stirrer, a thermometer, a reflux condenser topped with a nitrogen inlet, and a dropping funnel for a solid material[17] which had been charged with iodoform. The flask was flushed with prepurified nitrogen. In the flask we placed benzene and diethylzinc, and the stirred solution was heated to 40—45 °C. The iodoform was added, portion by portion, over a 1 hr period at 50 °C, and then the reaction was continued for another 5 hr. On the addition of the iodoform, an exothermic reaction was observed and the iodoform reacted smoothly. During the addition of the iodoform, white precipitates were formed in the reaction flask. At the end of the reaction, a small amount of water and then dilute nitric acid were added cautiously to the cooled mixture. The organic layer was washed successively with dilute nitric acid and water. The aqueous layer and combined aqueous washings were extracted with a small amount of benzene, and the content of the iodide ion was determined by Vorhard titration. The organic layer was washed with a dilute sodium carbonate solution and water, and then diluted with additional benzene to a 250 ml volume, from which a 10 ml portion was used for the quantitative determination of the ethyl iodide, cyclohepta-1,3,5-triene, and 7-ethylcyclohepta-1,3,5-triene formed. The remaining solution was dried over magnesium sulfate. After the removal of benzene and ethyl iodide by distillation, the residue was fractionated through a Vigreux column. Besides 7-ethylcyclohepta-1,3,5-triene, a high-boiling portion was obtained which was positive to the Beilstein test and which seemed to consist of the iodocyclopropanes derived from cyclo-

Table 4. NMR data for the 7-ethylcyclohepta-1,3,5-triene-d_6

Proton[a] Chemical shift (ppm)[b]	H_a 6.5 (b)[c]	H_b 6.05 (b)	H_c 5.07 (b)	H_d	H_e	H_f 1.0 (t,m)[e]
				1.69 (q,m)[d]		
Proton distribution						
Obsd	0.25H	0.27H	0.28H	2.12H		3H
Calcd for statistical distribution	0.286H[f]	0.286H	0.286H	0.143H[g]	2H	3H

a) 

b) Downfield from internal TMS.
c) Broad.
d) Complex quintette.
e) Complex triplet.
f) 2/7 H.
g) 1/7 H.

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13) D. Lloyd, "Carbocyclic Non-benzenoid Aromatic Compounds," Elsevier Publ. Co., Amsterdam-London-New York, (1966), p. 98.

14) Prof. M. Hida suggested that from the HMO calculations the frontier electron density of a methyltropylium ion for a nucleophilic reaction (f_r^N) is in the order of $f_1 > f_3 > f_2$.[15]

15) M. Hida, Private communication.

16) J. Villieras, *Bull. Soc. Chim. Fr.*, **1967**, 1511.

17) T. Suehiro, K. Tokumaru, and M. Yoshida, "Gendai no Yukikagaku Zikken," Gihodo, Tokyo, (1971), p. 139.

heptatrienes by the addition of the iodocarbenoid of zinc to the double bonds. Cyclohepta-1,3,5-triene was confirmed only by the retention time on glc because of its scarcity.

The isomer distributions of 7-ethylcycloheptatrienes from alkylbenzenes were determined by studying the glc[7a)] and NMR[18)] spectra (Table 2). The results of the separation of cycloheptatrienes are shown in Table 3.

Competition between Benzene and Isopropylbenzene. Benzene (0.30 mol) and isopropylbenzene (0.30 mol) competed for the iodocarbenoid reagent generated *in situ* from diethylzinc (0.050 mol) and iodoform (0.050 mol). Both gave the corresponding 7-ethylcycloheptatrienes, in yields of 0.00853 mol and 0.0126 mol respectively.

7-Ethylcyclohepta-1,3,5-triene-d_6. Under a nitrogen atmosphere, an 11 ml portion of commercial benzene-d_6 (Merck Co., deuterium content, 99%) was distilled over sodium into a reaction flask directly. The reaction was carried out as stated above using 1 ml (0.010 mol) of diethylzinc and 4.0 g (0.010 mol) of iodoform. A portion boiling at 70—72°C/45 mmHg, contaminated with a trace amount of ethyl iodide, was distilled into an NMR sample tube. The NMR analysis of the sample (*ca.* 5% solution in CCl_4, TMS) showed the statistical distribution of the hydrogen atom derived from iodoform throughout the cycloheptatriene ring within the limits of experimental error (Table 4).

The authors wish to acknowledge with pleasure their helpful discussions with Professor Mitsuhiko Hida.

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18) K. W. Egger and W. R. Moser, *J. Phys. Chem.*, **71**, 3699 (1967).