

at 56° under vacuum; therefore, drying at room temperature is recommended.

Acknowledgment.—The authors wish to thank Dr. Fred Kaplan for his helpful discussions and aid in interpreting the pmr spectra and to Mr. Francis E. Stary who ran the pmr spectra. Mr. Leslie Lytle's assistance with some of the syntheses is appreciated.

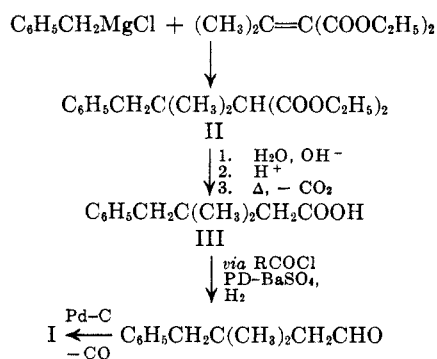
A New Method of Introducing the Neopentyl Group¹

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Because of interest in the behavior of compounds containing neopentyl groups,³ methods of synthesis for such compounds other than the known ones⁴ were in demand. In this paper, a new method by which one can construct the neopentyl group is illustrated by the synthesis of neopentylbenzene (I). Although this method of synthesis is not recommended over some known⁴ methods for neopentylbenzene itself, it may be of value in other cases involving neopentyl-like structures not so readily made by the previously published methods⁴ or where C¹⁴ or D are needed.



There is a feature of interest regarding the reaction of benzylmagnesium chloride with diethyl isopropylidenemalonate. The reaction takes place to give II exclusively, as shown by vpc analysis of the distilled product, and no ring-substitution products as are often found in reactions of benzyl-type Grignard reagents.

Originally, decarboxylation of III to I was intended. However, when attempted decarboxylation failed (copper or copper chromite in quinoline), the alternate route *via* the Rosenmund reduction and decarbonylation⁵ was followed. Although not generally practiced, this route may be generally preferable when decar-

boxylation of an acid occurs in poor yield or when the temperature needed for decarboxylation is too high for the molecule in question. Often, the temperature needed for decarbonylation may be lower than that needed for decarboxylation.

Experimental Section⁶

Diethyl (α,α -Dimethylphenethyl)malonate (II).—In the best of a few runs, a solution of the Grignard reagent, prepared in 97% yield (by titration) by the addition of 100 g of benzyl chloride to 20.0 g of magnesium (2300 ml of ether in all) at a rate sufficient to maintain the ether at reflux, was added to a solution of 155 g of diethyl isopropylidenemalonate,⁷ bp 110–112° (9 mm), in 200 ml of ether containing 12.0 g of purified cuprous chloride,⁸ at such a rate as to maintain a gentle reflux for 2 hr, and was then cooled, treated with saturated ammonium chloride solution, and worked up as usual. Distillation through a 30 × 2.5 cm column packed with glass helices yielded 122 g (54%) of pure IIa: bp 163–165° (4 mm); one peak by vpc analysis on a 2 ft × 0.25 in. 10% SE-30 (silicone gum rubber) on 60–80 Chromosorb P column; infrared band at 5.85 μ ; nmr (CCl₄), δ 1.08 (singlet, 6 H, CCH₃), 1.20 (triplet, 6 H, $J \approx 7$ cps, CH₃ of ethyl group), 2.83 (singlet, 2 H, CH₂), 3.20 (singlet, 1 H, CH), 4.11 (quartet, 4 H, $J \approx 7$ cps, COOCH₂), and 7.16 (singlet, 5 H, aromatic).

Anal. Calcd for C₁₇H₂₄O₄: C, 69.8; H, 8.2. Found: C, 69.7; H, 8.0.

(α,α -Dimethylphenethyl)malonic Acid (IIb).—After alkaline hydrolysis and acidification, acid IIb was isolated in 93% yield as a colorless solid, mp 167–168° dec, neut equiv 119 (calcd 118).

Anal. Calcd for C₁₃H₁₆O₄: C, 66.1; H, 6.8. Found: C, 66.0; H, 6.8.

3,3-Dimethyl-4-phenylbutanoic Acid (III).—After heating 54.0 g of IIb at 175–177° for 2 hr, the theoretical amount of carbon dioxide had been collected. Distillation afforded 41.6 g (95%) of III as a colorless, viscous liquid: bp 141–142° (2.5–3.0 mm); neut equiv 190 (calcd 192); nmr (CCl₄), δ 1.04 (CCH₃), 2.20 (CH₂COO), 2.66 (CH₂), 7.16 (aromatic), and 12.03 (COOH), all singlets of relative areas 6:2:2:5:1.

Anal. Calcd for C₁₂H₁₆O₂: C, 75.0; H, 8.3. Found: C, 75.2; H, 8.5.

3,3-Dimethyl-4-phenylbutanal (IV).—A suspension of 0.7 g of predried 5% palladium-on-barium sulfate catalyst⁹ in 100 ml of dry toluene was heated at reflux while nitrogen and then hydrogen were bubbled through for 1 hr. After cooling to 60°, 7.0 g of the distilled acid chloride, bp 113.0–113.5° (4.5–5.0 mm), infrared absorption at 5.55 μ , was added. As the temperature was raised to 95° the evolution of hydrogen chloride¹⁰ became brisk and 90% of the theoretical amount was accounted for by titration in 2.5 hr. After cooling under nitrogen the catalyst was filtered and the toluene was removed under reduced

(6) Nmr spectra were determined on a Varian A-60 spectrometer with tetramethylsilane (TMS) as internal standard; δ values are given in parts per million downfield from the TMS resonance (0 ppm). Microanalyses were by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The phrase, "worked up in the usual manner," refers to the following procedure. The organic layer of the reaction products in ether-benzene was washed successively with dilute hydrochloric acid, sodium bicarbonate solution, unless an organic acid was the product, and saturated sodium chloride solution, and was then filtered through an anhydrous magnesium sulfate bed. The solvent was usually removed in a rotary evaporator.

(7) Prepared in 53% yield as described by A. C. Cope and E. M. Hancock, *J. Am. Chem. Soc.*, **60**, 2645 (1938).

(8) This reagent contained 12.0 g of colorless cuprous chloride prepared by treating crude solid cuprous chloride (Baker Analyzed) in a mortar with 10% of its weight of moist hydroxylamine hydrochloride until fumes of nitrous oxide were no longer apparent. The paste was transferred to a filter under nitrogen and the solid was washed with a small amount of distilled water which had been boiled and allowed to cool under nitrogen, then with absolute alcohol and ether, similarly treated. The colorless cuprous chloride was stored in a vacuum desiccator until used. We thank Dr. K. Greenlee for telling us of this method of treatment.

(9) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 627.

(10) The absence of carbon monoxide in gas samples at different times showed that no carbon monoxide was being formed. Analysis was by gas chromatography as described by G. Kyriacos and C. E. Boord, *Anal. Chem.*, **29**, 787 (1957).

(1) This work, supported in part by the Petroleum Research Fund Grant No. 588-C and a special fund of the Ohio State University, formed part of the Ph.D. thesis of N. Gill, 1965.

(2) P. E. O. International Peace Scholarship holder, 1961–1963.

(3) See, for example, M. S. Newman, J. R. LeBlanc, H. A. Karnes, and G. Axelrad, *J. Am. Chem. Soc.*, **86**, 868 (1964).

(4) See for example, A. Bygden, *Ber.*, **45**, 3479 (1912); E. Berliner and F. Berliner, *J. Am. Chem. Soc.*, **71**, 1195 (1949); C. D. Nenitzescu, I. Necsoiu, A. Glatz, and M. Zahman, *Ber.*, **92**, 10 (1959); A. Friedman, W. Gugig, L. Mehr, and E. I. Becker, *J. Org. Chem.*, **24**, 516 (1959); J. H. Brewster, J. Patterson, and D. A. Fidler, *J. Am. Chem. Soc.*, **76**, 6368 (1954), and references cited therein.

(5) M. S. Newman and H. V. Zahm, *ibid.*, **65**, 1097 (1943).

pressure. Distillation afforded 4.5 g (77%) of colorless IV, bp 99–100° (3.5–4.0 mm), infrared absorption at 5.80 μ . This product was not purified further but was decarbonylated as described below. The 2,4-dinitrophenylhydrazone of IV, mp 134–135°, was obtained in high yield after two recrystallizations from ethanol–benzene.

Anal. Calcd for $C_{18}H_{20}N_4O_4$: C, 60.7; H, 5.6; N, 15.7. Found: C, 60.7; H, 5.7; N, 16.0.

Neopentylbenzene (I).—In the best of three runs, a mixture of 4.5 g of IV and 0.2 g of 10% palladium-on-charcoal catalyst⁶ in a small Claisen flask was heated in a fused salt bath. Gas evolution started at 160° and became rapid at 220°. After 4 hr the theoretical amount of carbon monoxide had been evolved. The crude distillate had almost no infrared absorption at 5.80 μ and weighed 3.6 g. A solution of this material in pentane was stirred with water, then worked up as usual except that the pentane was removed on a column to yield 3.4 g (90%) of I as a colorless liquid:¹¹ bp 186.0–187.5°; homogeneous by vpc analysis; nmr (CCl_4), δ 0.89 (singlet, 9 H, CCH_3), 2.43 (singlet, 2 H, CH_2), 7.11 (closely spaced multiplet, 5 H, aromatic); infrared absorption at 8.05, 12.95, and 13.90 μ .

(11) H. Pines and J. T. Arrigo, *J. Am. Chem. Soc.*, **79**, 4966 (1957), give bp 185.6–187.0°.

Reactions of Acetylenic Ketones and an Aldehyde with Phosphorus Pentachloride¹

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Because of interest in the mechanism of reactions of phosphorus pentachloride with ketones³ we report on the reactions of three compounds containing the phenylethynyl group: 3-phenylpropynal (I), 4-phenyl-3-butyn-2-one (II), and 1,3-diphenyl-2-propyn-1-one (III).

On treatment of I with phosphorus pentachloride in methylene chloride for 20 hr at room temperature and in carbon tetrachloride for 20 hr at reflux, there was obtained 1,1-dichloro-3-phenyl-2-propyne (IV) in 94 and 85% yields, respectively. As no dichloroallene was formed in this reaction, a chlorocarbenium ion mechanism³ is probably not involved. Hydrolysis using an aqueous suspension of calcium carbonate⁴ yielded the starting I.



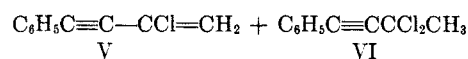
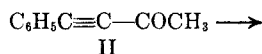
The reaction of II with phosphorus pentachloride was carried out only in methylene chloride at room temperature. A mixture of 2-chloro-4-phenyl-1-buten-3-yne (V) and 3,3-dichloro-1-phenyl-1-butyne (VI) in the ratio of about 3 to 1 was formed. The absence of any dichloroallene in the mixture was established by the lack of a band near 5.1 μ in the infrared spectrum. The compounds V and VI were not isolated in the pure

(1) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. AF-AFOSR-569-64.

(2) The material in this paper was taken from the Ph.D. thesis presented by B. C. Ream to The Ohio State University, 1965.

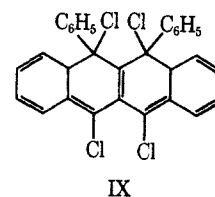
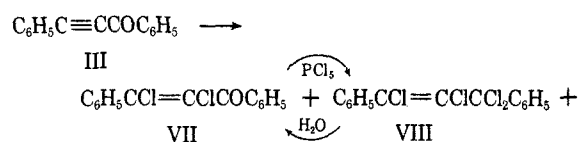
(3) M. S. Newman and L. L. Wood, *J. Am. Chem. Soc.*, **81**, 4300 (1959); M. S. Newman, G. Fraenkel, and W. N. Kirn, *J. Org. Chem.*, **28**, 1851 (1963).

(4) L. J. Andrews and S. L. Linden [*J. Am. Chem. Soc.*, **69**, 2091 (1947)] used this method to hydrolyze 1,1-dichloro-3-phenyl-2-propyne.



state because of decomposition on attempted fractionation. However, analyses and nmr data were sufficient to establish the structures beyond reasonable doubt (see the Experimental Section).

On reaction of III with phosphorus pentachloride in carbon tetrachloride or in methylene chloride, mixtures of 2,3-dichloro-1,3-diphenylpropenone (VII), 1,3-diphenyl-1,2,3,3-tetrachloropropene (VIII), 5,6,11,12-tetrachloro-11,12-diphenyl-10a,12a-dihydronaphthacene⁵ (IX), and III were obtained, the composition of which depended mainly on the ratio of phosphorus pentachloride to III used. We confirm the formation of IX but find it to be a very minor (2–6%) product, the main products in these solvents being VII and VIII, with the latter predominating when 2 equiv of phosphorus pentachloride are used.



The structure of VII was confirmed by adding chlorine to III. In addition, treatment of VII with phosphorus pentachloride yielded VIII which, on treatment with methanol, yielded α,β -dichlorochalcone dimethyl ketal (X) and, with dilute acid, VII.

In none of the ethynyl carbonyl compounds studied was there any evidence for the formation of a dichlorinated allene as might have been expected if reactions with phosphorus pentachloride had taken place *via* a chlorocarbenium ion.³

Experimental Section⁶

1,1-Dichloro-3-phenyl-2-propyne (IV).—3-Phenylpropynal (I), bp 66–69° (1 mm), was prepared by hydrolysis of its diethyl acetal as described.⁷ The diethyl acetal was prepared as described by reaction of phenylethynylmagnesium bromide with ethyl orthoformate.⁸ To a suspension of 29.2 g of PCl_5 in 100 ml of methylene chloride was added a solution of 17.0 g of I in 50 ml of CH_2Cl_2 during 2 hr. After 18 hr at room temperature the mixture was poured on ice and the organic layer was separated, washed, and dried over $MgSO_4$. Distillation afforded 22.6 g (94%) of IV, bp 82–83° (1 mm), infrared absorption at 4.50 μ . The nmr spectrum showed a singlet at τ 3.60 (CCl_2H) in addition to an aromatic complex centered near 2.7.

Anal. Calcd for $C_9H_6Cl_2$: C, 58.4; H, 3.3; Cl, 38.3. Found: C, 58.3; H, 3.2; Cl, 38.6.

(5) C. Dufraisse, A. Etienne, and M. Jolly, *Compt. Rend.*, **231**, 5 (1950). No experimental details or yields were cited.

(6) All melting points were determined on a Fisher-Johns apparatus and are uncorrected. All microanalyses by Micro-Analysis Inc., Wilmington, Del.

(7) C. R. H. Allen and C. O. Edens, Jr., "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 731.

(8) B. W. Howk and J. C. Sauer, *J. Am. Chem. Soc.*, **80**, 4607 (1958).