Anal. Calcd. for $C_{11}H_8BrNO_5$: C, 42.06; H, 2.56; Br, 25.44; N, 4.46. Found: C, 42.42; H, 2.78; Br, 25.62; N, 4.66.

***m*-Nitrobenzylidenepyruvic Acid Phenylhydrazone VI.**—This deep orange product was always accompanied by 30% of the tautomeric bright yellow pyrazolinecarboxylic acid (VII), even when the usual solvent, 50% acetic acid, was replaced by 50% methanol. Separation was accomplished by a tedious fractional crystallization, which was easily followed because of the marked difference in color of the two products.

A solution of 2.4 g. of sodium *m*-nitrobenzylidenepyruvate of 90% purity (0.009 mole) was dissolved in 25 ml. of 50% acetic acid at 60°, and 2.0 ml. (0.02 mole) of phenylhydrazine was added dropwise. Heating was continued for 15 min., during which time the original oil became granular. The orange solid was washed with 50% acetic acid, then with water, and air dried (weight of crude mixture of VI and VII, 2.8 g., 90%). The phenylhydrazone was less soluble in methanol and the pyrazoline was less soluble in ether. The product was conveniently purified and fractionated by dissolving in 150 ml. of ether, washing with 2% hydrochloric acid and with water, drying, and concentrating to crystallization at room temperature. Usually two crops of fairly pure pyrazoline (0.75 g.) were recovered in this way. The residual filtrate was then taken to dryness and the crude phenylhydrazone (1.62 g.) was recrystallized twice from methanol. The compact red-orange crystals melted at 180–181° dec. (melting point tube inserted in the bath 5° below the melting point). The carboxylic acid rather than an inner salt structure[12] was supported by the S-shaped pH titration curve and the pK' value of 4.2 in 50% methanol solution; $\lambda_{max}^{CH_3OH}$ 217 mμ, (ε 18,600), 266 (22,000), and 383 (30,000); $\lambda_{min}^{CH_3OH}$ 236 mμ (ε 13,750) and 320 (5500); and λ_{max}^{THF} 5.93 μ.

Anal. Calcd. for $C_{16}H_{13}N_3O_4$: C, 61.73; H, 4.21; N, 13.50. Found: C, 62.05; H, 4.48; N, 13.84.

5-*m*-Nitrophenyl-1-phenyl-$\Delta^{2,3}$-pyrazoline-3-carboxylic Acid VII.—The crude yellow pyrazoline which separated from ether solution in the previous preparation was recrystallized from acetone, m.p. 161–162°. The carboxylic acid structure is indicated by the pK' of 5.0 in 50% methanol and by the normal S-shaped titration curve. An intense purple color lasting for 2 days was obtained in the Knorr pyrazoline test[12]; the phenylhydrazone (VI) gave a pale orange color, a negative test; $\lambda_{max}^{CH_3OH}$ >215 mμ (ε 16,150), 264 (26,100), and 384 (20,750); $\lambda_{min}^{CH_3OH}$ 233 mμ (ε 15,250) and 322 mμ (ε 5,750); and λ_{max}^{THF} 5.75 and 5.85 μ.

Anal. Calcd. for $C_{16}H_{13}N_3O_4$: C, 61.73; H, 4.21; N, 13.50. Found: C, 61.57; H, 4.31; N, 13.75.

(12) L. Knorr, *Ber.*, **26**, 100 (1893). A few crystals are dissolved in 90% sulfuric acid and a drop of 1% aqueous ferric chloride solution is added. An intense purple color lasting for more than 24 hr. is a positive test.

Ring Openings of Substituted Cyclobutanes Induced by Grignard Reagents. II. 2,2,4,4-Tetramethyl-3-dimethylaminocyclobutanone*

LEONARD WEINTRAUB, ARMIN WILSON, DAVID L. GOLDHAMER, AND DONALD P. HOLLIS[1]

The Bristol-Myers Company, Products Division, Hillside, New Jersey, and Varian Associates, Palo Alto, California

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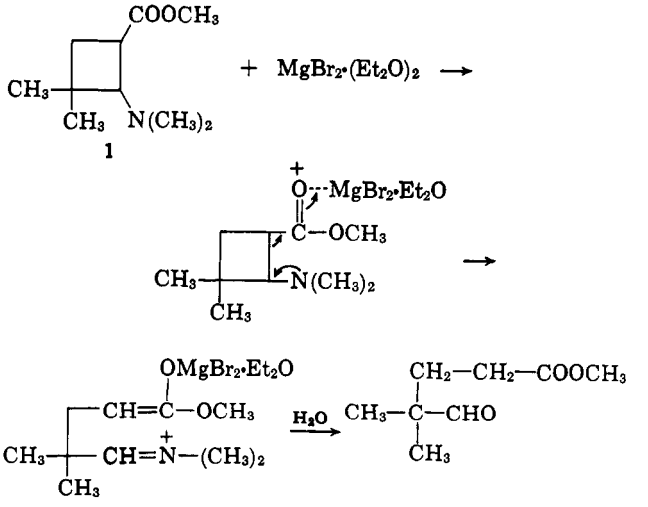
The reaction of 2,2,4,4-tetramethyl-3-dimethylaminocyclobutanone has been studied with (1) the Grignard reagent, (2) phenyllithium, and (3) magnesium bromide. In some instances the ring is opened in a manner analogous to the cyclobutanes studied previously, methyl 2-dimethylamino-3,3-dimethylcyclobutanecarboxylate and tetramethyl-1,3-cyclobutanedione. The extent of ring cleavage brought about by the various reagents is related to the nature of the specific reagent and the structure of a particular ring.

We have recently shown that aryl Grignard reagents react with methyl 2-dimethylamino-3,3-dimethylcyclobutanecarboxylate (1) to cleave completely the cyclobutane ring and produce only open-chain ketones of the type $ArCH(NMe_2)C(Me_2)CH_2CH_2COAr$.[2] With cycloalkyl and alkyl Grignard reagents higher than ethyl, a second open-chain ketone of the type $Me_2NCH_2C(Me_2)CH_2CH_2COR$ was obtained. The reaction of phenylmagnesium bromide with **1** produced 1,5-diphenyl-4,4-dimethyl-5-dimethylaminopentanone-1 in 90% yield. However, phenyllithium gave only the normal carbonyl addition product, diphenyl(2-dimethylamino-3,3-dimethyl)cyclobutylcarbinol.

The reaction of **1** with magnesium bromide etherate was also studied. This reagent effected a 15% conversion of **1** into methyl 4,4-dimethylglutaraldehydate. This reaction must have occurred as shown. First a complex is formed between the carbonyl oxygen and the magnesium bromide. This complex then withdraws the electrons from the α–β bond with the assistance of the unshared pair on the nitrogen atom. Grignard reagents may also open the cyclobutane ring by forming a similar electron-withdrawing complex. However, these reagents can function as nucleophiles as well as electrophiles. They could therefore open the ring by direct nucleophilic attack at the β-carbon. This attack would be facilitated by complex formation between the reagent and the amino nitrogen.



A study of the reactions of Grignard reagents, phenyllithium and magnesium bromide etherate, with other β-aminocarbonyl compounds in the cyclobutane series would be worthwhile. This study has now been ex-

* To Professor Louis F. Fieser.

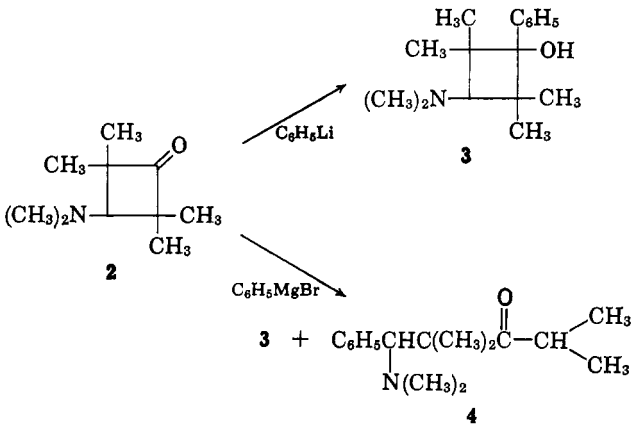
(1) Johns Hopkins School of Medicine, Department of Physiological Chemistry, Baltimore, Md.

(2) L. Weintraub, A. Wilson, D. L. Goldhamer, and D. P. Hollis, *J. Am. Chem. Soc.*, **86**, 4880 (1964).

tended to the available 2,2,4,4-tetramethyl-3-dimethylaminocyclobutanone.[3,4]

Results and Discussion

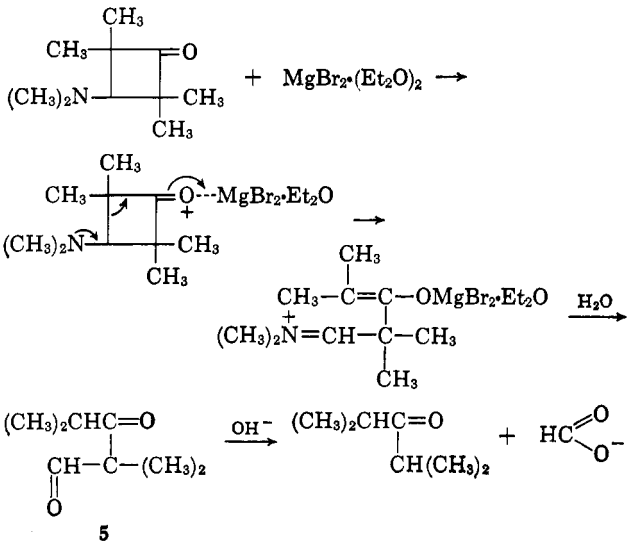
The only substance isolated (89%) from the reaction of phenyllithium with **2** was the carbonyl addition product, 1-phenyl-2,2,4,4-tetramethyl-3-dimethylaminocyclobutanol (**3**). A 90% yield of basic products, consisting mostly of two substances, was obtained from the reaction of **2** with phenylmagnesium bromide. The products were identified as 1-phenyl-1-dimethylamino-2,2,4-trimethyl-pentanone-3 (**4**, 38% of the total) and **3** (53% of the total).



A 73% recovery of basic products was obtained after treatment of **2** with isopropylmagnesium bromide. A very small amount of acyclic ketone, too small to isolate, was obtained as evidenced by very weak infrared absorption at 1705 cm.$^{-1}$. However, v.p.c. indicated only one peak corresponding in retention time to the carbonyl reduction product *trans*-2,2,4,4-tetramethyl-3-dimethylaminocyclobutanol.[5]

When **2** was refluxed in ether for 2 hr. with excess magnesium bromide etherate, and the reaction mixture was poured into water or ammonium chloride solution, a high yield of diisopropyl ketone was obtained as the main product, along with a very small amount of an aldehyde. Rupture of the ring was complete. The formation of diisopropyl ketone could be explained as shown at the top of col. 2.

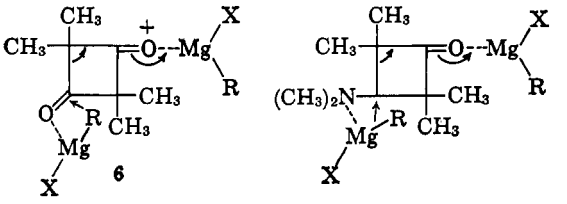
Indeed, when the reaction mixture was worked up in acid, only a small amount of diisopropyl ketone was obtained. The major product was the aldehyde **5**. Pearson and Mayerle have demonstrated the facile base-catalyzed cleavage of α-dimethyl β-diketones.[6] Analogously, **5** was completely converted into diisopropyl ketone by treatment with 1 *N* sodium hydroxide at room temperature for 1 hr.



In contrast to **2**, tetramethyl-1,3-cyclobutanedione, which is known to cleave completely with Grignard and organolithium reagents,[7] was unchanged after treatment with magnesium bromide.

It seems fairly certain that the reaction of **2** with magnesium bromide follows the course suggested for **1**. These reactions are analogous to the fragmentation reactions classified by Grob.[8] The failure of the tetramethyl-1,3-cyclobutanedione ring to open is due to the lack of an electron-donating group β to the electrophilic carbonyl group. The much greater amount of ring opening of **2** compared to **1** may be due to several factors. The ketone carbonyl, being more basic than that of the ester, should form a stronger, more electron-withdrawing complex with the magnesium bromide. Further, the greater angle strain of the cyclobutanone system[9] makes it generally more susceptible to cleavage.

Grignard reagents, as has been mentioned, could open the cyclobutane ring by an alternative mechanism. The ring could be opened by nucleophilic attack of the Grignard reagent at the β-carbon as the carbonyl group complex simultaneously withdraws the electrons from the broken bond. This is illustrated for tetramethyl-1,3-cyclobutanedione and for **2**.[10]



(3) A more meaningful analogy to **1** would have been 2-dimethylamino-3,3-dimethyl cyclobutyl methyl ketone. We have not yet been able to obtain this compound.

(4) After submission of this paper we learned of the work of Professor G. Opitz on reactions of Grignard reagents with β-amino-2,2,4,4-tetramethylcyclobutanones. The amino groups of his compounds were always part of a cyclic system, *viz.*, pyrollidino, hexamethyleneimino, piperidino, morpholino: see G. Opitz and M. Kleeman, *Angew. Chem.*, **76**, 598 (1964); G. Opitz, *ibid.*, **76**, 724 (1964). Professor Opitz obtained essentially the same types of products. He also observed a reductive ring-opening product similar to what we got with compound **1**. We gratefully acknowledge a personal communication from Professor Opitz.

(5) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **28**, 1468 (1963).

(6) R. G. Pearson and E. A. Mayerle, *J. Am. Chem. Soc.*, **73**, 926 (1951).

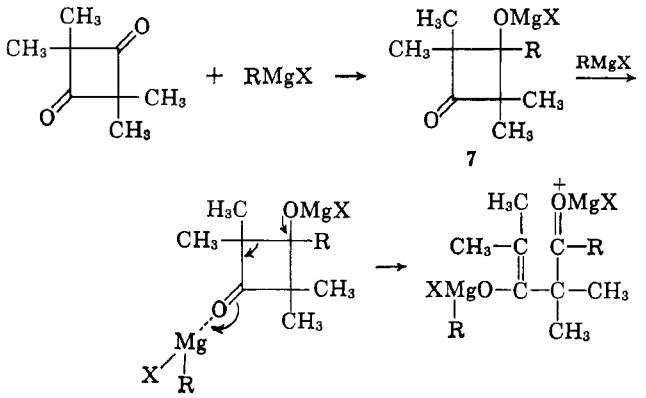
(7) J. L. E. Erickson and G. C. Kitchens, *ibid.*, **68**, 492 (1946).

(8) C. A. Grob, *Bull. soc. chim. France*, 1360 (1950). Grob's classification was kindly pointed out to us by Dr. R. E. Lyle, University of New Hampshire.

(9) Angle strain in small ring compounds can be calculated and correlated with experimental thermochemical values: *cf.* S. Kaarsemaker and J. Coops, *Rec. trav. chim.*, **71**, 261 (1952). The order of decreasing strain is estimated as tetramethyl-1,3-cyclobutanedione > 2,2,4,4-tetramethyl-3-dimethylaminocyclobutanone (**2**) > methyl 2-dimethylamino-3,3-dimethylcyclobutanecarboxylate (**1**) by approximately 6 kcal./mole between each ring system.

(10) In representing the Grignard reagent no implication as to the exact structure is intended. The reagent could be indicated as dimeric with the addition taking place through a six-membered transition state as proposed by J. Miller, G. Gregoriou, and H. S. Mosher [*J. Am. Chem. Soc.*, **83**, 3966 (1961)].

We have stated previously[2] that this mechanism may be preferable to explain the ring opening of **1** with Grignard reagents.[11] While we do not have sufficient evidence to make a choice of mechanism in the ring opening of **2**, we feel that the tetramethyl-1,3-cyclobutanedione ring may also be cleaved in the same manner *via* the transition state **6**. The alternative, which has been implied in the literature,[12] would involve addition of a molecule of Grignard to form intermediate **7**. This would be followed by ring opening as shown.



The intermediate **7** would not be expected to be any more susceptible to ring opening by electron withdrawal than **2**, which it resembles in structure. Its angle strain would be roughly comparable with that of **2** and the "OMgX" would be a poorer electron donor in aiding ring cleavage than the dimethylamino group of **2**. Thus, a mechanism which requires intermediate **7** as an essential step does not explain why the tetramethyl 1,3-cyclobutanedione ring is cleaved much more extensively than that of **2**. Nor does it explain why tetramethyl-1,3-cyclobutanedione undergoes ring opening with the weakly electrophilic organolithiums[13] while **2** does not. However, **6**, the transition state for ring opening by the other mechanism, retains the greater angle strain of the cyclobutanedione and ascribes the ring opening to the addition of the nucleophilic R group. In this case, the great nucleophilicity of organolithiums would be an advantage.[13] The ready ring opening of tetramethyl-1,3-cyclobutanedione upon nucleophilic attack has been reported.[14]

Experimental

Melting points are uncorrected. Microanalyses were performed by Geller Microanalytical Laboratory, Charleston, W. Va.

Magnesium turnings were cut on a lathe from a rod of magnesium of minimum 99.80% purity obtained from Fisher Scientific Co. Alkyl and aryl halides were highest purity grades obtained from Eastman or Matheson. All cyclobutanes were obtained from Tennessee Eastman Co. N.m.r. spectra were determined with a Varian A-60 spectrometer. Infrared spectra were recorded on a Beckman IR-7 spectrophotometer. Gas chromatographic analyses were performed with an F and M Model 500. In all v.p.c. runs reported, the carrier (helium) flow rate was 65 ± 2 cc./min., and the injection port temperature was 325°. Columns were 0.25 in. in diameter and 6 ft. long. The solid support was Chromosorb W.

Reaction of 2,2,4,4-Tetramethyl-3-dimethylaminocyclobutanone (2) with Phenyllithium.—Phenyllithium was prepared under nitrogen from 2.9 g. (0.42 g.-atom) of finely cut lithium in 125 ml. of anhydrous ether and 33.0 g. (0.21 mole) of bromobenzene in 100 ml. of anhydrous ether. After the reagent had been refluxed 1 hr. it was cooled to room temperature and a solution of 16.9 g. (0.1 mole) of 2,2,4,4-tetramethyl-3-dimethylaminocyclobutanone in 50 ml. of anhydrous ether was added with stirring at a rate which maintained gentle reflux. The solution was refluxed for 2 hr. following addition, cooled to room temperature, and added to an ice-cold solution of 75 g. of ammonium chloride in 200 ml. of water. The aqueous phase was extracted with ether. The ether extract was extracted with three 50-ml. portions of 2 *N* hydrochloric acid. The combined acid extracts were brought to pH 10 with 5 *N* sodium hydroxide, and the mixture was again extracted with ether. The ether extract was dried over anhydrous sodium sulfate, filtered free of drying agent, and evaporated *in vacuo* leaving 22.1 g. of gummy solid. A portion was set aside for v.p.c. The remainder was recrystallized twice from hexane to give 13.8 g. of 1-phenyl-2,2,4,4-tetramethyl-3-dimethylaminocyclobutanol (**3**) melting at 120–122°. Pertinent infrared peaks (KBr pellet) are 3360 s (broad), 3080 m, 3040 m, 2820 s, 2780 m, 1600 w, 1495 m, 1380 m, 1365 s, 770 s, 710 s cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{25}NO$: C, 77.68; H, 10.19; neut. equiv., 247.37. Found: C, 77.94; H, 10.19; neut. equiv., 229.

The crude sample was dissolved in ether and gas chromatographed on 10% SE 30 at 175°. There was only one peak with a retention time of 10.2 min. which was identical with that of the purified product.

Reaction of 2 with Phenylmagnesium Bromide.—The Grignard reagent was prepared from 2.67 g. (0.11 g.-atom) of magnesium and 17.4 g. (0.11 mole) of bromobenzene in 35 ml. of anhydrous ether. Titration of the reagent[15] indicated a yield of 0.106 mole. A solution of 16.9 g. (0.1 mole) of **2** in 35 ml. of anhydrous ether was added at a rate which maintained gentle reflux. After addition was complete the green solution was refluxed for 90 min. The reaction mixture was worked up like the phenyllithium reaction to yield 20.7 g. of a semisolid mass from the acid-soluble portion. One gram of acid-insoluble oil was also obtained. This contained a small amount of diisopropyl ketone and was mostly biphenyl as shown by v.p.c. on 10% SE 30 and infrared.

A sample of the acid-soluble material was held aside for v.p.c. The remainder was treated with 15 ml. of ice-cold hexane, and the insoluble solid was filtered. This solid, 10.2 g., melted at 115–122°. After one recrystallization from hexane it melted at 121–122° and its infrared spectrum was identical with that of **3**.

The filtrate from the hexane extraction was evaporated *in vacuo* leaving 8.4 g. of oil. This was distilled at 0.5 mm. through a 6-in. Vigreux column. A middle cut of 5.0 g. of water-white oil boiling at 109.5–111° was 1-phenyl-1-dimethylamino-2,4,4-trimethylpentanone-3 (**4**). Pertinent infrared peaks (smear) are 3090 w, 3060 w, 3030 m, 2830 m, 2790 m, 1705 s, 1600 w, 1585 w, 1493 m, 1380 m, 1365 m, 770 m, 707 s cm.$^{-1}$; n.m.r. doublet (3H) at 1.1 and doublet (3H) at 1.2 [CH (CH_3)$_2$], singlet (3H) at 0.9 and singlet (3H) at 1.4 [C(CH_3)$_2$], singlet (6H) at 2.1 [N(CH_3)$_2$], multiplet (1H) at 3.0–3.5 [CH(CH_3)$_2$], singlet (1H) at 3.9 (N–CH), and singlet (5H) at 7.3 p.p.m. (aromatic protons).

Anal. Calcd. for $C_{16}H_{25}NO$: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.83; H, 9.72; N, 5.66.

The sample of the crude acid-soluble material was gas chromatographed in ether solution on 10% SE 30 at 175°. There were three significant peaks with retention times of 1.15, 7.55, and 10.5 min. corresponding precisely to the retention times of starting material, **4**, and **3**, respectively. The ratios of the various components were determined from an integrated run on a Texas Instruments Servo/Riter integrating recorder. The starting material was 5% of the total, **4** was 38.2% of the total, and **3**

(11) Ring opening by electrophilic withdrawal, as with magnesium bromide, followed by nucleophilic addition of Grignard radical or hydride to the resulting carbonium ion should not be subject to any steric restriction. It was found, however, that steric factors were important in determining whether hydride added to produce $(CH_3)_2NCH_2C(CH_3)_2CH_2CH_2COR$ or Grignard radical added to produce $(CH_3)_2NCH(R)C(CH_3)_2CHCH_2COR$. On changing the Grignard from ethyl to isopropyl to *t*-butyl, the former type of product increased in percentage of the total from 0 to 29 to 100%; see ref. 2.

(12) R. A. Raphael in "Chemistry of Carbon Compounds," Vol. II, part A, E. H. Rodd, Ed., Elsevier Publishing Co., New York, N. Y., 1953, p. 57.

(13) F. A. Settle, M. Haggerty, and J. F. Eastham, *J. Am. Chem. Soc.*, **86**, 2076 (1964).

(14) R. H. Hasek, E. U. Elam, and J. C. Martin, *J. Org. Chem.*, **26**, 4340 (1961).

(15) H. Gilman, E. A. Zoellner, and J. B. Dickey, *J. Am. Chem. Soc.*, **51**, 1576 (1928).

was 53.4% of the total. When corrected for recovered starting material the over-all yield was 89.5% and the yields of **4** and **3** were 34.2 and 47.9%, respectively.

Reaction of 2 with Magnesium Bromide Etherate. Ammonium Chloride Work-Up.—Magnesium bromide etherate was prepared by the method of Storfer and Becker[16] from 30.5 g. of magnesium and 235 g. of ethylene bromide in a total of 2500 ml. of anhydrous ether. The lower, pale yellow, layer contained 2.55 mmoles of $MgBr_2$/ml. by titration for bromide. To a mixture of 200 ml. of this solution and 200 ml. of anhydrous ether was added, at a rapid dropwise rate, an ether solution of 42 g. (0.25 mole) of **2** in 100 ml. of anhydrous ether. The mixture was refluxed 3 hr. after addition during which time a precipitate separated. The mixture was poured into cold ammonium chloride solution, and the resulting mixture was extracted with ether. The combined ether extracts were dried over anhydrous sodium sulfate. After filtering free of drying agent, the ether was removed by distillation at atmospheric pressure through a 12-in. Vigreux column. A residue of 29 g. of light oil remained. This oil exhibited infrared absorption at 2720, 1738, 1715 cm.$^{-1}$ and no peaks at 2820 and 2780 cm.$^{-1}$ (dimethylamino group).[17] The oil was distilled at 75 mm.; 24 g. were collected at a bath temperature of 40°. This was redistilled through a 6-in. Vigreux column at 125–126° at 760 mm. The pure liquid was identified as diisopropyl ketone by comparison of its infrared spectrum to a known sample, refractive index, $n^{26}D$ 1.3988 (lit.[18] $n^{20}D$ 1.4001), and melting point of its 2,4-dinitrophenylhydrazone, 95.5–96° (lit.[18] m.p. 94–98°). The residue from the vacuum distillation was distilled at 75 mm. to give 3.1 g. of the keto aldehyde identified in the next experiment.

Acid Work-Up.—The reaction mixture from 0.48 mole of magnesium bromide etherate and 0.24 mole of **2** was poured into 1 l. of cold 1 *N* hydrochloric acid. A residue of 27.4 g. of oil remained following extraction and evaporation of the ether at 760 mm. through a 12-in. Vigreux column. A sample, gas chromatographed on 10% Carbowax 20M at 100°, was shown to be about 95% of the keto aldehyde previously obtained, retention time 15.5 min., and 5% diisopropyl ketone. The oil was distilled at 75 mm. through a 6-in. Vigreux column and a middle cut of 13 g. of 2-formyl-2,4-dimethylpentanone-3 (**5**) boiling at 103.5° was collected. Pertinent infrared peaks (smear) are 2720 m 1738 s, 1703 s, 1395 m, 1385 s, 1367 s, 1350 m cm.$^{-1}$; n.m.r. doublet (6H) at 1.00 and 1.12 [$(CH_3)_2CH$], singlet (6H) at 1.32 [$(CH_3)_2CC{=}O$], multiplet (1H) at 2.7–3.2 [$CH(CH_3)_2$], singlet (1H) at 8.81 p.p.m. ($HC{=}O$).

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.20; H, 9.71.

Conversion of 5 to Diisopropyl Ketone.—A two-phase system of 0.5 g. of **5** and 50 ml. of 1 *N* sodium hydroxide was stirred vigorously at room temperature for 1 hr. The system was extracted with ether, and the ether extract was dried over anhydrous sodium sulfate. The drying agent was filtered. Gas chromatography of the ether solution on 10% Carbowax 20M at 90° showed the sample to be pure diisopropyl ketone. The ether was removed by distillation at 760 mm. through a 6-in. Vigreux column and the residue was distilled to give 0.3 g. of diisopropyl ketone, b.p. 125–126°.

Treatment of Tetramethylcyclobutane-1,3-dione with Magnesium Bromide Etherate.—After refluxing 35 g. (0.25 mole) of tetramethylcyclobutane-1,3-dione with 0.5 mole of magnesium bromide etherate for 1 hr. and pouring the reaction mixture into ice, 34.5 g. of starting material was recovered.

Reaction of Isopropylmagnesium Bromide with 2.—The Grignard reagent was prepared from 6.1 g. (0.25 mole) of magnesium and 31 g. (0.25 mole) of isopropyl bromide in 75 ml. of anhydrous ether. The gas-collecting system used previously[2] was set up and 16.9 g. (0.1 mole) of **2** in 35 ml. of anhydrous ether were added dropwise. A white precipitate appeared during addition and 1500 cc. of propylene evolved. During the 1-hr. reflux after addition, an additional 50 cc. of propylene was collected. The reaction mixture was poured into cold ammonium chloride solution and worked up in the same fashion as the phenylmagnesium bromide reaction. A crude yield of 11.2 g. of white solid was obtained. The infrared spectrum (CCl_4 solution) was very similar to that of a sample of *trans*-2,2,4,4-tetramethyl-3-dimethylaminocyclobutanol obtained from Tennessee Eastman Co. A very weak C=O peak was present at 1705 cm.$^{-1}$. The crude material was dissolved in ether and gas chromatographed on 10% Carbowax 20M programmed at 15°/min. from 100 to 240°. It had only one peak with a retention time, 5.2 min., identical with that of the above cyclobutanol. After one recrystallization from petroleum ether (b.p. 30–60°), the infrared spectrum and melting point, 72–73°, were identical with those of the known sample.

Acknowledgment.—We wish to acknowledge a helpful discussion with Dr. P. A. Vaughan, Rutgers University, and the technical assistance of Mr. Stanley R. Oles.

(16) S. Storfer and E. I. Becker, *J. Org. Chem.*, **27**, 1868 (1962).
(17) W. B. Wright, Jr., *ibid.*, **24**, 1362 (1959).
(18) "Dictionary of Organic Compounds," Vol. 1, I. M. Heilbron and H. M. Bunbury, Ed., Oxford University Press, New York, N. Y., 1943, p. 875.

Aryl-Substituted Propargyl Alcohols and Related Compounds*,[1]

THOMAS L. JACOBS AND DONALD M. FENTON

Contribution 1779 from the Department of Chemistry, University of California, Los Angeles, California

Received November 16, 1964

The halides prepared from aryl-substituted propargyl alcohols Ia, Ib, and Ic, previously reported to have propargyl structures, III, were shown to have allenyl structures, II. Ethers formed from 1,1,3-triphenyl-2-propyn-1-ol (Ib) or from allenyl halide IIb have propargyl structures. Methyl ethers corresponding to both propargyl and allenyl structures were prepared in the 4,4-dimethyl-1,3-diphenyl-1-pentyn-3-ol series (Ic and IIc). The various acetylene–allene rearrangements involved in reactions of these compounds have been explained on the basis of the stabilized carbonium ions, IV.

Investigations of rubenes[2] and of the possibility of dissociation of highly substituted dipropargyl derivatives into radicals[3–10] involved the synthesis of a variety of aryl-substituted, tertiary propargyl alcohols, I, and replacement of the hydroxyls of these alcohols by halogens. The possibility of an acetylene–allene

* To Professor Louis F. Fieser.

(1) This paper is taken from the Ph.D. Thesis of D. M. Fenton, June 1958. A summary of the work was presented before the Organic Chemistry Division at the 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959; Abstracts, p. 56O. This research was supported by the U. S. Army Research Office (Durham).

(2) See A. Willemart, "Traite de chimie Organique," Vol. 17, V. Grignard, G. Dupont, and R. Lorquin, Ed., Maisson et Cie, Paris, 1949, pp. 1241–1298, and also a series of articles by C. Dufraisse [*Bull. soc. chim. France*, [5] **3**, 1847–1913 (1936)] which discusses the revision of the rubene structure from the incorrect biindanyl to the naphthacene. The latter lists, with references, old and new structures for many rubenes (pp. 1866–1871).

(3) K. Hess and W. Weltzien, *Ber.*, **54**, 2511 (1921).
(4) C. Moureu, C. Dufraisse, and A. S. Houghton, *Bull. soc. chim. France*, [4] **41**, 56 (1927).
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(8) R. S. Sweet and C. S. Marvel, *ibid.*, **54**, 1184 (1932).
(9) J. C. Tsao and C. S. Marvel, *ibid.*, **55**, 4709 (1933).
(10) J. H. Ford, C. D. Thompson, and C. S. Marvel, *ibid.*, **57**, 2619 (1935).