[COMMUNICATION NO. 1686 FROM THE KODAK RESEARCH LABORATORIES]

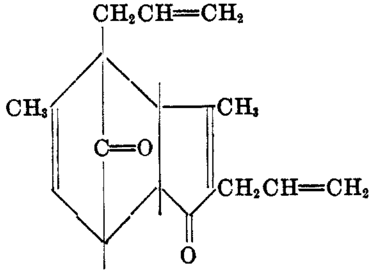
A CARBONYL BRIDGE COMPOUND IN WHICH THE BRIDGED RING IS SATURATED

C. F. H. ALLEN AND J. A. VANALLAN

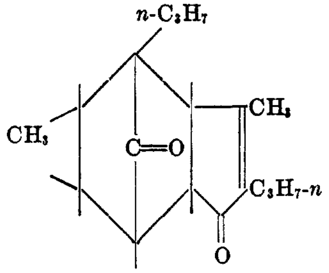
Received October 4, 1953

Up to the present, practically all six-membered rings containing a carbonyl bridge have been of the same general type; there has been a double bond, with aryl substituents in the β,γ-position. The ease with which decarbonylation takes place has been assumed to be connected with the relative position of these two structural features. Attempts to reduce the double bond have been unsuccessful; this failure has been attributed to the presence of the aryl groups which hinder adsorption of the catalyst (1). The purpose of the work described in the present paper was to prepare and study a saturated six-membered carbonyl bridge compound.

A cyclopentadienone having only hydrogen atoms or small substituents should give a dimer that could be successfully reduced. Such a substance is now available in allethrolone, which has recently been shown to form a dimer (I) having the desired linkages (2).



I

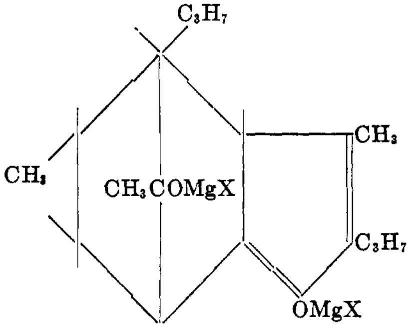


II

The 5-methyl group would not be expected to offer any hindrance to catalytic reduction. The dimer (I) contains four ethylenic linkages, two of which are alike, and two carbonyl groups; three of the former are readily reduced in the presence of the Adams platinum catalyst, the two carbonyl groups remaining unchanged. The product is the tricyclic diketone, II. It is a thick oil, having a spicy, woody odor. It does not decolorize bromine. It forms a mono-2,4-dinitrophenylhydrazone, and a monosemicarbazone which can be converted easily to the dinitrophenylhydrazone. The reagents attack the carbonyl bridge, leaving the α,β-unsaturated ketonic system intact; this is shown by an examination of the absorption spectra, as will be discussed later.

It distills unchanged in spite of the high boiling point (206–210°/3 mm.); there is no change in refractive index after two hours at 240°. This behavior affords proof of the assumption previously made, that easy decarbonylation of carbonyl bridge compounds in six-membered unsaturated rings is dependent upon the presence of a double bond in the β,γ-position. It also shows that saturated six-membered, carbonyl bridge rings are stable to heat, as compared with their unsaturated analogs.

The new diketone (II) resembles all other previously known carbonyl bridge compounds in its quantitative behavior with methylmagnesium iodide; there is one addition and one active hydrogen (evolution of methane). By analogy, the addition has occurred on the bridge, and the active hydrogen arises from the enolic form; the Grignard complex may be represented by structure III.



III

The di-*n*-propyl analog of I was made by similarly dehydrating the phthalate of the corresponding anhydroacetonebenzil, 3-methyl-2-*n*-propyl-2-cyclopenten-4-olone (IV). The reaction was not clean, so the crude product was at once catalytically reduced to give the diketone (II), which was then converted to the semicarbazone for identification.

DISCUSSION OF ABSORPTION SPECTRA

A. Infrared. The specific band at 5.64 μ has recently been shown to be a property of carbonyl bridge across (*para*) a six-membered ring (3). From Cupples' correlation of wavelengths with functional groups, the characteristic absorptions of the latter in compounds with structures similar to the ones described in this paper are known (4). The correspondence of these with the substances described in this paper affords sufficient evidence of similarity of structure. The infrared data are collected in Table I.

TABLE I

INFRARED ABSORPTION

No.	Substance	Endo CO	Conj. CO	C=C	CH_3	CH_3—C	OH
	Allethrolone		5.86	6.06	3.42, 6.96	7.23	2.91
	Cinerolone (3)		5.86	6.06	3.42, 6.96	7.23	2.91
I	Dimer of allethrolone	5.64	5.92	6.12	3.42, 6.94	7.23	
	Monosemicarbazone of I	5.64	6.0[a]	6.45[a]	3.42, 7.02	7.23	
II	Diketone	5.64	5.92	6.15	3.42, 6.85	7.23	
	Monosemicarbazone of II		5.95	6.20	3.42, 6.89	7.23	
	Dinitrophenylhydrazone of II, m.p. 229°		5.98	6.21	3.42, 7.05	7.23	

[a] = CONHR

TABLE II

ULTRAVIOLET ABSORPTION

No.	Substance	λ_{max}	log ϵ	λ_{max}	log ϵ
	Allethrolone	230	4.34	306	1.81
	Semicarbazone of allethrolone	263	4.38		
I	Dimer of allethrolone	239	3.97	310	2.14
	Monosemicarbazone of I	270	4.32		
	Disemicarbazone of I	272	4.25	314	4.86
II	Diketone	239	3.98	309	2.10
	Monosemicarbazone of II	227	4.58	314	1.90

Of particular interest are the structures of the monosemicarbazones. The derivative of the dimer (I) has a band at 5.64 μ, which indicates that the semicarbazide reagent has attacked the carbonyl group of the five-membered ring, whereas in the reduced diketone (II) this band is missing, showing that the semicarbazone is on the bridge. These conclusions are confirmed by the ultraviolet data (Table II).

B. Ultraviolet. It can be seen from Fig. 1 that allethrolone, I, II, and the monosemicarbazone of II have typical α,β-unsaturated carbonyl systems as evidenced by the ultraviolet spectra (5). It has been noted that semicarbazone formation causes (a) a bathochromic and hyperchromic effect in the maximum absorption band over the corresponding carbonyl compound, and (b) a disappearance of the α,β-unsaturated carbonyl R band and that all the λ_{max} fall within the range 267 ± 7.5 mμ (5). All these effects are noted in the semicarbazone of allethrolone, the mono and disemicarbazone of I indicating that, in the case of monosemicarbazone of I, semicarbazone formation has occurred at the α,β-unsaturated carbonyl group. Conversely, the spectrum of the monosemicarbazone of II indicates the endocarbonyl bridge as being the site of attack. The above evidence supports the assignment of structure as given in II.

The ultraviolet curves were obtained with a Cary double-beam recording spectrophotometer, Model 11. The solutions were run against the same thickness of pure solvent (methanol).

The infrared spectra were obtained on a Baird double-beam spectrophotometer using rock-salt optics. Samples were prepared as Nujol mulls or as pressed plates in potassium bromide.

EXPERIMENTAL

3-Methyl-2-n-propyl-2-cyclopenten-4-olone (IV). A mixture of 30 g. of allethrolone (2),[1] 100 ml. of ethyl acetate, 1 ml. of acetic acid, and 0.3 g. of platinum oxide catalyst (6) was reduced at 25–30° and 30-lb. pressure. After removal of the catalyst, the solution was distilled; the fraction, b.p. 80–136°/1 mm., was redistilled, collecting as product the portion, b.p. 123–125°/0.7 mm. The yield was 22 g.; n_D^{25} 1.4960.

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[1] The gift of a generous supply of allethrolone from the Carbide and Carbon Chemicals Company division of the Union Carbide and Carbon Corporation is gratefully acknowledged.

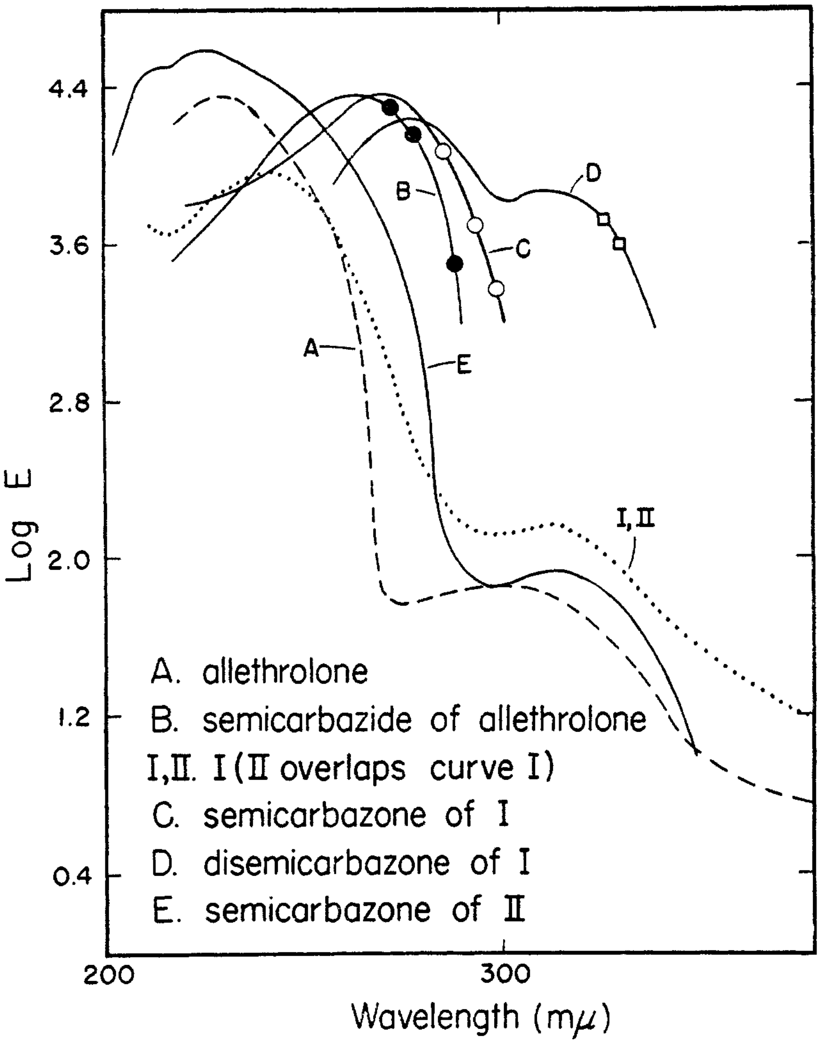

FIG. 1. ULTRAVIOLET ABSORPTION.

Anal. Calc'd for $C_9H_{14}O_2$: C, 70.0; H, 9.1.
Found: C, 69.2; H, 9.1.

The *2,4-dinitrophenylhydrazone*, obtained in the usual way, formed deep red needles from *n*-butyl alcohol, m.p. 203–204°.

Anal. Calc'd for $C_{15}H_{18}N_4O_5$: C, 53.8; H, 5.4.
Found: C, 54.5; H, 5.5.

The acid phthalate (V) of the above was prepared by 7 hours' heating at 110° of 12.5 g. of phthalic anhydride and 12.5 g. of the above ketone. On cooling, the solid was broken up and stirred with dilute aqueous ammonia, followed by extraction with ether. The clear, residual solution was acidified. After standing overnight, the precipitated acid salt was collected, dried in the air, and twice recrystallized from benzene-ligroin; the yield was 14 g., m.p. 124–126°.

Anal. Calc'd for $C_{17}H_{18}O_5$: C, 67.6; H, 6.0.
Found: C, 67.8; H, 6.1.

The allethrolone dimer (I) was obtained as directed by LaForge (2). The *mono-* and *di-semicarbazones* had melting points of 209–210° and 246–247°, respectively. Upon catalytic reduction only three molecular equivalents of hydrogen were taken up, the reduction product having the structure II.

3,5-Dimethyl-1,8-dioxo-2,4-di-n-propyl-3a,4,5,6,7,7a-hexahydro-4,7-methanoindene (II). A mixture of 4.9 g. of allethrolone dimer (I), 0.4 g. of platinum oxide catalyst (6), 150 ml. of dry ethyl acetate, and 3 ml. of glacial acetic acid was reduced, with shaking at room temperature and room pressure. Hydrogen was rapidly taken up, a total of 1530 ml. (84% of the calculated four molecular equivalents) being used. After removal of the catalyst by filtration through Doucil and the solvent by evaporation, the residual oil was taken up in benzene, washed with aqueous sodium carbonate, and distilled. There was obtained 2.6 g. of a clear, pale yellow oil, b.p. 206–210°/3 mm.; n_D^{25} 1.5179. It had not crystallized after one year.

Anal. Calc'd for $C_{18}H_{28}O_2$: C, 78.0; H, 10.2; Act. H, 1.0; Addn., 1.0.
Found: C, 78.1; H, 9.6; Act. H, 0.8; Addn., 0.9 (cold; 1.2 if heated).

The *8-semicarbazone* was obtained by the usual procedure and was recrystallized from ethanol; m.p. 246° dec.

Anal. Calc'd for $C_{19}H_{29}N_3O_2$: C, 69.0; H, 8.8.
Found: C, 69.3; H, 9.0.

The *8-(2,4-dinitrophenylhydrazone)* was prepared both from the diketone and from the semicarbazone in alcoholic solution. Bright yellow crystals, m.p. 229°, were obtained on crystallization from alcohol.

Anal. Calc'd for $C_{24}H_{31}N_4O_5$: C, 63.4; H, 6.8; N, 12.3.
Found: C, 63.6; H, 7.1; N, 12.2.

The same reduced dimer (II) was obtained by treatment of the acid phthalate (V) with alkali; 14 g. of the acid salt was added to a solution of 5 g. of sodium hydroxide in 100 ml. of water. An oil began to separate as soon as the addition was complete; the next day this oil was taken up in benzene, dried, this solvent was removed *in vacuo*, and the residual oil was dissolved in 50 ml. of ethyl acetate. The latter solution was then reduced catalytically as above, using a platinum oxide catalyst (6). The oil (4.1 g., n_D^{25} 1.5165) was then refluxed overnight with 4 g. of semicarbazide hydrochloride in 50 ml. of methanol containing 4 ml. of pyridine. After appropriate manipulation, the semicarbazone, m.p. 246–247°, was obtained, identical by mixture melting point with that of the reduced dimer (II).

Acknowledgment. We are indebted to Miss Davis and Dr. Stewart for the absorption data.

SUMMARY

A carbonyl bridge compound has been prepared, in which there is a saturated six-membered ring, across which the carbonyl group is attached to *para* atoms. The new substance is stable to heat, being distillable and unchanged by long heating. This behavior justifies the previous assumption that easy decarbonylation of unsaturated carbonyl bridge compounds was related to the presence of the ethylenic linkage.

ROCHESTER 4, NEW YORK

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