distillation, the residue was dissolved in 150 ml. of benzene and hydrogenated over 3 g. of 5% palladium on charcoal catalyst in a bottle shaken at 50 pounds pressure and room temperature. Hydrogenation was halted after 0.5 hr. and 0.09 mole absorption of hydrogen. After removal of catalyst by filtration, the solution was Claisen-distilled to give 79 g. of crude product, b.p. 65–90° (0.5 mm.). Redistillation through a 10-tray Oldershaw column afforded 34 g. (24% yield) of β-phenylglycidaldehyde, b.p. 70–72° (0.3 mm.); n_D^{20} 1.5448 [lit.[3] values: b.p. 66–68° (0.2 mm.); n_D^{20} 1.5447].

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(5) A sample was added to a mixture of 5 ml. of acetic acid and 50 ml. of 2-propanol; 2 ml. of saturated aqueous sodium iodide was added and the stoppered solution held in the dark for 30 min. at room temperature. The liberated iodine was titrated with 0.1*N* sodium thiosulfate to the disappearance of yellow color.

2,6-Diethyl Homologs of Bromobenzene, Benzonitrile, Benzamide, and Benzoic Acid

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In connection with another project, we had occasion to prepare the heretofore unknown 2,6-diethylbenzoic acid. The conversion of the readily available[1] 2,6-diethylaniline to 2,6-diethylbenzoic acid was carried out by two alternate sequences of reactions. The 2,6-diethyl homologs of bromobenzene, benzonitrile, and benzamide are also unreported in the literature. These intermediates were isolated and their physical properties determined. The hydrolysis of 2,6-diethylbenzonitrile to 2,6-diethylbenzamide rather than 2,6-diethylbenzoic acid, even under the vigorous conditions employed, indicates a considerable steric factor.[2]

EXPERIMENTAL

2,6-Diethylbenzonitrile. 2,6-Diethylaniline was converted into 2,6-diethylbenzonitrile, b.p. 85–86° (1 mm.), n_D^{20} 1.5210; d_4^{27} 0.9614 in a 21% yield *via* the diazonium salt.[3] 2,6-Diethylbenzonitrile was also prepared from 2,6-diethylbromobenzene and cuprous cyanide[4] in an 86% yield.

Anal. Calcd. for $C_{11}H_{13}N$: C, 82.97; H, 8.23. Found: C, 83.02; H, 8.2.

2,6-Diethylbromobenzene. 2,6-Diethylaniline was converted into 2,6-diethylbromobenzene, b.p. 234° (742 mm.); n_D^{20}, 1.5456; d_4^{27}, 1.264 in a 24% yield according to the general direction for the Gatterman reaction.[5]

Anal. Calcd. for $C_{10}H_{13}Br$: C, 56.36; H, 6.15. Found: C, 56.31; H, 6.2.

2,6-Diethylbenzamide. Basic hydrolysis[4] of 2,6-diethylbenzonitrile gave a 91% yield of 2,6-diethylbenzamide, m.p. 136–136.5°, after recrystallization from hexane or water. Hydrolysis of 2,6-diethylbenzonitrile with 90% sulfuric acid gave a 55% yield of 2,6-diethylbenzamide. There was no evidence for the formation of 2,6-diethylbenzoic acid in either the acidic or basic hydrolysis even after an extended reaction time.

Anal. Calcd. for $C_{11}H_{15}NO$: N, 7.90. Found: N, 7.82.

2,6-Diethylbenzoic acid. Eighteen grams (0.1 mole) of 2,6-diethylbenzamide was dissolved in 180 g. of 85% phosphoric acid and heated to 130°. Within 15 min. the clear reaction mixture became opaque and after 1-hr. two layers had formed. The organic layer solidified on cooling and after recrystallization from hexane 2,6-diethylbenzoic acid, m.p. 92–93°, was obtained in a 91% yield.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.36; H, 8.1.

2,6-Diethylbenzoic acid was also obtained in a 72% yield from the carbonation of 2,6-diethylphenyllithium, prepared from 2,6-diethylbromobenzene and lithium wire in ethyl ether. The physical and spectroscopic properties of 2,6-diethylbenzoic acid prepared by the two alternate methods were identical.

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The Stereochemistry of the Free Radical Addition of Hydrogen Bromide to 1-Methylcycloheptene[1]

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Since the work of Goering[2] and his group on the stereochemistry of the radical addition of hydrogen bromide to 1-bromocyclohexene and 1-methylcyclohexene, in which stereospecific *trans* addition was observed, the use of cyclic olefins in the study of free radical reactions has become increasingly more important. The effect of a number of factors on radical additions to cyclic olefins has been studied. Of considerable interest has been the influence of ring size on the stereospecificity of the reaction. King Howe[3] reported that the free radical addition of hydrogen bromide to 1-methylcyclopentene afforded at least 94.3% of the *trans* addition product, *cis*-1-methyl-2-bromocyclopentane. Abell and Chiao[4] investigated the radical addition of hydrogen bromide to 1-bromocyclobutane, 1-bromocyclo-

(1) G. G. Ecke, J. P. Napolitano, A. H. Filbey, and A. J. Kolka, *J. Org. Chem.*, 22, 639 (1957).

(2) M. S. Newman, *Steric Effects in Organic Chemistry*, John Wiley and Sons, Inc., New York, 1956, p. 232.

(3) H. T. Clark and R. R. Read, *Org. Syntheses*, Coll. Vol. I, 514 (1941).

(4) H. R. Snyder, R. R. Adams, and A. V. McIntosh, *J. Am. Chem. Soc.*, 63, 3280 (1941).

(5) L. A. Biglow, *Org. Syntheses*, Coll. Vol. I, 135 (1941).

(1) This work was performed under Contract No. DA-19-020-ORD-3171, OOR Project 1037, of the Office of Ordnance Research, U. S. Army. Support for this work is gratefully acknowledged.

(2) (a) H. L. Goering, P. I. Abell, and B. F. Aycock, *J. Am. Chem. Soc.*, 74, 3588 (1952). (b) H. L. Goering and L. L. Sims, *J. Am. Chem. Soc.*, 77, 3465 (1955).

(3) King Howe, Ph.D. Thesis, University of Wisconsin, 1957.

(4) P. I. Abell and C. Chiao, *J. Am. Chem. Soc.*, 82, 3610 (1960).

pentene, and 1-bromocycloheptene. The ratios of *cis* to *trans* isomers of the 1,2-dibromocycloalkanes obtained were, respectively, 79:21, 94:6, and 91:9. These results were explained in terms of a balance between preference for a *trans* addition process and steric inhibition to the formation of the *cis* isomers. The next step in the study seemed to be an extension of the ring-methyl series to include the seven-membered ring.

It is the purpose of this note to present the preliminary report of our work on the radical addition of hydrogen bromide to 1-methylcycloheptene. It was thought that the increased flexibility of the seven-membered ring might have some effect on the reaction, especially in the chain transfer step, where the cycloheptane ring should be capable of distorting slightly, enabling closer approach of the hydrogen bromide molecule.

Three products may result from the addition of hydrogen bromide to 1-methylcycloheptene, *cis*- and *trans*-1-methyl-2-bromocycloheptanes by the free radical process and 1-methyl-1-bromocycloheptane by the ionic process. The method of analysis employed in this work consisted of dehydrobromination of the free radical product followed by infrared analysis of the resultant olefins. The presence of ionic addition product, however, would interfere with this procedure, hence removal of this material was necessary. Preferential solvolysis of the tertiary bromide with aqueous acetone was found to give quite satisfactory results. According to Cristol[5] dehydrohalogenation proceeds preferentially by a *trans* elimination process. Therefore, *trans* addition of hydrogen bromide to 1-methylcycloheptene would give *cis*-1-methyl-2-bromocycloheptane, which would give the original olefin upon dehydrohalogenation. If *trans*-1-methyl-2-bromocycloheptane were formed in the addition reaction, 3-methylcycloheptene would be expected to be formed in the dehydrobromination. A mixture of these olefins would, of course, indicate the presence of both isomers of 1-methyl-2-bromocycloheptane and the absence of a stereospecific addition process.

Examination of the infrared spectra and the physical constants of the olefin from the dehydrobromination of the radical addition product and an authentic sample of 1-methylcycloheptene showed them to be virtually identical. The absence of absorption bands of 3-methylcycloheptene in the infrared spectrum and the fact that 3-methylcycloheptene does not isomerize to 1-methylcycloheptene under the conditions of the dehydrobromination reaction indicate that the free radical addition proceeds probably better than 95% by the *trans* mechanism. It would appear from these results that the increased flexibility of the seven-membered ring does not affect the addition process to any substantial degree.

(5) S. J. Cristol, *J. Am. Chem. Soc.*, **69**, 338 (1947).

EXPERIMENTAL

1-Methylcycloheptene. This compound was synthesized according to the method of Arnold, Smith, and Dodson[6] and Bartlett and Rosenwald[7] in 61.2% yield. The physical constants of this olefin were: b.p. 135.5–136.0°, n_D^{24} 1.4562 (lit.[8] b.p. 136°, n_D^{25} 1.4563).

3-Methylcycloheptene. This olefin was prepared according to the method of Arnold, Smith, and Dodson[6] by the Ziegler bromination of cycloheptene (47.2%) to give 3-bromocycloheptene, followed by coupling of this product with methyl magnesium iodide. Purification of the 3-methylcycloheptene gave a product with the following physical constants: b.p. 130–132°, n_D^{25} 1.4562.

Free radical additions. The addition reactions were run in a fused silica flask fitted with an addition funnel, a gas inlet adapter fitted with a fritted glass bubbler tube, and a reflux condenser protected from the atmosphere by a drying tube filled with anhydrous calcium sulfate. Energy for the homolysis of the hydrogen bromide was provided by a Hanovia type 30600, medium pressure, mercury vapor lamp. The reaction flask was partially immersed in a water bath which was held at about 70°. 1-Methylcycloheptene in *n*-heptane was added through the addition funnel which contained a glass wool pad upon which was placed a layer of sodium hydride. Hydrogen bromide, dried by passing over anhydrous calcium sulfate, was bubbled through the reaction mixture for 2–3 hr. The reaction product was isolated by removal of the solvent under reduced pressure followed by distillation of the residual material in one fraction. Analysis for tertiary halide (ionic addition product) was performed at this stage. The results of a number of runs are given in Table I.

TABLE I

FREE RADICAL ADDITION OF HYDROGEN BROMIDE TO 1-METHYLCYCLOHEPTENE

Run	Olefin Used, G.	Product, G.	Yield, %	B.P./Mm.	*tert*-Halide Analysis
4	8.7	11.2	74	91–95°/17	17.1
6	8.4	11.0	75	85–89°/16	19.3
7	10.0	14.6	84	95–97°/20	15.4
8	10.0	13.7	79	97–99°/25	22.1

Tertiary halide analysis. An accurately weighed bromide sample of about 0.2 g. was mixed with 5 ml. of a 4:1 acetone-water mixture and allowed to stand at room temperature for 0.5 hr. The mixture was diluted with a large excess of cold water and titrated against standard sodium hydroxide using a 1% solution of phenolphthalein in alcohol as indicator. The end point was taken when the color held for about 1 min.

Isolation of the free radical addition product. The free radical bromide was isolated by selective hydrolysis of the tertiary halide with a 4:1 acetone-water mixture. The mixture was allowed to stand at room temperature for 1 hr. After dilution with water, the organic material was extracted with ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate. Purification by distillation gave a product which had an analysis corresponding to less than 1% tertiary halide. The secondary halide (from run number 6) had the following physical properties: b.p. 106°/32 mm., n_D^{25} 1.5003.

(6) R. T. Arnold, G. G. Smith, and R. M. Dodson, *J. Org. Chem.*, **15**, 1256 (1950).

(7) P. D. Bartlett and R. H. Rosenwald, *J. Am. Chem. Soc.*, **56**, 1990 (1934).

(8) R. B. Turner and R. H. Garner, *J. Am. Chem. Soc.*, **80**, 1424 (1958).

Dehydrobromination of the free radical bromide. Dehydrobromination of the free radical bromide, purified as described in the preceeding paragraph, was done by refluxing 6 hr. with anhydrous pyridine. At the end of the heating period the mixture was poured into ice-cold water which had been acidified with hydrochloric acid. The ether extract was washed with water and dried over anhydrous magnesium sulfate. Distillation at atmospheric pressure gave a product with b.p. 133–135°, $n_D^{25.5}$ 1.4560 (lit.[3] for 1-methylcycloheptene: b.p. 136°, n_D^{25} 1.4563).

Isomerization experiment. 3-Methylcycloheptene, prepared as indicated above, was refluxed in a pyridine–pyridine hydrobromide mixture to simulate the dehydrobromination reaction conditions. The reaction mixture was poured into cold, dilute hydrochloric acid, the olefin extracted with several portions of ether, and the ether extracts were combined and dried over anhydrous magnesium sulfate. After the ether was removed under reduced pressure the infrared spectrum of the residual oil was obtained, and this spectrum was found to be identical to the spectrum of an authentic sample of 3-methylcycloheptene.

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Decolorization of Triphenylmethyl Carbonium Ion by Ethyl Ether

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In 1921 Hantzsch noted that the addition of ethyl ether to various solutions containing the triphenylmethyl carbonium ion caused a diminution of the characteristic yellow color of the ion.[1] This he attributed to a reversal of the ion forming reaction with the regeneration of the colorless precursor to the ion. Since solid triphenylmethyl perchlorate is itself highly colored this explanation can hardly hold for the decolorization of solutions of triphenylmethyl perchlorate.

Leffler, in speculating on these observations, proposed the formation of a colorless oxonium salt with the ether as a more likely possibility.[2] If so, then the formation of the complex should follow a regular diminution in color as a function of ether concentration, and one should be able to calculate an equilibrium constant for the complex formation. Such a study has been carried out for triphenylmethyl perchlorate in acetic anhydride and for triphenylmethyl chloride in nitromethane. The results are reported below.

Solutions of triphenylmethyl perchlorate in acetic anhydride were prepared *in situ* by the addition of a stoichiometric excess of perchloric acid to a solution of triphenylcarbinol. The characteristic spectrum of the triphenylmethyl carbonium ion in this solvent is given in Fig. 1A. The solution

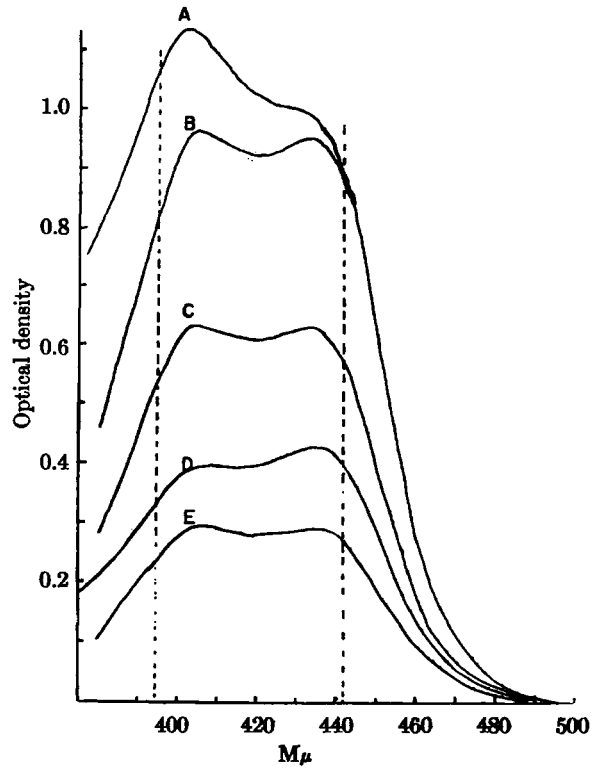

Fig. 1. The spectrum of the triphenylmethyl carbonium ion under various conditions: A, Ph_3CClO_4 ($2.75 \times 10^{-5}M$) in acetic anhydride; B, Ph_3CCl ($0.0804M$) in nitromethane; C, Ph_3CCl ($0.0777M$), Et_2O ($0.192M$) in nitromethane; D, Ph_3CClO_4 ($2.75 \times 10^{-5}M$) and Et_2O ($1.65M$) in acetic anhydride; and E, Ph_3CCl ($0.0791M$) and Et_2O ($0.736M$) in nitromethane

was stable for thirty to sixty minutes after which the bands due to the carbonium ion slowly decreased in intensity. After twenty-four hours the solution was still deep orange, but the carbonium ion band had entirely disappeared. The addition of ethyl ether lessened the intensity of the carbonium ion bands, Fig. 1C. The data for a series of ether concentrations are given in Table I as are the values

TABLE I

EFFECT OF ETHYL ETHER ON A $2.75 \times 10^{-5}M$ SOLUTION OF TRIPHENYLMETHYL PERCHLORATE IN ACETIC ANHYDRIDE

$(C_2H_5)_2O$	$(Ph_3C^+) \times 10^5$	$[Ph_3C{-}O(C_2H_5)^+_2] \times 10^7$	K
0.0946	2.51	24	0.99
0.1519	2.42	33	0.90
0.3952	2.10	65	0.78
0.4600	1.85	90	0.94
0.8340	1.59	116	0.88
1.650	1.06	169	0.97
2.240	0.84	191	1.02
			K_{av} = 0.93

of the equilibrium constant calculated for the individual points assuming a one to one complex. The assumption of a two to one complex led to a great variation in the value of K. A plot of carbonium ion concentration *versus* the concentration

(1) A. Hantzsch, *Ber.*, 54, 2573 (1921).

(2) J. E. Leffler, *The Reactive Intermediates of Organic Chemistry*, p. 97, Interscience Publishers, New York, 1956.