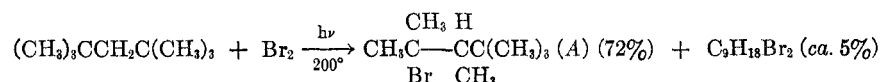


REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XXXV.
MIGRATION OF A METHYL GROUP IN THE REARRANGEMENT
OF THE FREE DI-*TERT*-BUTYLCARBINYL RADICAL. THE REAC-
TION OF DI-*TERT*-BUTYLCARBINYL CHLORIDE WITH A GRI-
GNARD REAGENT IN THE PRESENCE OF COBALTOUS BROMIDE

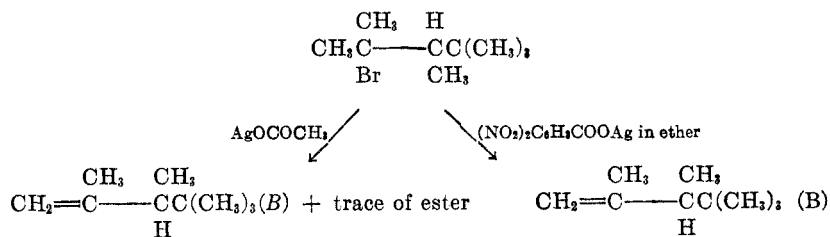
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During a study of bromination of alkyl halides and saturated hydrocarbons, we examined the products formed in the vapor-phase photochemical bromination of 2,2,4,4-tetramethylpentane (di-*tert*-butylmethane). The design of the apparatus and the specific details of operation will be described in a subsequent article. Suffice it to say at this time that no bromination of 2,2,4,4-tetramethylpentane takes place at 100°, but ready bromination takes place at 200°. The yield of the bromination products, on the basis of the bromine used, is high provided the concentration of the bromine in the vapor-phase is low.



The structure assigned to compound *A* is based on the following considerations: (a) analyses and molecular weight determination; (b) reaction of *A*, dissolved in 75% ethanol, with silver acetate to give within a short time (30 minutes) an almost quantitative yield of silver bromide and an olefin (*B*); (c) identification of the olefin (*B*) formed in *b* as 2,3,4,4-tetramethylpent-1-ene.

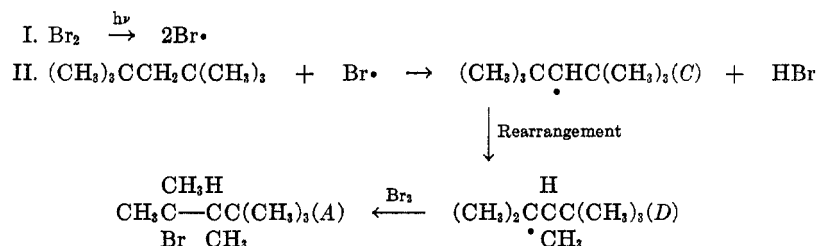


The olefin *B* upon ozonolysis gave formaldehyde (identified as the methone derivative) and a ketone, 3,4,4-trimethylpentan-2-one. The melting point of the 2,4-dinitrophenyl hydrazone of this ketone was the same as the one described in the literature for 3,4,4-trimethylpentan-2-one.

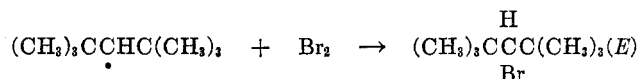
The data here presented strongly suggest that the bromination of di-*tert*-

¹ The authors wish to acknowledge the generous support of the United States Rubber Company which made this research possible.

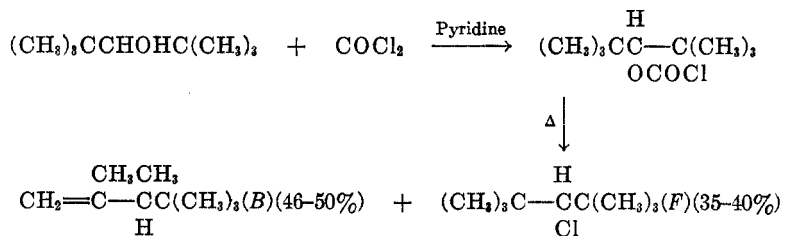
butylmethane proceeds by a free radical mechanism with rearrangement of a methyl group.



On the other hand one might argue (although somewhat less convincingly) that the free radical *C* reacted with bromine to give compound *E*, and the latter in the presence of hydrogen bromide rearranged (by an ionic mechanism) to give compound *A*.

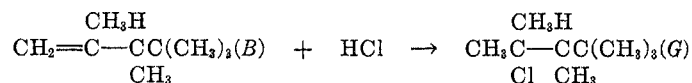


Obviously the data presented do not admit of an unequivocal choice of the mechanism of rearrangement of the methyl group. The answer to the question whether migration of the methyl group occurs in the free radical *C* depended upon the preparation of compound *E*, or the chloro-derivative of this compound, and generation of the free radical *C* from this halide. The chloro-derivative of *E*, namely compound *F*, was prepared by thermal decomposition of di-*tert*-butylcarbinyl chloroformate.



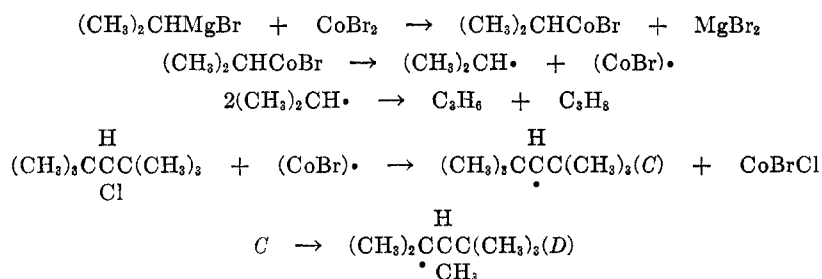
The olefin *B* obtained in this reaction had the same boiling point and index of refraction as the olefin obtained in the dehydrohalogenation of compound *A*. Infrared analysis indicated the presence of a terminal double bond and neither a non-terminal double bond nor a cyclopropane ring. The olefin absorbed one mole of hydrogen to give the saturated hydrocarbon which had the same physical constants (b. p. and index of refraction) as those reported for 2,2,3,4-tetramethylpentane. Furthermore, the infrared spectrum of the hydrocarbon obtained as here described agreed in every detail with the reported spectrum of 2,2,3,4-tetramethylpentane. Upon ozonolysis it gave formaldehyde and 3,4,4-trimethylpentan-2-one. When the olefin *B* obtained as outlined above was treated with hydrogen chloride, compound *G* was formed. This substance was

hydrolyzed very rapidly (95% in 20 minutes at room temperature) when treated with an alcoholic solution of silver nitrate.

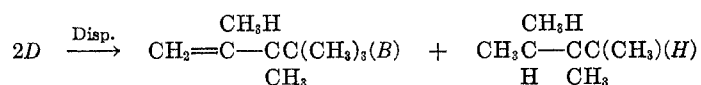


Previous to this work, compound *F* had not been isolated in the pure state.² The structure assigned to the compound isolated by us (compound *F*) is based in part on the differences in the refractive indices of this compound (n_D^{20} 1.4470) and compound *G* (n_D^{20} 1.4527) (the structure of which has been definitely established by us) and in part on the difference in reactivity of these compounds with silver nitrate. Compound *F* reacted very slowly when treated with an alcoholic solution of silver nitrate (ca. 6% reaction in 24 hours) at room temperature, while *G* reacted very rapidly (95% in 20 minutes at room temperature).

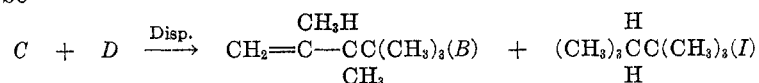
To generate the free radical *C* from compound *F*, the latter substance was slowly added to a solution of isopropylmagnesium bromide, containing some cobaltous bromide. Immediate gas evolution took place. Upon working up the reaction mixture some unchanged compound *F* was recovered as well as a mixture of a saturated and unsaturated hydrocarbon.



Disproportionation could take place between two free radicals *D*,



or between the free radicals *C* and *D*. In the latter case, the expected products would be



Actually, the products of this reaction are compound *B*, and the hydrocarbon *I*. The structure of compound *I* was confirmed by its complete identity with the infrared absorption spectrum of an authentic sample of this hydrocarbon.

² Hughes, *Bull. soc. chim.*, [5] **18**, 41 (1951) states that compound *F* is one of the products of the mixture of chlorinated products formed upon chlorination of 2,2,4,4-tetramethylpentane. The authors were unable to separate the individual compounds by conventional means. The presence of compound *F* is deduced from the data on the rate of solvolysis of the reaction mixture.

A more attractive mechanism of formation of compounds *B* and *I* is the disproportionation of two free radicals *C*, *i.e.* that migration and disproportionation occur during the collision of the free radicals. This concept has an important bearing on rearrangements in general, and it is regrettable that no simple and direct experimental method is as yet available for determining which of these mechanisms is responsible for formation of compounds *B* and *I*. It is hoped that additional useful information for evaluation of this problem will be forthcoming from the study now under way on mechanism of disproportionation of two dissimilar free radicals.³

EXPERIMENTAL

Preparation of di-tert-butyl ketone. This ketone was prepared by the procedure of Cook and Percival (1) except that copper powder was added to the reaction mixture.

Preparation of di-tert-butylcarbinol. The ketone, prepared as described above, was reduced with lithium aluminum hydride to the corresponding alcohol (82%, m.p. 53–54°). The phenylurethan of the alcohol melted at 119–120°.

Preparation of di-tert-butylcarbinyl chloroformate. Phosgene (139 g., 1.4 moles) was introduced into an ice-cooled 500-ml. three-necked flask equipped with a mercury-sealed stirrer, a dropping-funnel, and a Dry-Ice condenser. Anhydrous pyridine (0.76 mole) was then added dropwise, followed by a solution of 96 g. (0.67 mole) of di-tert-butylcarbinol in 200 ml. of ether. The mixture was agitated during the addition of these reagents. The ice-bath was removed and the mixture was stirred for 8 hours at room temperature. The excess phosgene was removed, and the reaction mixture was poured on ice and the whole was extracted with ether. The ether extract was washed with water, the layers were separated, and the ether extract was dried with sodium sulfate. The ether was then removed and the residue was distilled at reduced pressure. A colorless oil (b.p. 45–46°/0.7 mm.; n_D^{20} 1.4400; 128.2 g. [93% of calc'd amount]) was collected.

Anal. Calc'd for $C_{10}H_{19}ClO_2$: C, 58.10; H, 9.27; Cl, 17.15.

Found: C, 58.11; H, 9.27; Cl, 17.02.

A few drops of the ester were treated with dilute ammonia and warmed for 5 minutes on a steam-bath. The urethan formed was crystallized from medium-boiling petroleum ether. Colorless needles were thus obtained. The substance melted at 96–97°.

Anal. Calc'd for $C_{10}H_{21}NO_2$: N, 7.48. Found: N, 7.23.

Thermal decomposition of the di-tert-butylcarbinyl chloroformate. The ester (128 g.) was placed in a flask (fitted with a reflux condenser) and the air in the flask was replaced by nitrogen gas. A slow stream of nitrogen gas was passed through the liquid while the whole was heated to 110°. The evolved gases were collected in 10% sodium hydroxide solution. Examination of the latter showed that carbon dioxide and hydrogen chloride were eliminated from the ester. The temperature of the oil-bath was kept at 110° for 13 hours and then was raised to 120–140° for 3.5 hours longer. The residue was fractionated at reduced pressure. Four fractions were collected: Fraction I: b.p. 27° (13 mm.), n_D^{20} 1.4260, 43.8 g.; Fraction II: b.p. 27–36° (13 mm.), n_D^{20} 1.4315, 3.1 g.; Fraction III: b.p. 37–38° (5 mm.), n_D^{20} 1.4470, 13.0 g.; Fraction IV: b.p. 38–39° (5 mm.), n_D^{20} 1.4475, 8.8 g. From the cold trap a material was collected (9.9 g.) which had an index of refraction of 1.4356 at 20°.

(a) *Identification of Fraction I.* This material was identified as 2,3,4,4-tetramethylpent-1-ene. A similar fraction (b.p. 27–31.5° (18 mm.), n_D^{20} 1.4266, 14.5 g.) which was obtained from the thermal decomposition of 30 g. of the chloroformic ester at somewhat

³ For the sake of simplicity we have not assessed the importance of the disproportionation of the free radicals *D* and *C* with the free isopropyl radicals generated in the reaction. These items will be discussed in a paper now nearing completion on mechanism of disproportionation of free radicals.

higher temperatures, was carefully fractionated through a small Podbielniak column, and the distillate was cut into 12 fractions (b.p. 128.5–131.5°). The indices of refraction varied from 1.4241 to 1.4257. However, the analyses of these fractions for carbon and hydrogen were essentially the same.

(i) *Anal.* Calc'd for C_9H_{18} : C, 85.63; H, 14.37.

Found: C, 85.50; H, 14.58.

(ii) *Infrared spectrum.* The infrared spectrum was made on a Perkin-Elmer 12-C infrared spectrometer in the region 4000 cm^{-1} to 600 cm^{-1} . A fixed cell of thickness 0.1 mm. was used. The spectrum had the following bands which were characteristic of a terminal double bond of the type $>C=CH_2$ — 3076 cm^{-1} ; 1785 cm^{-1} ; 891 cm^{-1} . The remainder of the spectrum insofar as other groups were concerned, was similar to the spectrum of the groups of 2,2,3,4-tetramethylpentane (2), suggesting that the carbon skeleton was similar in both cases.

(iii) *Upon hydrogenation* Fraction I absorbed 0.96 mole of the calculated amount of gas. The saturated hydrocarbon boiled at 129° (747 mm.), n_D^{20} 1.4151. 2,2,3,4-Tetramethylpentane (3) boils at 133° (760 mm.), n_D^{20} 1.4146. The infrared spectrum was also identical with the standard spectrum of this compound (2).

(iv) *Ozonolysis.* A solution of 0.3 g. of Fraction I (0.3 g.) dissolved carbon tetrachloride (100 ml.) was cooled to 0° and ozone was passed through the solution for 10 minutes. The gaseous products were absorbed in distilled water (25 ml.). When the aqueous solution was treated with a saturated solution of methone in 20% alcohol, a crystalline derivative readily formed. This compound (m.p. 191 – 192°) did not depress the melting point of an authentic sample of the methone derivative of formaldehyde.

Fraction I (2.2 g.) was dissolved in ethyl acetate (100 ml.), cooled to -40° , and ozone was passed through the solution for 40 minutes. After removal of the solvent under reduced pressure the residue was dissolved in absolute alcohol and was subjected to the action of hydrogen gas in the presence of PtO_2 , until the decomposition of the ozonide was complete. The catalyst was then collected, and the solution was distilled through a Vigreux column to recover the alcohol and other low-boiling materials. An aliquot of the distillate was treated with 2,4-dinitrophenylhydrazine solution. The precipitate which formed was crystallized twice from aqueous alcohol. The solid thus obtained sintered at 130° and melted at 140° . On admixture with the 2,4-dinitrophenylhydrazone of acetone a depression of 30° in the melting point was noted. These data indicate that acetone was not present in the distillate. The residue (2.2 g.) was fractionated in a small Claisen flask under reduced pressure and two fractions were collected: Fraction A: b.p. 25 – 43° (21 mm.), n_D^{20} 1.3924, 1.5 g.; Fraction B: b.p. 71° (3 mm.), n_D^{20} 1.4308.

Fraction A was shown to contain methyl pinacolyl ketone (3,4,4-trimethylpentan-2-one). The semicarbazone was prepared in the usual manner and melted at 150° . Crystallization, from dilute alcohol, did not change the melting point (m.p. 150.5 – 151°). The value reported in the literature (4) for the melting point of this semicarbazone is 148° .

Anal. Calc'd for $C_9H_{19}N_3O$: C, 58.34; H, 10.34; N, 22.44.

Found: C, 59.07; H, 10.36; N, 22.14.

Fraction B was an acid which presumably was formed during working up of the ozonide.

Another portion (1 g.) of the Fraction I was ozonized in ethyl acetate at -40° . After removal of the solvent under reduced pressure, the oily ozonide was warmed with water (25 ml.) for 30 minutes and cooled. The mixture was extracted with ether, the ether extract washed with water and 5% sodium carbonate solution, and dried with sodium sulfate, and the solvent was then removed. The residue was treated with 2,4-dinitrophenylhydrazine and the orange precipitate which formed was recrystallized from aqueous alcohol (m.p. 109.5 – 110°). The melting point of 2,4-dinitrophenylhydrazone (4) of methyl pinacolyl ketone recorded in the literature is 109.5° .

Anal. Calc'd for $C_{14}H_{26}N_4O_4$: C, 54.53; H, 6.54; N, 18.17.

Found: C, 54.43; H, 6.75; N, 18.10.

(b) *Identification of Fractions III and IV.* The analyses and the behavior of these frac-

tions with silver nitrate in alcohol suggest that these fractions are 3-chloro-2,2,4,4-tetramethylpentane.

Anal. Calc'd for $C_9H_{19}Cl$: C, 66.44; H, 11.77; Cl, 21.79.

Found: C, 66.20; H, 11.34; Cl, 21.16.

Towards silver nitrate in 85% alcohol, Fractions III and IV are similar to *sec*-butyl chloride. About 4-6% of the compounds were hydrolyzed in 24 hours at room temperature.

The amount of unsaturation in the chloride fraction was determined by the bromate-bromide titration method. No detectable amount of unsaturation beyond the experimental error of the method was found.

The yields of the pure fractions of the olefin and the secondary chloride were 56% and 22% respectively. The material of Fraction II and that collected from the cold trap was a mixture of the olefin and the chloride. Assuming that the refractive indices were of a linear relationship with the composition of the mixture, the combined mixture would contain 0.052 mole of the olefin and 0.032 mole of the secondary chloride. Thus the yield of the olefin and the chloride were 66% and 27% respectively.

Addition of hydrogen chloride to 2,3,4,4-tetramethylpent-1-ene. Dry hydrogen chloride gas (in excess of the calculated amount) was passed into the liquid olefin maintained at -80° . The reaction mixture was gradually allowed to come to room temperature, and the excess hydrogen chloride removed with dry nitrogen gas. Distillation of the residue under reduced pressure gave a material which boiled at $48-50^\circ/8$ mm. (n_D^{20} 1.4527, 1.6 g.). The product hydrolyzed almost completely in 20 minutes in aqueous alcohol in the presence of silver nitrate.

Anal. Calc'd for $C_9H_{19}Cl$: Cl, 21.8. Found: Cl, 20.7.

Reaction of 3-chloro-2,2,4,4-tetramethylpentane with isopropylmagnesium bromide in the presence of cobaltous bromide. An ether solution (500 ml.) of isopropylmagnesium bromide (0.39 mole) was introduced into a one-liter three-necked flask equipped with a mercury-sealed stirrer, a Friedrich condenser, and a dropping-funnel. A solution of 3-chloro-2,2,4,4-tetramethylpentane (21 g., 0.13 mole) in 200 ml. of anhydrous ether and 2.8 g. of anhydrous cobaltous chloride was added dropwise to the Grignard solution. The addition of these reagents required 2.5 hours. The mixture was vigorously stirred during the entire period. After the addition was over, the mixture was gently warmed on a steam-bath for 1 hour. Two liters of gas were evolved during the course of the reaction. An additional amount (0.6 g.) of cobaltous bromide was then added and the mixture again was warmed for 1 hour on a steam-bath. The reaction mixture was decomposed with ice and 30 ml. of glacial acetic acid then was added. The ether layer was washed with water and 5% sodium bicarbonate solution and dried over sodium sulfate. The ether was removed using a Vigreux column. The residue was distilled in a Claisen flask and the fractions were collected: Fraction 1: a low-boiling fraction (11.6 g.) which distilled over at ordinary pressure; Fraction 2: a high-boiling fraction (7.9 g.) which distilled over at 5 mm.; Fraction 3: a residue (1.1 g.).

(a) The low-boiling fraction was fractionated in a small Podbielniak column and the following fractions were obtained: Fraction A: b.p. $121-122^\circ$, n_D^{20} 1.4065, 2.8 g.; Fraction B: b.p. $122-123^\circ$, n_D^{20} 1.4086, 2.4 g.; Fraction C: b.p. $122-123^\circ$, n_D^{20} 1.4085, 1.6 g. The residue was distilled in a Hickman flask to yield a Fraction D: b.p. $129-133^\circ$, n_D^{20} 1.4244, 1.5 g. All these four fractions were halogen-free.

The infrared spectra of Fractions A-D were run on a Perkin Elmer 12-C infrared spectrometer in the region 4000 cm^{-1} , to 650 cm^{-1} . A fixed cell of thickness 0.1 mm. was used. Fraction A contained mainly 2,2,4,4-tetramethylpentane (bands at 1170 cm^{-1} , 972 cm^{-1} , 916.5 cm^{-1} and 855 cm^{-1} in agreement with the A.P.I. #584 spectrum for 2,2,4,4-tetramethylpentane, and a small amount of the olefin, 2,3,4,4-tetramethylpent-1-ene (bands characteristic of a terminal double bond at 3076 cm^{-1} , 1785 cm^{-1} and 891 cm^{-1}). Fractions B-C contained a larger percentage of the olefin. Fraction D was a mixture of 2,2,4,4-tetramethylpentane and 2,3,4,4-tetramethylpent-1-ene with the olefin predominating.

Bromate-bromide titration method showed Fractions A, B, and C contained 4%, 5%, and 6% of unsaturation, respectively. Fraction D contained 82% of unsaturation. Thus the total yields of 2,2,4,4-tetramethylpentane and 2,3,4,4-tetramethylpent-1-ene were 0.053 and 0.013 mole, respectively. The combined yield of these two compounds was 50% on the basis of the starting material.

The identity of the olefin component was further established through ozonolysis. The ketone obtained formed a 2,4-dinitrophenylhydrazone which crystallized from aqueous alcohol in fine, orange needles, m.p. 109–110°. This compound did not depress the melting point of the 2,4-dinitrophenylhydrazone of methyl pinacolyl ketone.

(b) The high-boiling fraction was redistilled in a Claisen flask to give three fractions: Fraction E: b.p. 45–50° (5 mm.), n_D^{20} 1.4449, 2.3 g.; Fraction F: b.p. 51–54° (5 mm.), n_D^{20} 1.4444, 1.7 g.; Fraction G: b.p. 57–61° (5 mm.), n_D^{20} 1.4426, 3.2 g. All three fractions were found to contain halogen. Fraction E (Found: C, 72.76; H, 13.61) was unsaturated and contained presumably a mixture of the olefin and the secondary chloride. Fractions F and G (Found: Mol. wt., 195) were probably a mixture of the secondary chloride, the coupling product (C₁₂ compound) with the Grignard reagent, and some dimeric substance. The combined yield of these three fractions corresponded to 34–38% of the starting material.

(c) The residue (1.1 g.; Found: Mol. wt., 244) was purified by molecular distillation. A viscous liquid was obtained (n_D^{20} 1.4650) which was free of halogen. It was probably a dimer (6%).

Calc'd for C₁₈H₃₈: Mol. wt., 254. Found: Mol. wt., 244.

The gas obtained from the reaction was analyzed by the method of Kharasch, Lewis, and Reynolds (5). It was found to contain 60% of propane and 40% of propylene.

SUMMARY

1. It has been established that di-*tert*-butylcarbonyl chloroformate decomposes when heated at 110° into di-*tert*-butylcarbonyl chloride and 2,3,4,4-tetramethylpent-1-ene.

2. Di-*tert*-butylcarbonyl chloride decomposes when treated with a Grignard reagent and cobaltous bromide to give 2,3,4,4-tetramethylpent-1-ene and 2,2,4,4-tetramethylpentane.

3. The results recorded in 2 suggest that migration of a methyl group takes place in the rearrangement of the free di-*tert*-butylcarbonyl radical.

4. The preparation of a number of new compounds is described.

CHICAGO 37, ILLINOIS

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