

terminated n.m.r. spectra for diphenyl-, methyldiphenyl-, and triphenylcarbonium ions are given in Fig. 1a-c.

The structures of the carbonium ions were established by several observations. In cases 2, 3, 5, and 7 (Table I), the starting materials were recovered in 60% yield or greater by addition of aged solutions in chlorosulfonic acid to excess, ice-cold, vigorously stirred, aqueous base. The phenyl proton regions of the n.m.r. spectra in cases 2, 4, and 8 were very similar in appearance, though different in position. The ratio of the area of the phenyl proton resonances to that of the methyl (or methine) proton resonance in cases 4, 6, 7, and 8 was very close to the calculated value. The position of the methyl (or methine) proton resonance in cases 4, 6, 7, and 8 was as expected for the carbonium ions (see Table I). The spectra were stable and reproducible under the conditions of the n.m.r. determination.

The data in Table I show that the position of the *para* proton resonance is a reasonable measure of the extent of positive charge on the phenyl ring. Thus, the cases 1 through 8 are arranged in the anticipated order of increasing stabilization of the benzylic carbonium ion by electron release from the phenyl group. Collaterally, the *para* proton resonance moves progressively downfield. By contrast, the *ortho* proton chemical shifts show wide, noncorrelating variations. Columns 5 and 6 show that the separation of the *ortho* and *para* proton resonances fluctuates dramatically, while the separation of the *meta* and *para* proton resonances is more uniform.

A closer consideration of cases 3, 5, 6, and 7, however, puts the behavior of the *ortho* protons on a rational basis. Thus, as the substituent group on the benzylic carbon atom increases in size from hydrogen (case 7) to hydroxyl (case 3) to methyl (case 6) to phenyl (case 5), the *ortho* proton resonance moves upfield relative to the *para*. This is the expected behavior if the increasing bulk of the substituent causes the phenyl groups to twist further out of the plane of the carbonium ion, thus bringing the *ortho* protons more into the shielding region of the adjacent phenyl group. In order to account for the shielding of approximately 0.5 p.p.m. observed for the *ortho* protons of the triphenylcarbonium ion, an angle in the neighborhood of 40° from coplanarity is necessary. This may be compared with the 35° suggested by X-ray analysis of trityl perchlorate.⁸⁻¹¹

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(1961). We thank Dr. Bothner-By for a copy of the program and a deck of IBM cards.

(7) The computer program was run, after minor modifications, on a CDC 1604 computer. A resolution factor of 0.8 (approximately equal to the band width at half-height) gave calculated curves comparable in appearance to the best determined n.m.r. spectra.

(8) K. A. Eriks, A. H. Gomes de Mesquita, and P. S. Aggarwal, 5th Annual Report of the Petroleum Research Fund, 1960, p. 35.

(9) The large *ortho* shielding which we observe for the carbonium ion is claimed to be absent in the corresponding carbanion.¹⁰ Neither data nor space permits a detailed discussion of this discrepancy at present.

(10) V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963).

(11) After the completion of this work we were made aware of related work done independently by George A. Olah on the preparation of stable salts of some of the carbonium ions reported. We thank Dr. Olah for a prepublication account of his results and for his agreement to simultaneous publication.

(12) Fellow of the Alfred P. Sloan Foundation.

DEPARTMENT OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK

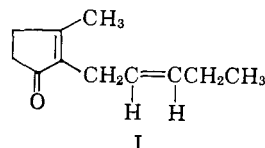
DONALD G. FARNUM¹²

RECEIVED DECEMBER 14, 1963

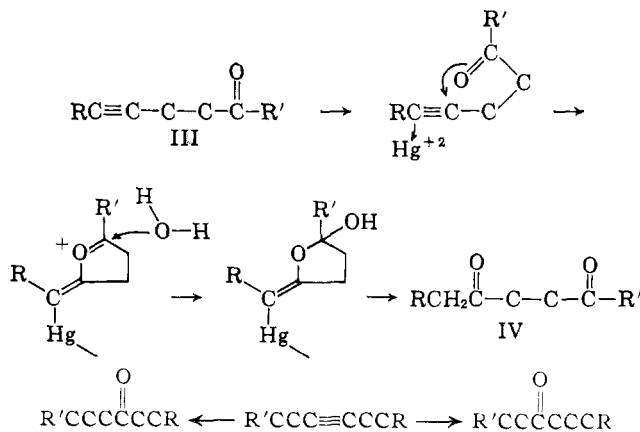
A New Synthesis of 1,4- and 1,5-Diketones

Sir:

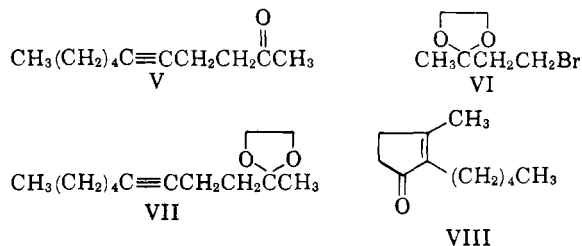
We have devised a new general synthesis of 1,4 and 1,5-dicarbonyl compounds which we have then utilized, *inter alia*, in an efficient synthesis of jasmone (I).¹ It is well known that an unsymmetrically disubstituted acetylene such as II will undergo mercuric ion catalyzed hydrolysis to form both possible carbonyl compounds,² and such hydrations are therefore not normally suited to synthetic purposes.



We were, however, attracted by the possibility that the hydration of an unsymmetrical acetylene of type II could become completely unidirectional when R (or R') is an acyl group (*cf.* III). In such a situation the participation of the carbonyl oxygen in the transition state for the hydration should sufficiently lower its energy to lead to only one of the two possible products, in this case the 1,4-diketone (IV).



The ketones of type III, which were necessary to test this hypothesis, were made by two different routes which we will illustrate with the synthesis of 5-undecyn-2-one (V). In the first sequence, methyl vinyl ketone was converted, by addition of hydrogen bromide followed by exchange ketalization, into the cyclic ketal of 2-bromoethyl methyl ketone (VI)³ which thus becomes readily available, and which served to alkylate



the lithium salt of 1-heptyne in refluxing dioxane to give acetylenic ketal VII in 50% yield, b.p. 85-88° (0.05 mm.). Deketalization with methanolic sulfuric acid led to the desired V in 93% yield, b.p. 79-81° (0.3 mm.), semicarbazone m.p. 104-104.5°.

(1) G. Stork and R. Borch, *J. Am. Chem. Soc.*, **86**, 936 (1964).

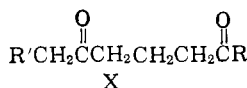
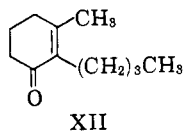
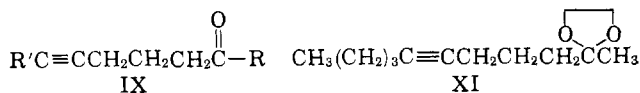
(2) For general references, *cf.* R. Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworths Publications Ltd., London, England, 1955.

(3) For an earlier synthesis of this substance see L. Willmann and H. Schinz, *Helv. Chim. Acta*, **32**, 2151 (1949).

In the second sequence propargylacetone⁴ was converted in 80% yield into its cyclic ketal (VI),⁵ b.p. 75–76° (15 mm.), and this was then alkylated (sodamide–liquid ammonia) with *n*-amyl bromide to give VII, identical with the product from the first route.

When the acetylenic ketone (V) was hydrated by refluxing with hot aqueous methanolic sulfuric acid in the presence of mercuric sulfate *exclusive formation of the 1,4-diketone*, the known 2,5-undecanedione⁶ (IV, R' = CH₃; R = CH₃(CH₂)₄) was observed, b.p. 80–85° (0.1 mm.), 85% yield. The structure of the 1,4-dione was proved by its almost quantitative cyclization to dihydrojasmane (2-*n*-amyl-3-methyl-Δ²-cyclopentenone-VIII), b.p. 79–81° (0.2 mm.), single peak on gas chromatography (20% SE-30 at 175°), λ_{max}^{EtOH} 237 mμ (ε 12,000); further identified as its semicarbazone, m.p. 175–176° as reported.⁷

The exclusive formation of a 1,4-diketone requires carbonyl participation in the hydration step *via* a kinetically and geometrically favored five-membered ring. Participation *via* a six-membered ring should however be possible in acetylenic ketones of type IX, thus *leading specifically to 1,5-diketones X*. This turned out also to be the case: Alkylation of the cyclic ketal of 6-heptyn-2-one (made by alkylation of sodium



acetylide in liquid ammonia with the dioxolane of 3-bromopropyl methyl ketone) with butyl iodide, using sodamide in liquid ammonia, gave the corresponding disubstituted acetylene (XI) in 60% yield. Deketalization with aqueous perchloric acid at room temperature led to the required 6-undecyn-2-one (IX, R = CH₃; R' = CH₃(CH₂)₃) in 93% yield, b.p. 85–87° (0.3 mm.). The acetylenic ketone was transformed on refluxing with aqueous methanolic sulfuric acid and mercuric sulfate into a single diketone (one peak on 20% Craig column at 190°), the structure of which as 2,6-undecanedione (X, R = CH₃; R' = CH₃(CH₂)₃) was confirmed by its base-catalyzed cyclization to 2-butyl-3-methyl-Δ²-cyclohexenone (XII, 82% yield from the acetylenic ketone), b.p. 63–65° (0.2 mm.), λ_{max}^{EtOH} 242 mμ (ε 13,400), only one peak on gas chromatography (Craig, 190°), 2,4-dinitrophenylhydrazone m.p. 142–143° as reported.⁸

Specific hydration of acetylenes to 1,5-diketones *via* δ-carbonyl participation can thus also take place, but it is significant that this hydration is, as expected, markedly slower than with the γ-carbonyl analog. This is shown by the fact that it is possible to define conditions which will result in complete hydration of γ-ketoacetylenes while leaving the δ-keto compounds unchanged.

(4) J. Colonge and R. Gelin, *Bull. soc. chim. France*, 208 (1954).

(5) A different synthesis of this ketal has recently been published by C. Feugeas, *ibid.*, 2579 (1963).

(6) H. Hunsdiecker, *Ber.*, **75**, 447 (1942).

(7) W. Tieff and H. Werner, *ibid.*, **68**, 640 (1935).

(8) A. J. B. Edgar, J. H. Harper, and M. A. Kazi, *J. Chem. Soc.*, 1083 (1957).

(9) Predoctoral Fellow, National Institutes of Health.

THE CHANDLER LABORATORY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK

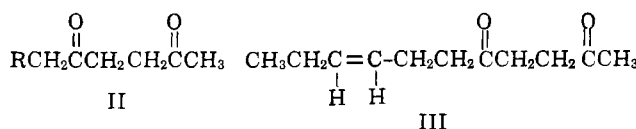
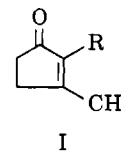
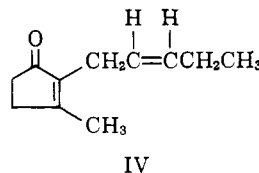
GILBERT STORK
RICHARD BORCH⁹

RECEIVED JANUARY 28, 1964

A Synthesis of *cis*-Jasmone

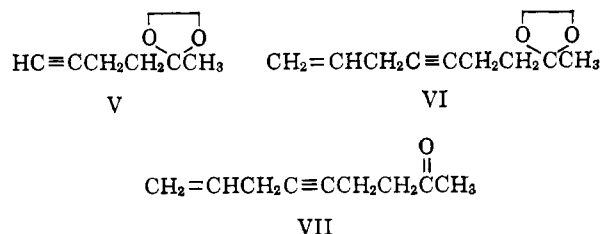
Sir:

It was demonstrated by Hunsdiecker¹ that 2-alkyl 3-methyl-Δ²-cyclopentenones (I) are readily prepared by base-catalyzed cyclization of 1,4-diketones of the general formula II, which were themselves available by a variety of classical methods. The discovery in our laboratory of a new synthesis of 1,4-diketones² suggested the possibility of its use for the preparation of diketone III, the precursor of the well-known jasmone (IV), the important constituent of the essential oil of jasmine.³



We first demonstrated the feasibility of the synthesis for the preparation of 3-methyl-Δ²-cyclopentenones with an unsaturated side chain in the 2-position by synthesizing I (R = allyl).

Alkylation of the magnesium halide complex of V with allyl chloride in the presence of cuprous chloride led to cyclic ketal VI obtained in 61% yield (b.p. 78–81° at 0.5 mm.) and deketalized (91%) as usual to VII, b.p. 70–77° (0.5 mm.), semicarbazone m.p. 99–101°. Hydration in the standard manner gave 83% of 8-nonene-2,5-dione (II, R = allyl), b.p. 75–77° (0.5 mm.), cyclized in 93% yield to the known 2-allyl 3-methyl-Δ²-cyclopentenone (I, R = allyl), b.p. 71–73°, λ_{max}^{EtOH} 236 mμ (ε 12,000), 2,4-dinitrophenylhydrazone m.p. 174–175°.⁴



In the synthesis of diketone III, the precursor of jasmone, two problems were faced which are absent with the simple allyl derivative just described.

The first of these was the occurrence of rearrangements, which we could not suppress, in the formation of *cis*-1-halo 2-pentene. This was solved when it was found that *cis*-2-pentene-1-ol⁵ (VIII) could be transformed in 95% yield, upon treatment with toluene-sulfonyl chloride and powdered sodium hydroxide in the cold, into a crude tosylate which was satisfactory for use in the alkylation of V. In that alkylation, the use of the magnesium complex of V proved unsatisfactory, but success was achieved by the use of the lithium salt of V in liquid ammonia which gave ketal IX in 45% yield, b.p. 100–103°. Deketalization of IX with aqueous perchloric acid (94% yield) at room

(1) H. Hunsdiecker, *Ber.*, **75**, 447 (1942).

(2) G. Stork and R. Borch, *J. Am. Chem. Soc.*, **86**, 935 (1964).

(3) For a review see E. L. Saul, *Am. Perfumer*, **45**, 27 (1943).

(4) L. Crombie, A. J. B. Edgar, S. H. Harper, M. W. Lowe, and D. Thompson, *J. Chem. Soc.*, 3552 (1950).

(5) Cf. J. Colonge and J. Poilane, *Bull. soc. chim. France*, 953 (1955).