H, 12.76, 12.54; N, 13.02, 13.06; neut. equiv., 105.2.

An isomer melting at 31–33° was obtained by the German workers.[2,3] Their sample of the *cis–trans* isomer apparently was impure.

C. *cis–cis* II.—Whereas the first crop of crystalline material obtained on acetylation of Fraction F yielded diacetyl *cis–trans* II, the third isomer was concentrated in the succeeding crops in spite of its lower solubility because of the relatively small amount of this isomer produced under the conditions of hydrogenation. Thus, on working up Fraction H and the mother liquors from Fractions H and I, according to the scheme outlined in Table IV, there were obtained two relatively pure samples of diacetyl *cis–cis* II (Fractions I4 and H3) totaling 11.87 g. After two additional recrystallizations from boiling 95% ethanol, in which it is relatively insoluble, pure diacetyl *cis–cis* II (Fraction J) was obtained as colorless, waxy, butterfly-shaped plates or small plate-like prisms melting at 241.5–243.2°.

Pure *cis–cis* II was isolated as follows: To 106 g. (0.36 mole) of pure diacetyl *cis–cis* II was added 300 ml. (3.6 mole) of concentrated hydrochloric acid and 100 ml. of water and the mixture refluxed for 13.5 hours, the derivative dissolving almost immediately in the hot acid. An additional 100 ml. of concentrated hydrochloric acid was then added and the mixture again refluxed for 8 hours. This procedure was repeated three times using a total of 250 ml. of concentrated hydrochloric acid after which hydrolysis appeared to be complete. On interrupting the hydrolysis overnight, the hydrolysate deposited colorless crystals, presumably of the dihydrochloride, which again dissolved on heating. To the cooled reaction mixture (containing solid hydrochloride) was added with cooling a solution of 290 g. (7.25 moles) of sodium hydroxide in 600 ml. of water, whereupon the diamine precipitated as a white amorphous hydrate. The diamine was extracted with 500 ml. of *n*-butyl alcohol in four portions, the combined alcohol solutions washed with two 50-ml. portions of water and the alcohol removed by distillation *in vacuo*, leaving a clear light yellow sirup which crystallized spontaneously. On distillation *in vacuo* through a 10-inch packed column, there was obtained, after rejecting 0.4 g. of crystalline foreshot, 71.8 g. (94.8% yield) of *cis–cis* II as a colorless liquid which immediately set to a colorless crystalline solid; b.p. 141° (2 mm.). On redistillation there was obtained 68.6 g. of *cis–cis* II boiling at 139.8–139.3° (1.9–1.8 mm.): m.p. (cor.) 60.5–61.9°.[14]

Anal. Calcd. for $C_{13}H_{26}N_2$: C, 74.22; H, 12.46; N, 13.32; neut. equiv., 105.2. Found: C, 74.73, 74.64; H, 12.47, 12.55; N, 13.35, 13.27; neut. equiv., 105.0, 105.5.

By taking into account the actual amounts of the three isomers isolated and the fraction of the initial amount of II accounted for as pure isomers, it is estimated that the three isomers occur in II in the following proportions: 50–60% *trans–trans* II, 30–40% *cis–trans* II and 5–10% *cis–cis* II.

Preparation of Derivatives.—The melting points and analytical data for the picrates and the diformyl, diacetyl and dibenzoyl derivatives of the isomers of II are listed in Table V. The general procedure employed for acetylation and formylation has been previously described. Ethanol was used as solvent in the preparation of the picrates. The dibenzoyl derivatives were prepared by reaction of II with benzoyl chloride in pyridine.

Summary

The isolation and characterization of the three geometric isomers of bis-(4-aminocyclohexyl)-methane are described. Spatial configurations are assigned on the basis of (1) the melting points of the isomers in comparison with analogous systems and (2) the relative abundance of the three isomers under the conditions of formation.

WILMINGTON, DELAWARE RECEIVED JUNE 26, 1950

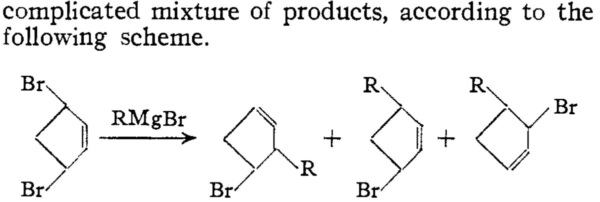
[CONTRIBUTION FROM THE STERLING MEMORIAL LABORATORY, YALE UNIVERSITY]

Reaction of 3,5-Dibromocyclopentene with Grignard Reagents

BY GEORGE W. BARBER[1] AND J. ENGLISH, JR.

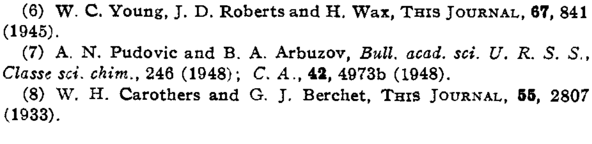
A recent paper by Reid and Yost[2] in which they report unsuccessful attempts to effect reaction of 3,5-dibromocyclopentene with Grignard reagents prompts us to report at this time some preliminary results obtained in this Laboratory in the spring of 1947. Like Reid and Yost we were attracted by the possibility of utilizing the readily available *cis*- and *trans*-3,5-dibromocyclopentenes for the synthesis of 3,5-dialkylcyclopentenes related to the structures proposed for the plant-growth hormones, auxin-a and auxin-b.[3] Although partial success on treating 3,5-dibromocyclopentene with Grignard reagents is reported here, this approach to the auxin ring structure was subsequently abandoned in favor of the more promising synthesis of substituted cyclopentene carboxaldehydes from substituted catechols.[4]

The action of Grignard reagents on unsymmetrically substituted allyl halides has been investigated only slightly, but in a few instances allylic rearrangement during the reaction has been observed to take place to a greater or less extent, mixtures of products invariably having been obtained.[5,6,7,8]



$$\underset{\displaystyle X}{\text{R—CH}}\text{—CH=CH—R}' + \text{R}''\text{—MgBr} \longrightarrow \underset{\displaystyle R''}{\text{R—CH}}\text{—CH=CH—R}' + \text{R—CH=CH—}\underset{\displaystyle R''}{\text{CH}}\text{—R}'$$

In view of these reports, it seemed likely that the reaction of 3,5-dibromocyclopentene with a Grignard reagent would yield a similar but more complicated mixture of products, according to the following scheme.



I II III

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[1] George S. Cox Medical Research Institute, University of Pennsylvania. Taken from a thesis submitted by George W. Barber to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree.

[2] E. B. Reid and J. F. Yost, THIS JOURNAL, **72**, 1807 (1950).

[3] F. Kögl, *Ber.*, **68A**, 16 (1935).

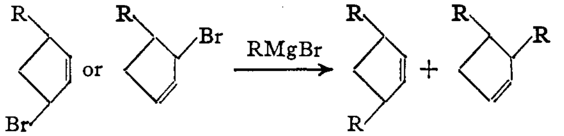
[4] J. English and G. W. Barber, THIS JOURNAL, **71**, 3310 (1949).

[5] C. Prevost and J. Daujat, *Bull. soc. chim.*, [4] **47**, 588 (1930).

[6] W. C. Young, J. D. Roberts and H. Wax, THIS JOURNAL, **67**, 841 (1945).

[7] A. N. Pudovic and B. A. Arbuzov, *Bull. acad. sci. U. R. S. S., Classe sci. chim.*, 246 (1948); *C. A.*, **42**, 4973b (1948).

[8] W. H. Carothers and G. J. Berchet, THIS JOURNAL, **55**, 2807 (1933).



II III IV V

If two equivalents of the Grignard reagent were used, II would probably not be obtained, but would be expected to react further to give IV and V. Compound II might also rearrange to give III, the further reaction of which should also produce IV and V. Compound I is not an allyl type halide, however, and might well be expected among the products of the reaction. On investigating this reaction with ethyl- and *n*-octylmagnesium bromides, these predictions were partially verified.

The reactions with ethylmagnesium bromide of both the *cis* and *trans* forms of 3,5-dibromocyclopentene were investigated. On addition of either isomer to slightly more than two equivalents of the Grignard reagent, exothermic reactions were observed, which did not produce directly the polymeric material described by Reid and Yost[2] as the only product of this type of reaction. Rather, each reaction yielded a mixture of liquid products from which by fractional distillation, 3-ethyl-4-bromocyclopentene (I), a diethylcyclopentene fraction (IV and/or V) and a large non-distillable residue were obtained. Each of these reactions was conducted several times, a larger combined yield and a higher proportion of the diethylcyclopentene fraction invariably being obtained from the *cis*-dibromide. When the Grignard reagent was added to the *trans*-dibromide, 3-ethyl-4-bromocyclopentene (I) was the only distillable product.

The presence of the desired 3,5-diethylcyclopentene (IV) in the hydrocarbon fraction obtained from the *cis*-3,5-dibromocyclopentene was demonstrated by ozonolysis and oxidation, a small amount of the high melting form of the known 2,4-diethylglutaric acid[9] having been obtained, but inasmuch as the major portion of this degradation product failed to crystallize, the constitution of the diethylcyclopentene fraction is not completely established. Attempts to separate the diethylcyclopentene fractions from each of the isomeric dibromides into the two possible constituents (IV and V) were unsuccessful, however.

Each of the 3-ethyl-4-bromocyclopentene (I) fractions obtained from the *cis*- and *trans*-3,5-dibromocyclopentenes appeared to be homogeneous, for on fractional distillation in each case, the material boiled over a very narrow range with quite constant refractive index. Moreover, the physical constants of the products obtained from the isomeric starting materials were nearly identical. The relative positions of the substituents were demonstrated in each product by hydrogenation to the saturated bromide and the action on the latter of silver oxide and water to give the corresponding cyclopentanol. In each instance, the physical constants of the alcohol so obtained were practically identical with those reported for the known *cis*-2-ethylcyclopentanol,[10] and the melting point of the acid phthalate obtained from each alcohol also agreed with the value reported for the *cis* isomer. The identity of the 2-ethylcyclopentanol obtained from the Grignard reaction products was further confirmed by oxidation to the ketone and comparison of the semicarbazone with that of an authentic sample of 2-ethylcyclopentanone.

On the basis of the above evidence, it is concluded that the 3-ethyl-4-bromocyclopentene (I) fractions obtained on reaction of the *cis*- and *trans*-3,5-dibromocyclopentenes with ethylmagnesium bromide are geometrically identical. The position of the double bond in this product is surmised from the fact that the compound did not possess the properties of reactivity and instability characteristic of the 3-halocyclopentenes.[11]

Furthermore, it is suggested that this rearrangement product, obtained from either of the isomeric dibromides, is probably *trans*-3-ethyl-4-bromocyclopentene. The reasons for this suggestion are the following. Whether the mechanism of this rearrangement involves a resonating allylic carbonium ion[12] or a cyclic coördination complex such as that proposed by Carothers,[8] resonance stabilization of the activated complex[13] requires a planar structure, so that some additional factor is required to determine the final orientation of the entering ethyl group. The mutual repulsion to be expected of the bromine and ethyl substituents should favor the predominant formation of the *trans* isomer. The reaction of alkyl halides with silver oxide and water has been shown to proceed with inversion of configuration accompanied by more or less extensive racemization.[14]

The reaction of *trans*-3,5-dibromocyclopentene with *n*-octylmagnesium bromide was also briefly investigated. In this reaction the principal product isolated was the coupling product, *n*-hexadecane. A very low yield of a dioctylcyclopentene was obtained, which appeared to be homogeneous in that it melted quite sharply, but no attempt was made to determine which of the two possible formulas (IV and V, R = *n*-octyl) represents the structure of this product.

Experimental[15]

***cis*- and *trans*-3,5-Dibromocyclopentene.**—Cyclopentadiene was brominated in petroleum ether (b.p. 30–60°) at Dry Ice temperature. The *trans* isomer crystallized on the walls of the reaction vessel and was separated by decantation and recrystallized from ether to give a white, crystalline product, m.p. 45°, in 30–40% yield. The *cis* isomer was obtained by evaporation of the petroleum ether mother liquor and distillation of the residue at reduced pressure. In this manner, a colorless, constant-boiling liquid was obtained in 25–30% yield, b.p. 53–55° at 2.5 mm., $n^{20}\mathrm{D}$ 1.5820; reported[16] $n^{20}\mathrm{D}$ 1.5822. Although both isomers decomposed rather rapidly at room temperature, they could be stored at Dry Ice temperature for several weeks without

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(9) O. Dressel, *Ann.*, **256**, 185 (1890); A. Reformatski, *J. Russ. Phys.-Chem. Soc.*, **34**, 364 (1902).

(10) G. Vavon and A. Horeau, *Bull. soc. chim.*, [5] **1**, 1703 (1934).

(11) P. J. Wilson and J. H. Wells, *Chem. Revs.*, **34**, 1 (1944).

(12) A. G. Catchpole, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 8 (1948).

(13) G. W. Wheland, "The Theory of Resonance and its Application to Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, Chapter 8.

(14) E. D. Hughes, C. K. Ingold and S. Masterman, *J. Chem. Soc.*, 1236 (1937); A. McKenzie and G. W. Clough, *ibid.*, 687 (1913).

(15) All melting and boiling points are corrected.

(16) A. T. Blomquist and W. G. Mayes, *J. Org. Chem.*, **10**, 134 (1945).

any evident decomposition, and no decomposition was observed when ether solutions of either isomer were kept at room temperature for as long as 2 days.

Reaction of *cis*- and *trans*-3,5-Dibromocyclopentene with Ethylmagnesium Bromide.—Ether solutions of the *cis*- and *trans*-dibromides (1 cc. ether per g. dibromide) were added slowly under nitrogen and with stirring to 2.1 to 2.2 equivalents of a 3.28 *N* stock solution of ethylmagnesium bromide in ether. Cooling was employed in some runs, but with no noticeable effect on the course of the reaction other than preventing loss of the more volatile products. After complete addition, stirring was continued for 18 to 20 hours at room temperature, whereupon titration of aliquots from a number of reactions indicated that 70–80% of the theoretical two equivalents of Grignard reagent had been consumed. The reaction mixtures were then poured onto ice and shaken with saturated aqueous ammonium chloride. The ether solutions were dried over anhydrous sodium sulfate and the ether removed. Distillation of the liquid residues at moderately reduced pressure gave in each case a colorless or pale yellow distillate and a considerable amount of non-distillable tar.

Products from *cis*-3,5-Dibromocyclopentene.—From 290 g. of *cis*-dibromide, there was obtained a distillate of 74 g., b.p. 57–75° at 43 mm. This was readily separated into two different fractions by distillation at reduced pressure through a one-foot Podbielniak type column. The lower boiling fraction amounted to 47.5 g., b.p. 47–50° at 27 mm., and appeared to consist of hydrocarbons, although it did not seem to be completely homogeneous. The second fraction was 23.4 g., b.p. 61–67° at 25 mm. Each of these fractions was carefully redistilled with the following results.

(1) The lower fraction boiled over too small a range to permit a clear separation of the constituents. The spread of $n^{20}\text{D}$ was 1.4390–1.4420. The fractions were recombined, and after refluxing over sodium for 1 hour, the material was refractionated slowly at atmospheric pressure through a two-foot Podbielniak type column. The major portion, which now appeared to be homogeneous, boiled at 141.5–142° with constant refractive index, $n^{20}\text{D}$ 1.4390; d_{20} 0.7921; *MR* calcd. for diethylcyclopentene 41.0; *MR* found 41.2. The results of ozonization demonstrate that this material consisted, at least in part, of 3,5-diethylcyclopentene. The yield was 40.5 g. (25%).

Anal. Calcd. for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 87.07; H, 13.13.

(2) When the higher boiling fraction was subjected to fractionation under vacuum, there was obtained a stable, water-white liquid boiling constantly at 65° at 23 mm., with a constant refractive index for the five fractions collected, $n^{20}\text{D}$ 1.4878; d_{20} 1.2674; *MR* calcd. for ethylbromocyclopentene 39.7; *MR* found 39.8; b.p. 165° by the Siwoloboff micro method.[17] This material was shown to be 3-ethyl-4-bromocyclopentene by conversion to the known *cis*-2-ethylcyclopentanol. The yield was 23.4 g. (10%).

Products from *trans*-3,5-Dibromocyclopentene.—From 166 g. of *trans*-dibromide, a distillate of 41 g. was obtained, b.p. 40–70° at 30 mm. Redistillation through a one foot Podbielniak type column gave two major fractions: (1) 13.2 g., b.p. 35–38° at 12.5 mm., $n^{20}\text{D}$ 1.439–1.448; (2) 21.6 g., b.p. 51–52° at 12.5 mm., $n^{20}\text{D}$ 1.4870. Each of these fractions was carefully redistilled.

(1) The lower boiling diethylcyclopentene fraction did not appear to be completely homogeneous, but it was not possible to effect a separation by distillation. When what appeared to be the best and principal fraction was refluxed for an hour over sodium and then distilled, however, there was obtained an apparently homogeneous, water-white liquid, b.p. 141.5–142.5°; $n^{20}\text{D}$ 1.4404; d_{20} 0.7948; *MR* calcd. for diethylcyclopentene 41.0; *MR* found 41.2.

Anal. Calcd. for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 86.95; H, 13.03.

(2) On distillation of the higher fraction through the one foot column, 3-ethyl-4-bromocyclopentene was obtained as a stable, water-white liquid boiling constantly at 50° at 12 mm., with constant $n^{20}\text{D}$ 1.4880; d_{20} 1.2661; *MR* calcd. 39.7; *MR* found 39.8; sapon. equiv. calcd., 175.1; found, 175.1. The identity of this product was established by conversion to the known *cis*-2-ethylcyclopentanol.

Anal. Calcd. for $C_7H_{11}Br$: C, 48.02; H, 6.33; Br, 45.65. Found: C, 47.83; H, 6.45; Br, 45.77.

Reverse Reaction with *trans*-3,5-Dibromocyclopentene.—3-Ethyl-4-bromocyclopentene was obtained as the only distillable product when 200 cc. of the stock 3.28 *N* ethylmagnesium bromide in ether was added slowly with stirring, cooling in cold water and under nitrogen to a solution of 45.5 g. (0.2 mole) of *trans*-3,5-dibromocyclopentene in 400 cc. of ether. After the homogeneous reaction mixture had stood overnight at room temperature, titration of an aliquot with standard hydrochloric acid revealed that 0.157 mole of Grignard reagent had been consumed, or 0.78 mole per mole of dibromide. On standing 4 more days, there was no further consumption of Grignard reagent. On working up as before, 17 g. of light yellow distillate, b.p. 60–70° at 20 mm., was obtained. Fractional distillation of this material revealed that it consisted almost entirely of 3-ethyl-4-bromocyclopentene, b.p. 52° at 13 mm., $n^{20}\text{D}$ 1.4879. The yield was 47% of the theoretical.

Ozonization of 3,5-Diethylcyclopentene (?).—Two grams of the diethylcyclopentene fraction from the reaction of *cis*-3,5-dibromocyclopentene with ethylmagnesium bromide was dissolved in 20 cc. of chloroform and oxygen containing 9% of ozone was passed through at such a rate that 0.01 mole of ozone was passed in 20 minutes. After 40 minutes, during which the solution was cooled in ice, ozone was detected at the exit. The ozonide was reduced with powdered zinc and water and the product oxidized by stirring at room temperature with alkaline permanganate. About 1 g. of an oily acid fraction was so obtained. By extraction of this material with petroleum ether (b.p. 30–60°) and cooling the extract in Dry Ice, a small amount of white powder was obtained. Several recrystallizations from petroleum ether gave 10 mg. of microcrystalline 2,4-diethylglutaric acid, m.p. 116–117°; neut. equiv.: calcd. for $C_9H_{16}O_4$, 94; found (in 50% alcohol), 92. The remainder of the acid material could not be induced to crystallize. Authentic 2,4-diethylglutaric acid was prepared according to Dressel[9] and also proved difficult to crystallize. The portion obtained in crystalline form melted at 117–118° and gave no depression when mixed with the product from ozonolysis.

2-Ethylcyclopentyl Bromide.—Approximately 20-g. portions of the 3-ethyl-4-bromocyclopentene fractions obtained from each of the isomeric 3,5-dibromocyclopentenes were individually hydrogenated by shaking with Adams platinum catalyst in 50 cc. of 95% ethanol under 40 pounds initial pressure of hydrogen. Because the hydrogenated products were found to codistill with alcohol at water-pump pressure, the filtered reaction mixtures were diluted with water and extracted with ether. The ether extracts were dried and evaporated and the residues were distilled at reduced pressure through the one-foot Podbielniak column.

From 20 g. of 3-ethyl-4-bromocyclopentene from the *cis*-dibromide, there was obtained 14.3 g. of colorless 2-ethylcyclopentyl bromide, b.p. 70–71° at 24 mm.; $n^{20}\text{D}$ 1.4787; d_{20} 1.2372; *MR* calcd. 40.1; *MR* found 40.6.

From 21.6 g. of 3-ethyl-4-bromocyclopentene from the *trans*-dibromide, 14.9 g. of 2-ethylcyclopentyl bromide was obtained, b.p. 65° at 20 mm.; $n^{20}\text{D}$ 1.4792; d_{20} 1.2407; *MR* calcd. 40.1; *MR* found 40.5.

Anal. Calcd. for $C_7H_{13}Br$: Br, 45.12. Found: Br, 45.15.

***cis*-2-Ethylcyclopentanol.**—This product was obtained by stirring each of the above hydrogenation products in aqueous suspension with an equal weight of freshly prepared silver oxide for 20 to 40 hours. The reaction mixtures were extracted with ether, the extracts were dried and evaporated and the residues were fractionated at reduced pressure. Each of the alcoholic products was accompanied by a much lower boiling fore-fraction (caught in the Dry Ice trap) and a still residue.

From 14 g. of the 2-ethylcyclopentyl bromide whose original source was the *cis*-3,5-dibromocyclopentene, 3.7 g. of colorless *cis*-2-ethylcyclopentanol was obtained, b.p. 67° at 23 mm., 162–163° at 757 mm. (micro method[17]); $n^{22}\text{D}$ 1.4550; d_{20} 0.9208; *MR* calcd. 33.7; *MR* found 33.7. An acid phthalate was prepared from 1 g. of this alcohol. After several recrystallizations from petroleum ether (b.p. 30–60°), the product melted at 91.5–92°.

From 13 g. of the 2-ethylcyclopentyl bromide whose source was the *trans*-3,5-dibromocyclopentene, 4 g. of *cis*-2-ethylcyclopentanol was obtained, b.p. 66° at 23 mm., 161–163° at 759 mm. (micro method); $n^{20}\text{D}$ 1.4555; d_{20} 0.9206;

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[17] A. Siwoloboff, *Ber.*, **19**, 795 (1886).

MR calcd. 33.7; *MR* found 33.7. The acid phthalate prepared from 1 g. of this product melted at 90–91.5° after several recrystallizations from petroleum ether.

The following properties were reported by Vavon and Horeau[10] for the two isomers of 2-ethylcyclopentanol: *cis* isomer: b.p. 163°; $n^{19}\mathrm{D}$ 1.4556; d_{19} 0.9198; acid phthalate m.p. 92°. *trans* isomer: b.p. 165°; $n^{19}\mathrm{D}$ 1.4529; d_{19} 0.9149; acid phthalate m.p. 54.5–55°.

2-Ethylcyclopentanone.—Two grams of 2-ethylcyclopentanol obtained from the *trans*-3,5-dibromocyclopentene as described above was added dropwise with stirring to a solution of 3.6 g. of potassium dichromate and 3 cc. of sulfuric acid in 10 cc. of water. After completion of the reaction, the mixture was extracted with ether. The ether solution was dried over anhydrous sodium sulfate, the ether was removed and the residue was distilled at reduced pressure. One-half gram of 2-ethylcyclopentanone was obtained, b.p. 57° at 24 mm. The boiling point determined by the Siwoloboff micro method[17] was 159° at 760 mm.; reported for 2-ethylcyclopentanone: 149°,[18] 157–158°,[10] 160–161°.[19]

A semicarbazone was prepared from this material, m.p. 178–179° after several recrystallizations from dilute ethanol. The semicarbazone prepared from an authentic sample of 2-ethylcyclpentanone (prepared by alkylation of 2-carbethoxycyclopentanone[10,19]) melted at 182°, and there was no depression of the melting point on admixture of these two semicarbazones.

Reaction of *trans*-3,5-Dibromocyclopentene with *n*-Octylmagnesium Bromide.—A Grignard reagent was prepared from 150 g. (0.78 mole) of redistilled *n*-octyl bromide and 20 g. of magnesium in 700 cc. of dry ether. Titration of an aliquot indicated that the resulting solution contained 0.65 mole of *n*-octylmagnesium bromide. A solution of 91 g. (0.40 mole) of *trans*-3,5-dibromocyclopentene in 100 cc. of ether was added slowly under nitrogen while stirring and cooling in a water-bath. There was marked evolution of heat and the reaction mixture became bright yellow in color. After complete addition, which required 4 hours, two liquid layers were observed, but after standing overnight, the flask contained a slushy suspension of white solid. The mixture was poured onto ice and the ether layer shaken with saturated ammonium chloride solution, saturated sodium carbonate and water. The ether solution was dried over anhydrous sodium sulfate, the ether was removed and the residue was distilled at reduced pressure. Four fractions were eventually obtained.

(1) The first fraction, 20 g. of *n*-octane, boiled below 20° at 10 mm. and was caught in the Dry Ice trap. On redistillation at atmospheric pressure this material had b.p. 125–126°; m.p. −57 to −54°, uncorrected; $n^{20}\mathrm{D}$ 1.4002.

(2) The second fraction of 25 g., b.p. 100–110° at 1 mm., was a pale yellow liquid which darkened on standing. A portion was crystallized several times from ether by cooling in Dry Ice to give a mass of long white needles. This material was then redistilled to give a colorless liquid, b.p. 86° at 0.5 mm.; $n^{20}\mathrm{D}$ 1.4350; d_{20} 0.7748; m.p. 18°. This was demonstrated to be *n*-hexadecane by a mixed m.p. with an authentic sample, there being no depression.

(3) The third fraction of 10 g., b.p. 115–120° at 0.02 mm., was a yellow liquid which was crystallized from ether several times by cooling in Dry Ice and decanting. The residual ether was finally removed by protracted evacuation to give a colorless liquid, m.p. 17.5–18°; $n^{20}\mathrm{D}$ 1.4592; d_{20} 0.8265. The b.p. at 2.5 mm. was 155°, from which it is calculated that the b.p. at atmospheric pressure would be approximately 355°. The b.p. calcd. for a dioctylcyclopentene by the method of boiling point numbers[20] is 362°. The analysis confirms the identity of this product as a dioctylcyclopentene, possibly the desired 3,5-di-*n*-octylcyclopentene.

Anal. Calcd. for $C_{21}H_{40}$: C, 86.22; H, 13.78. Found: C, 86.25; H, 13.83.

(4) The fact that the hexadecane fraction remaining after crystallization of a portion from ether darkened on standing led to the suspicion that it might contain a small amount of an octylbromocyclopentene. The b.p. calcd. for such a compound from b.p. numbers[20] is approximately 290° (hexadecane b.p. 287.5°). Repeated fractionations of this material at reduced pressure eventually produced a fraction with $n^{20}\mathrm{D}$ 1.4600, boiling a fraction of a degree below the main fraction of hexadecane. This material was cooled in ice until mostly solid and the liquid portion was withdrawn to give 0.7 g. of pale yellow liquid, $n^{22}\mathrm{D}$ 1.4721; d_{22} 1.027; *MR* calcd. for an octylbromocyclopentene 63.8; *MR* found 70.7. This material was still not pure, but the quantity was not sufficient to permit further purification.

Anal. Calcd. for $C_{13}H_{23}Br$: Br, 30.83. Found: Br, 25.58.

Summary

The reactions of *cis*- and *trans*-3,5-dibromocyclopentene with ethylmagnesium bromide gave hydrocarbon fractions shown to consist, in part at least, of 3,5-diethylcyclopentene, but which may contain 3,4-diethylcyclopentene also. Identical bromine containing fractions were also obtained from the two reactions. This material was demonstrated to be 3-ethyl-4-bromocyclopentene and is believed to be the *trans* isomer. Similar results were obtained on reaction of *trans*-3,5-dibromocyclopentene with *n*-octylmagnesium bromide.

NEW HAVEN, CONNECTICUT RECEIVED JUNE 27, 1950

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[18] S. R. Best and J. F. Thorpe, *J. Chem. Soc.*, **95**, 713 (1909).

[19] F. H. Case and E. B. Reid, THIS JOURNAL, **50**, 3062 (1928).

[20] C. R. Kinney, *Ind. Eng. Chem.*, **32**, 559 (1940).

[CONTRIBUTION FROM RESEARCH LABORATORY OF AEROJET ENGINEERING CORP.]

The Chemistry of Aliphatic Dinitro Compounds. I. The Michael Reaction[1]

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Aliphatic mononitro compounds are known to undergo Michael type condensations with compounds having an activated double bond.[2–7]. This reaction has now been extended to aliphatic gem-dinitro compounds.

Potassium dinitromethane upon reaction with methyl acrylate (I) and acrylonitrile (II) gave dimethyl 4,4-dinitroheptanedioate (III) in 60% yield and 4,4-dinitroheptanedinitrile (IV) in 34% yield, respectively.

The reactions proceed readily in water solution at 35–45°. Aqueous potassium dinitromethane is sufficiently basic to effect the condensation without further addition of catalyst. Best results in the preparation of III were obtained when a 2.5-fold excess of methyl acrylate was used.

Potassium dinitroethanol underwent reaction with two molecules of methyl acrylate, in the same

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[2] Kohler and Engelbrecht, THIS JOURNAL, **38**, 889 (1916); **41**, 764 (1919).

[3] Bruson and Riener, *ibid.*, **65**, 23 (1943).

[4] Kloetzel, *ibid.*, **70**, 3571 (1948).

[5] Leonard and Beck, *ibid.*, **70**. 2504 (1948).

[6] Leonard and Shoemaker, *ibid.*, **71**, 1758–1876 (1949).

[7] Bruson, "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 99.