Vinyl cyanoacetate,[16] b.p. 49–50° (0.45 mm.), $n^{20}D$ 1.4410; infrared bands at 2240 (CN), 1754 (C=O), 1644 cm.$^{-1}$ (C=C).

Anal. Calcd. for $C_5H_5O_2N$: C, 54.05; H, 4.50; N, 12.61. Found: C, 54.36; H, 4.41; N, 12.56.

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[16] Prepared by the method of R. L. Adelman, *J. Org. Chem.*, **14**, 1057 (1949).

Acknowledgment.—The writer wishes to acknowledge gratefully helpful discussions with Drs. G. S. Hammond, W. D. Emmons, M. F. Hawthorne and K. S. McCallum.

HUNTSVILLE, ALABAMA

[CONTRIBUTION FROM HICKRILL CHEMICAL RESEARCH LABORATORY]

The Reaction of Carbalkoxycarbene with Saturated Hydrocarbons[1]

BY W. VON E. DOERING[2] AND L. H. KNOX

RECEIVED APRIL 27, 1956

In a previously unknown reaction, the photochemical decomposition of diazoacetic ester in saturated hydrocarbons R–H leads to the formation of saturated esters, RCH_2COOR', in yields of 30–50% of theory based on diazoacetic ester. Cyclopentane and cyclohexane give the esters of cyclopentane- and cyclohexaneacetic acids, respectively. The reaction of *n*-pentane and methyl diazoacetate gives the methyl esters of 3-ethylpentanoic, 3-methylhexanoic and heptanoic acids; 2,3-dimethylbutane and methyl diazoacetate give the methyl esters of 4,5-dimethylhexanoic and 3,3,4-trimethylpentanoic acids. A slight preference for the more highly substituted C–H bonds can be detected.

In our study of the photochemically induced reactions of aliphatic diazo compounds with various classes of organic molecules, this paper is a report on some of the results obtained with diazoacetic ester and saturated hydrocarbons. Although reactions of ethyl diazoacetate with a variety of unsaturated compounds are widely recorded in the literature,[3] there are no instances of reaction with saturated hydrocarbons and few that appear to have involved the carbon–hydrogen bond. In the thermally induced reaction of *p*-xylene,[4] mesitylene[5] and durene[6] with diazoacetic ester, 4-methyl-, 3,5-dimethyl- and 2,4,5-trimethylhydrocinnamic ester, respectively, have been isolated. In a pioneering study of the photolysis of diazomethane in organic solvents, Meerwein, Rathjen and Werner[7] isolated ethyl *n*-propyl and ethyl isopropyl ether from ethyl ether, α- and β-methyltetrahydrofuran from tetrahydrofuran and methyl isopropyl ether and *sec*- and *t*-butyl alcohols from isopropyl alcohol. From the photolysis of diazomethane in benzene, Doering and Knox[8] obtained toluene in addition to tropilidene.

In each of these examples, the structure of the product is consistent with direct attack on the carbon–hydrogen bond, but the presence of unsaturation or an oxygen atom in the examples cited obliges one to consider more involved mechanisms. Indeed, Huisgen[3] proposed the initial formation of an "ylid" intermediate to explain the ethyl ether–diazomethane reaction.

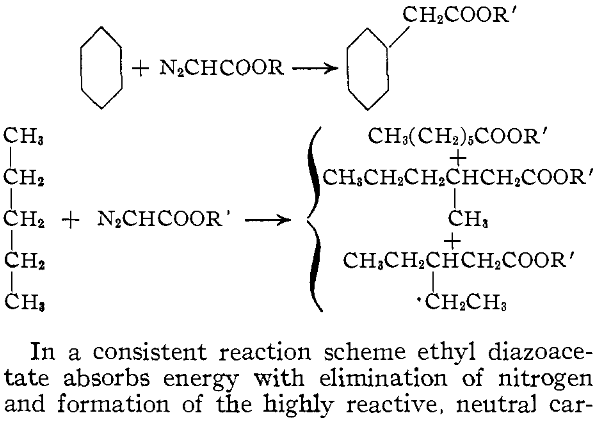
Reaction with saturated hydrocarbons offers no possibility for initial complex formation nor for reaction with unshared electrons or unsaturated bonds. Both its apparent simplicity and novelty encouraged the present study.

When dilute solutions of ethyl diazoacetate in saturated hydrocarbon solvent are irradiated, upwards of 80% of the nitrogen is smoothly evolved at a rate (measured semiquantitatively) which is independent of the temperature, the nature of the hydrocarbon and the dilutions employed. With a molar ratio of ethyl diazoacetate to hydrocarbon of 1:100 the rates of nitrogen evolution in cyclohexane at 12 and 80° and in 2,3-dimethylbutane at 12° were identical.

The reaction of cyclopentane and cyclohexane with ethyl diazoacetate afforded cyclopentaneacetic acid ethyl ester and cyclohexaneacetic acid ethyl ester in 48 and 42% yields, respectively. Ethyl cyclohexaneacetate was also obtained in comparable yield by heating cyclohexane and ethyl diazoacetate in a sealed tube at 150° for 8 hr. In the presence of copper powder, however, addition of ethyl diazoacetate to refluxing cyclohexane afforded only ethyl fumarate.

$$N_2CHCOOR' \xrightarrow[\text{or heat}]{\text{light}} N_2 + H—\ddot{C}—COOR'$$

$$H—\ddot{C}—COOR' + RH \longrightarrow RCH_2COOR'$$



In a consistent reaction scheme ethyl diazoacetate absorbs energy with elimination of nitrogen and formation of the highly reactive, neutral car-

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[1] Presented at the 119th Meeting of the American Chemical Society, Boston, Mass., April 2, 1951, "Abstracts of Papers," p. 2M.

[2] Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

[3] R. Huisgen, *Angew. Chem.*, **67**, 439 (1955).

[4] E. Buchner and P. Schulze, *Ann.*, **377**, 259 (1910).

[5] E. Buchner and K. Scholtenhammer, *Ber.*, **53**, 865 (1920).

[6] L. I. Smith and P. O. Tawney, THIS JOURNAL, **56**, 2167 (1934).

[7] H. Meerwein, H. Rathjen and H. Werner, *Ber.*, **75**, 1610 (1942).

[8] W. von E. Doering and L. H. Knox, *ibid.*, **72**, 2305 (1950); **73**, 828 (1951); **75**, 297 (1953).

bethoxy carbene.[9] The carbene then attacks a carbon–hydrogen bond of the hydrocarbon inserting itself between the two atoms forming the saturated ester.

Whether methylene and other carbenes are diamagnetic or paramagnetic will not be discussed in this paper nor will a choice between a single transition state formulation and several, obvious mechanisms with discrete intermediates be made. No complex of diazoacetic ester and the hydrocarbon can reasonably precede the loss of nitrogen, whether photochemically or thermally induced. The copper-induced decomposition appears not to lead to the same, highly reactive intermediate produced thermally or photochemically. In return for the lower temperature at which copper effects the loss of nitrogen, a less reactive intermediate is formed. Although it is still sufficiently reactive to add to a double bond (*cf.* the formation of ethyl norcaranecarboxylate from cyclohexene and ethyl diazoacetate),[10] it does not react with either the saturated carbon–hydrogen bond or with benzene.[11] Yates has observed a similar effect on the reactivity of the intermediate in the copper-catalyzed decomposition of diazoketones. He offers an explanation[12] which seems to be generally applicable and certainly accommodates the present observation.

From the reaction of 2,3-dimethylbutane and *n*-pentane with diazoacetic ester two and three products, respectively, are to be expected. With ethyl diazoacetate in each case only a single product was isolated: 4,5-dimethylhexanoic acid ethyl ester from 2,3-dimethylbutane and 3-methylhexanoic acid ethyl ester from *n*-pentane. It was clear, however, that mixtures had been formed.

Reactions of the four hydrocarbons were repeated with methyl diazoacetate when it was found that the methyl esters were sufficiently more volatile to be conveniently separable by vapor–liquid partition.

The product from cyclopentane and methyl diazoacetate had an infrared spectrum truly superimposable on that of authentic methyl cyclopentaneacetate and appeared to be homogeneous on vapor–liquid partition. Accordingly, there is still no evidence for the insertion of a carbene into a saturated carbon–carbon bond. However, the search for such a reaction is being continued.

From pentane and methyl diazoacetate, two fractions were isolated by vapor–liquid partition: one identified as pure methyl heptanoate, the second as a mixture of 68 ± 2% of methyl 3-methylhexanoate and 32 ± 2% of methyl 3-ethylpentanoate. The relative amounts of the products show little selectivity: methyl heptanoate, 38%; methyl 3-methylhexanoate, 42%; and methyl 3-ethylpentanoate, 20%. Based on the relative number of the three types of hydrogen in *n*-pentane and no selectivity, the theoretical ratios would have been 50.0, 33.3 and 16.7, respectively. There is clearly a little discrimination between primary and secondary hydrogens favoring the secondary which react 1.62 times faster than the primary. There is no discrimination between the two types of secondary hydrogen.

With 2,3-dimethylbutane and methyl diazoacetate a mixture of methyl 4,5-dimethylhexanoate (76.5%) and (presumably) methyl 3,3,4-trimethylpentanoate (23.5%)[12a] was formed in a total yield of 30% of the theoretical. The statistical, non-discriminatory ratio of these products would have been 85.7 to 14.3. From these data it appears that the tertiary hydrogen reacts 1.84 times faster than the primary.[13]

Experimental[14]

General Procedure for the Photochemical Decomposition of Ethyl and Methyl Diazoacetate in Saturated Hydrocarbons.—Solutions of one molar equivalent of ethyl diazoacetate in 75–100 molar equivalents of the hydrocarbon were irradiated in a round-bottom, Pyrex flask fitted with an upright, water-cooled condenser. General Electric RS reflector sun-lamps served as the light source. The condenser was attached through a drying tube packed with Drierite to a gas buret and the evolved nitrogen was collected over water. The temperature of the reaction mixtures was maintained between 12–17° by means of water running over the flask.

Semi-quantitative measurements of the rate of nitrogen evolution were made in cyclohexane at 12° and at 80° (the temperature of the refluxing mixture) and in 2,3-dimethylbutane at 12° employing 5.0 g. (0.044 mole) of ethyl diazoacetate dissolved in 4.4 moles (1:100) of the hydrocarbon. The volume of nitrogen evolved (uncorrected for the vapor pressure of the hydrocarbon) amounted to 85, 88 and 91%

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[9] Although the word "carbene" has been defined ("A bitumen soluble in carbon disulfide but insoluble in carbon tetrachloride"; "Webster's New International Dictionary," 2nd Ed., G. & C. Merriman Co., Springfield, Mass., 1952, p. 402) and has appeared in *Chemical Abstracts* 15 times during its history, the word seems so well suited to describe the class of divalent carbon compounds having two, singly covalently bonded substituents and two unshared electrons that one appears justified in assuming the innoxious risk that the new meaning become known in the same, presumably chemical, circle presently aware of the old. In its new meaning (collaboratively conceived by W. von E. Doering, S. Winstein and R. B. Woodward in a nocturnal Chicago taxi and later delivered diurnally in Boston[1]) "carbene" is synonymous with one of the several definitions of "methylene" and has already begun to find use in the chemical literature [C. D. Gutsche and M. Hillmann, *ibid.*, **76**, 2236 (1954); W. von E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954); E. Vogel, *Fortschr. chem. Forsch.*, **3**, 430 (1955), see pp. 438–440; W. E. Parham, H. E. Reiff and P. Swartzentruber, This Journal, **78**, 1437 (1956)].

[10] F. Ebel, R. Brunner and P. Mangelli, *Helv. Chim. Acta*, **12**, 19 (1929).

[11] W. von E. Doering and L. H. Knox, unpublished results.

[12] P. Yates, This Journal, **74**, 5376 (1952).

[12a] The structure of this compound has been proved neither by synthesis nor by degradation; it is assigned by analogy.

[13] Although these data lack sufficient accuracy to justify a refined discussion, they indicate an order of reactivity 3° > 2° > 1°. In a single transition state mechanism this order would be interpreted by examining the resonance structures written below and noting that the electronegative substituent on the carbene leaves a partial positive

charge on the carbon atom of the C–H bond being attacked. Discounting all other factors, the expected variation of energies would then be 3° < 2° < 1°.

[14] Melting points are corrected

of theory, respectively. The time curves of nitrogen evolution were essentially identical in all three examples.

Photochemical Decomposition of Ethyl Diazoacetate in Cyclohexane. (a) **At 15°.**—A solution of 10.0 g. (0.088 mole) of ethyl diazoacetate in 950 ml. (8.8 mole) of cyclohexane (Phillips Petroleum Co., Tech. Grade; >95%) was irradiated with two sun-lamps, at 14–16° until nitrogen ceased to be evolved (27 hr.). Distillation of the residual oil remaining after removal of cyclohexane gave 6.3 g. (42.6%) of ethyl cyclohexaneacetate, b.p. 102–103° at 25 mm. with no forerun (reported[15] b.p. 100° at 17 mm.).

Saponification of 3.4 g. (0.02 mole) of the ester by refluxing for 8 hr. with aqueous potassium hydroxide solution (5.6 g. in 25 ml.) and isolation of the product in the usual manner afforded 2.3 g. (79.2%) of cyclohexaneacetic acid, b.p. 111–112° at 3 mm. (reported[16] b.p. 117° at 5 mm.). The infrared spectrum was identical with that of an authentic sample, m.p. 28°, kindly furnished by the Dow Chemical Company. The amide, prepared from the acid with thionyl chloride and aqueous ammonia, melted at 168–169° in admixture with an authentic sample, m.p. 167–168°.

Anal. Calcd. for $C_8H_{15}NO$: C, 68.0; H, 10.7; N, 9.9. Found: C, 67.7; H, 10.3; N, 9.7.[17]

(b) **At 80°.**—A solution of 10.0 g. of ethyl diazoacetate in 950 ml. of cyclohexane was irradiated *under reflux* with one sun-lamp which served as a source of both heat and light, until nitrogen ceased to be evolved (28 hr.). The yield of ethyl cyclohexaneacetate, b.p. 62–63° at 1.5 mm., amounted to 6.1 g. (41.2%).

Thermal Reaction of Ethyl Diazoacetate and Cyclohexane.—A mixture of 5.0 g. of ethyl diazoacetate and 25 ml. of dry cyclohexane was heated in a sealed tube at 180° for 8 hr. From three such runs, 8.3 g. (37.4%) of ethyl cyclohexaneacetate was obtained, b.p. 89–91° at 13 mm. The ester was saponified by refluxing 7 hr. with 100 ml. of 7% alcoholic potassium hydroxide to give 4.9 g. (71.1%) of cyclohexaneacetic acid, b.p. 116–118° at 5 mm.; amide, m.p. 168–169°, undepressed on admixture with an authentic sample.

Reaction of Ethyl Diazoacetate with Cyclohexane in the Presence of Powdered Copper.—To a vigorously stirred suspension of 5 g. of copper powder in 550 ml. of refluxing, dry cyclohexane, 10.0 g. of ethyl diazoacetate in 200 ml. of cyclohexane was added dropwise over a period of 9.5 hr. Nitrogen was evolved smoothly during the addition. Removal of catalyst by filtration and solvent by distillation afforded an oil from which 3.0 g. of colorless product was obtained, b.p. 93–97° at 12 mm. Saponification of 2.5 g. of the ester with aqueous potassium hydroxide (5 g. in 25 ml. of water) afforded a solid acid which was recrystallized from water to give 0.91 g. (54.2%) of fumaric acid, m.p. 294–296°; m.p. 293–296° in admixture with an authentic sample of m.p. 293–296°.

Photochemical Decomposition of Ethyl Diazoacetate in Cyclopentane.—A solution of 10.0 g. of ethyl diazoacetate in 600 ml. of dry cyclopentane (Phillips Petroleum Co., Pure Grade, >99%) was irradiated with two sun-lamps until nitrogen ceased to be evolved (44 hr.). Distillation of the oil remaining after removal of cyclopentane gave 6.5 g. (48%) of ethyl cyclopentaneacetate, b.p. 73–77° at 12 mm. Redistillation afforded 4.9 g. of the ester, b.p. 77° at 12 mm., n^{20}_{D} 1.4366 (reported[18] b.p. 74–75° at 12 mm.; n^{20}_{D} 1.4357).

A mixture of 4.6 g. (0.03 mole) of the ester and 8.4 g. of potassium hydroxide in 35 ml. of water was refluxed for 9 hr. to give 2.5 g. (65.9%) of cyclopentaneacetic acid, b.p. 117–118° at 12 mm.; n^{19}_{D} 1.4540 (reported[18] b.p. 119–120° at 13 mm.; n^{19}_{D} 1.4527).

The amide, obtained from the acid with thionyl chloride and aqueous ammonia, melted at 150° after two recrystallizations from 50% aqueous methanol (reported[19] m.p. 151°).

Anal. Calcd. for $C_7H_{13}NO$: C, 66.1; H, 10.3; N, 11.0. Found: C, 65.8; H, 10.5; N, 10.9.[17]

Photochemical Decomposition of Ethyl Diazoacetate in *n*-Pentane.—A solution of 10.0 g. of ethyl diazoacetate in 900 ml. of *n*-pentane (Phillips Petroleum Co., Pure Grade, >99%) was irradiated with three sun-lamps until nitrogen ceased to be evolved (22.5 hr.). Distillation of the oil obtained after removal of pentane gave 5.2 g. (38.2%) of 3-methylhexanoic acid ethyl ester as a colorless oil, b.p. 57–58° at 11 mm. On redistillation at 17 mm.; n^{20}_{D} 1.4140 (reported[20] b.p. 176–177° at 756 mm.; n^{20}_{D} 1.4119).

Anal. Calcd. for $C_9H_{18}O_2$: C, 68.3; H, 11.5. Found: C, 68.5; H, 11.4.[21]

The ester obtained above, 3.16 g. (0.02 mole) was saponified by boiling with aqueous potassium hydroxide (5.6 g. in 25 ml. of water) for 9 hr. On working the saponification mixture, the acid, 2.6 g. (88.5%) was obtained as a colorless oil boiling uniformly at 113° and 15 mm.; n^{20}_{D} 1.4230; d^{20}_{4} 0.9216 (reported[22] b.p. 116° at 15 mm.; n^{20}_{D} 1.4222[20]).

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.6; H, 10.8. Found: C, 64.9; H, 10.6.[21]

The amide, obtained from the acid with thionyl chloride and aqueous ammonia, melted at 97–97.5° after two recrystallizations from 25% aqueous ethanol (reported m.p. 97°[20]); m.p. 78–85° in admixture with an authentic sample of heptanoic acid amide, m.p. 95–96°.

Photochemical Decomposition of Ethyl Diazoacetate in 2,3-Dimethylbutane.—A solution of 10.0 g. of ethyl diazoacetate in 900 ml. of 2,3-dimethylbutane (Phillips Petroleum Co., Pure Grade, >99%) was irradiated with two sun-lamps until nitrogen ceased to be evolved (26 hr.). The residual oil obtained after removal of solvent from two such runs was distilled *in vacuo* and the volatile colorless oil, 12.87 g., collected up to 82° at 14 mm. Redistillation afforded 10.4 g. (34.4%) of 4,5-dimethylhexanoic acid ethyl ester, b.p. 80–82° at 13 mm., b.p. 191–193° at atmospheric pressure, n^{20}_{D} 1.4230, d^{20}_{4} 0.9002.

Saponification of 6.9 g. (0.04 mole) of the ester by refluxing with aqueous potassium hydroxide (11.2 g. in 50 ml. of water) for 16 hr. afforded 4.0 g. (69.6%) of 4,5-dimethylhexanoic acid. This acid distilled without forerun at 112° and 7 mm.; n^{25}_{D} 1.4335; d^{25}_{4} 0.9269 (reported, b.p. 80–82° at 1 mm.; $n^{24.5}_{\mathrm{D}}$ 1.4315[23a]; b.p. 92° at 1 mm.; n^{25}_{D}, 1.4278.[23b]).

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.6; H, 11.2. Found: C, 66.6; H, 11.1.[17]

The *p*-bromophenacyl ester, recrystallized twice from 50% aqueous ethanol, melted at 53–54° (reported[23a] m.p. 56–57.5°).

Anal. Calcd. for $C_{16}H_{21}BrO_3$: C, 56.3; H, 6.2; Br, 23.3. Found: C, 55.9; H, 6.4; Br, 22.7.[17]

Photochemical Decomposition of Methyl Diazoacetate in Hydrocarbons.—The general procedure was the same as that used for ethyl diazoacetate described above. Isolation and quantitative analysis in the sequel is mainly by vapor-liquid partition. The Perkin–Elmer Vapor Fractometer Model 154 with the 2-m. stainless steel, type "A" (di-*n*-decyl phthalate) column was employed. Identification of components was based on comparison of infrared spectra of isolated components with those of the authentic material. Quantitative analysis, unless otherwise stated, was obtained from the areas of the curves assuming the thermal conductivity of isomeric materials to be identical.

(a) **Cyclohexane.**—From the irradiation (29 hr.) of 10.0 g. of methyl diazoacetate in 900 ml. of cyclohexane (*vide supra*), distillation gave 5.26 g. (33.7%) of methyl cyclohexaneacetate: b.p. 85–87° at 25 mm.; n^{25}_{D} 1.4442. This material appeared homogeneous in the Vapor Fractometer (N_2; 20 lb.; 145°) and had an infrared spectrum completely superimposable (neat; 0.025 mm. cell) on that of authentic methyl cyclohexaneacetate, prepared from cyclohexaneacetic acid and diazomethane; b.p. 201° at 760 mm.; n^{25}_{D} 1.4458.

(b) **Cyclopentane.**—Distillation of the irradiation (34 hr.) product from 10.0 g. of methyl diazoacetate and 550 ml. of cyclopentane (*vide supra*) gave 4.89 g. (34%) of crude

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[15] G. Darzens, *Compt. rend.*, **144**, 330 (1909).

[16] J. Eijkman, *Chem. Zentr.*, **80**, **II**, 2146 (1909).

[17] Analysis by Dr. W. Manser, Mikrolabor, Universitätsstr. 6, Zürich, Switzerland.

[18] K. Benschkies and J. Scholl, *Arch. Pharm.*, **281**, 328 (1943).

[19] C. D. Nenitzescu, D. A. Isacescu and T. A. Voltrap, *Ber.*, **71**, 2056 (1938).

[20] A. Dewael and A. Weckering, *Bull. soc. chim. Belg.*, **33**, 495 (1924).

[21] Analysis by the Schwarzkopf Microanalytical Laboratory, 56-19 37th Avenue, Woodside 77, New York.

[22] E. Bergmann, *Helv. Chim. Acta*, **20**, 590 (1937).

[23] (a) N. Levin, D. Papa and E. Schwenk, THIS JOURNAL, **69**, 1830 (1947); (b) P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **111**, 299 (1935).

methyl cyclopentaneacetate: b.p. 51–79° at 30 mm.; $n^{25}\mathrm{D}$ 1.4369. Vapor–liquid partition of this material showed a much more volatile contaminant (not yet identified) in addition to the main, homogeneous product. The infrared spectrum (neat; 0.025 mm. cell) of this sample was completely superimposable on that of an authentic sample.

Methyl cyclopentaneacetate was made by condensing sodiomalonic ester with cyclopentyl bromide in boiling toluene (N. Chaudhuri). Saponification of the ester followed by two recrystallizations from ether gave diacid, m.p. 164–165°. Decarboxylation gave cyclopentaneacetic acid, b.p. 115–116° at 5 mm., $n^{25}\mathrm{D}$ 1.4524. The corresponding methyl cyclopentaneacetate, from the acid and diazomethane, boiled at 76–77° at 25 mm., $n^{25}\mathrm{D}$ 1.4368.

(c) **n-Pentane.**—From 10.0 g. of methyl diazoacetate and 900 ml. of pentane (*vide supra*) distillation gave 4.44 g. of liquid; b.p. 63–74° at 40 mm.; $n^{25}\mathrm{D}$ 1.4124. Vapor-liquid partition gave three clearly separated fractions: the first was obtained from *all* reactions and, in amount (19.3%), depended on the way distillation fractions were made; its structure is not yet known but is being determined. The second was not resolved, amounted to 50.0% and by making known mixtures of authentic materials was shown by infrared analysis to consist of 68 ± 2% of methyl 3-methylhexanoate and 32∓% of methyl 3-ethylpentanoate. The third and last fraction was infrared spectroscopically identical with pure methyl n-heptanoate.

Methyl n-heptanoate, from authentic acid and diazomethane, boiled at 174–175°, $n^{25}\mathrm{D}$ 1.4102.

Methyl 3-methylhexanoate was prepared (N. Chaudhuri) (1) by condensing 2-bromopentane and malonic ester to methyl (2-pentyl)-malonic ester (70% of th. yield); b.p. 109–110° at 1 mm.; (2) saponifying to the dicarboxylic acid, m.p. 92–93° after 4 recrystallizations from cyclohexane. Decarboxylation followed by esterification gave the ester, b.p. 163–164°, $n^{25}\mathrm{D}$ 1.4092.

Methyl β-ethylpentanoate was synthesized by N. Chaudhuri by the application of the Arndt–Eistert synthesis to diethylacetic acid. The ester had b.p. 164° and $n^{25}\mathrm{D}$ 1.4130.

(d) **2,3-Dimethylbutane.**—Distillation of the product from 10.0 g. of methyl diazoacetate and 900 ml. of 2,3-dimethylbutane gave 4.74 g. of ester, $n^{25}\mathrm{D}$ 1.4206. Vapor-liquid partition (N_2; 20 lb.; 135°) separated two fractions: the first was identical with the low-boiling impurity reported above. The second (23.5%) was presumed to be methyl 3,3,4-trimethylpentanoate, $n^{25}\mathrm{D}$ 1.4220. *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.3; H, 11.5. Found: C, 68.5; H, 11.6. The third component (76.5%) was methyl 4,5-dimethylhexanoate, $n^{25}\mathrm{D}$ 1.4198. Its infrared spectrum was identical with that of an authentic sample prepared by the method of Levin, Papa and Schwenk.[23a] The methyl ester (b.p. 181°, $n^{25}\mathrm{D}$ 1.4230) was prepared from the acid (b.p. 114–117° at 17 mm., $n^{25}\mathrm{D}$ 1.4378) by diazomethane.

KATONAH, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Disproportionative Condensations. III. Reciprocal Routes to β-Phenylpropiophenones

BY ERNEST F. PRATT AND ALLAN P. EVANS[1]

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It has been shown that a variety of *para*-substituted β-phenylpropiophenones may be prepared in good yield by the reaction of an acetophenone with a benzyl alcohol in the presence of a catalytic amount of the corresponding lithium benzylate. The reaction was facilitated and followed by distilling the by-product water into a trap. It was possible, by this means, to determine readily the effects on the rate of changing the main variables. Predictions, based on the proposed reaction course, that a given β-phenylpropiophenone would be formed as readily from a benzaldehyde and a phenylmethylcarbinol as from the corresponding benzyl alcohol and acetophenone were confirmed experimentally.

In preceding papers of this series the condensation of a primary alcohol at the *beta* carbon of a second alcohol molecule[2] and at the nitrogen of an aniline[3] were discussed. It has now been found that when a xylene solution containing benzyl alcohol, acetophenone and catalytic amounts of lithium benzylate is refluxed until the theoretical amount of water is removed β-phenylpropiophenone is obtained in about 70% yield.

$$C_6H_5CH_2OH + CH_3COC_6H_5 \longrightarrow C_6H_5CH_2CH_2COC_6H_5 + H_2O \quad (1)$$

The related condensation of normal aliphatic alcohols[4] and of benzyl alcohol[5] with fluorene has been reported recently.

Since, as shown in Table I, various *para*-substituted β-phenylpropiophenones are obtained in good yields in one step this method offers advantages over the two-step process *via* benzalacetophenones[6] and the four-step processes *via* dibenzyl[7] or di-*t*-butyl malonates.[8]

TABLE I

EFFECT OF CHANGING THE *para*-SUBSTITUENTS

para-Substit.	$t_{50\%}$, min.	Water, %	Product, % A[b]	B[c]
para-Substd. acetophenones and benzyl alcohol				
Cl–	355	105	62	75
H–	530	101	69	82
CH_3–	635	97	69	79
CH_3O–	690	99	74	81
CH_3O–[a]	490	100	65	71
para-Substd. benzyl alcohols and acetophenone				
Cl–	445	101	68	78
H–	530	101	69	82
CH_3–	350	105	67	71
CH_3O–	385	99	69	75

[a] In this experiment both reactants contained a *p*-methoxyl group. [b] The yield of pure recrystallized product obtained directly. [c] The yield including material obtained by treatment of by-product with chromic anhydride.

The action on acetophenone of potassium benzylate in dilute (1 *N*) solution in benzyl alcohol at the reflux temperature was studied by Mastagli.[9] 1,3-Diphenyl-1-propanol, the product desired in that study, was obtained free of β-phenylpropiophenone when the reaction time was two hours. From a single experiment, not described in detail, at a shorter reaction time a good yield of crude β-phenylpropiophenone was reported. It is evident

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(1) From the M.S. thesis of A. P. Evans, May, 1953.

(2) E. F. Pratt and D. G. Kubler, THIS JOURNAL, **76**, 52 (1954). See also H. Machemer, *Angew. Chem.*, **64**, 213 (1952).

(3) E. F. Pratt and E. J. Frazza, THIS JOURNAL, **76**, 6174 (1954).

(4) K. L. Schoen and E. I. Becker, *ibid.*, **77**, 6030 (1955).

(5) Y. Sprinzak, *ibid.*, **78**, 466 (1956).

(6) R. Adams, J. W. Kern and R. L. Shriner, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1954, p. 101.

(7) R. E. Bowman, *J. Chem. Soc.*, 325 (1950).

(8) G. S. Fonken and W. S. Johnson, THIS JOURNAL, **74**, 831 (1952).

(9) P. Mastagli, *Ann. chim.*, **10**, 281 (1938).