Additional Spectroscopic Evidence for Cyclopropyl Ring Conjugation

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During the course of other work the 2,4-dinitrophenylhydrazones of methylcyclopropyl and dicyclopropyl ketone were prepared. These derivatives were strikingly red in the crystalline state and appeared to be anomalously colored when compared with the 2,4-dinitrophenylhydrazones of simple dialkyl ketones. Accordingly the ketones listed in Table I were converted to their 2,4-dinitrophenylhydrazones and the ultraviolet absorption spectra of these derivatives were determined in the 350–400 mμ region. As seen in Table I the cyclopropyl derivatives absorb at longer wave lengths than do their open ring model compounds.

TABLE I

Ultraviolet Absorption Spectra of 2,4-Dinitrophenylhydrazones in Methylene Chloride

Parent Ketone	λ_{max} (mμ)	$\epsilon \times 10^{-4}$
Methyl ethyl	368	2.40
Methyl isopropyl	368	2.29
Diisopropyl	369	2.41
Methyl vinyl[a]	374	2.74
Methyl cyclopropyl[b]	375	2.68
Dicyclopropyl[b]	381	2.56

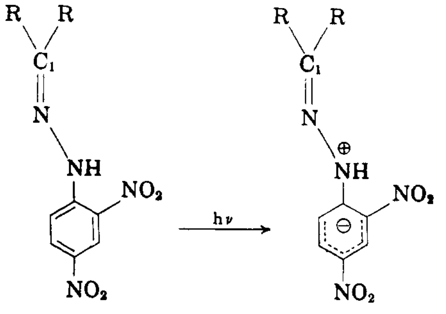
[a] The structure of this compound is verified by characteristic infrared alkene bands at 3020 cm.$^{-1}$ and 1830 cm.$^{-1}$. The absorption characteristic of 2,4-dinitrophenylhydrazones was observed in the 1700–1400 cm.$^{-1}$ region. [b] No alkene bands were found in the infrared spectra of these compounds. Cyclopropyl bands could not be assigned due to the complexity of the spectrum in the 9–10μ region.

DISCUSSION

Ramirez and Kirby[1] have recently presented the results of a very thorough examination of the ultraviolet and infrared absorption spectra of a number of 2,4-dinitrophenylhydrazones. Their results clearly show the dependence of the ultraviolet absorption spectrum of a 2,4-dinitrophenylhydrazone upon the electronic nature of substituent groups and in cases where it was possible to make assignments upon the steric configuration about the C=N bond of the 2,4-dinitrophenylhydrazone. As these authors pointed out, accurate comparisons of spectra can only be made within a stereochemical series. The present study must necessarily ignore this latter effect since no configurational data is available in this series of compounds. However, the comparison of the diisopropyl and the dicyclopropyl derivatives is independent of configuration and it is assumed[2] that in all the other cases compared that the model compound has the same configuration as the compound of prime interest.

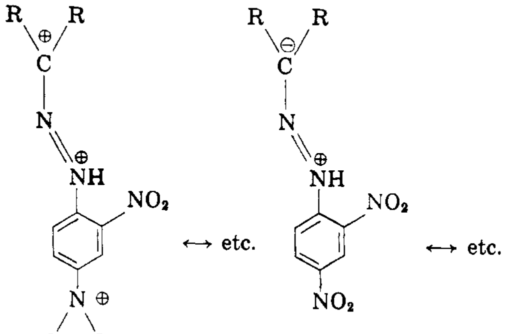
If the electronic transition which produces the 350–400 mμ band of 2,4-dinitrophenylhydrazones is of the type (1) then it is apparent that the ex-

(1)



A

cited state contains a highly conjugated system. As previously stated[1] the *p*-orbital of carbon atom C_1 of structure A may interact with this conjugated system in the manner described by structures B and C.



B C

If R is an unsaturated or aryl group additional stabilization may be given the excited state by virtue of the delocalization of the non-bonding electrons of this group.[1] As shown in Table I the fact that methyl cyclopropyl, dicyclopropyl, and methyl vinyl ketone 2,4-dinitrophenylhydrazones absorb at longer wave lengths than their purely aliphatic model compounds strongly suggests that the cyclopropyl ring may stabilize a 2,4-dinitrophenylhydrazone excited state much as does a conventionally unsaturated vinyl group. This observation provides additional evidence for the already well supported thesis that the cyclopropyl ring may stabilize excited states by conjugative electron release.[3]

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(1) F. Ramirez and A. F. Kirby, *J. Am. Chem. Soc.*, **76**, 1037 (1954).

(2) This assumption is perhaps justified by the similar steric requirements of the model compounds and the compounds of interest.

(3) See R. H. Eastman and S. K. Freeman, *J. Am. Chem. Soc.*, **77**, 6642 (1955), for examples of this phenomenon related to ultraviolet spectroscopy.

EXPERIMENTAL

All spectra were determined in pure, distilled methylene chloride using matched 1-cm. glass stoppered absorption cells and a Beckman Model DK-1 recording ultraviolet spectrophotometer.

All 2,4-dinitrophenylhydrazones were prepared from the pure ketones and 2,4-dinitrophenylhydrazine hydrochloride in 50% aqueous ethanol containing hydrochloric acid catalyst and were recrystallized to constant melting point[4] from ethanol.

Dicyclopropyl ketone 2,4-dinitrophenylhydrazone, prepared as described above, was obtained as bright red crystals melting at 193–194°.

Anal. Calc'd for $C_{13}H_{14}N_4O_4$: C, 53.78; H, 4.86. Found: C, 53.78; H, 4.81.

Methyl cyclopropyl ketone 2,4-dinitrophenylhydrazone was obtained as reddish-orange crystals, m.p. 155°.

Anal. Calc'd for $C_{11}H_{12}N_4O_4$: C, 49.99; H, 4.57. Found: C, 50.27; H, 4.84.

Methyl vinyl ketone 2,4-dinitrophenylhydrazone was obtained as orange crystals, m.p. 142°.

Anal. Calc'd for $C_{10}H_{10}N_4O_4$: C, 47.99; H, 4.02. Found: C, 48.13; H, 4.02.

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(4) With the exception of those compounds presented below, all melting points checked those given by R. L. Shriner and R. C. Fuson, *Identification of Organic Compounds*, Second Edition, 1947, John Wiley and Sons, Inc., New York, N. Y.

The Alkylation of Ethyl and *tert*-Butyl Acetates[1]

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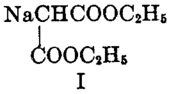
The common alkylation of ethyl malonate, accompanied by hydrolysis and decarboxylation, amounts to the indirect alkylation of ethyl acetate in which ethyl malonate would be regarded as α-carbethoxy ethyl acetate. The direct alkylation of ethyl acetate is difficult to achieve because this ester tends to undergo self-condensation when its α-hydrogen is ionized by a base, as would be required for the alkylation. Thus, whereas ethyl malonate shows no tendency to self-condense when its α-hydrogen is ionized by sodium ethoxide in its alkylation, ethyl acetate evidently underwent considerable self-condensation when its α-hydrogen was ionized by sodium triphenylmethide in an attempt to effect its benzylation.[2] The intermediates in these reactions would be I and II respectively.



$NaCH(COOC_2H_5)COOC_2H_5$
I

$NaCH_2COOC_2H_5$
II

In the present investigation ethyl and *tert*-butyl acetates were alkylated in low to fair yields by means of sodium amide in liquid ammonia.

The addition of ethyl acetate to a molecular equivalent of sodium amide in liquid ammonia, followed within a few seconds by an equivalent of benzyl chloride, produced the dibenzylated ester which was isolated in 16% yield as the corresponding acid (IV). No monobenzylated ester, which would have been isolated as acid III, was found. Some acetamide was probably produced although none of it was isolated.

$C_6H_5CH_2CH_2COOH$
III

$(C_6H_5CH_2)_2CHCOOH$
IV

In line with a recent observation[3] that lithium amide when used in excess favors certain condensations involving ethyl acetate, the addition of ethyl acetate to two equivalents of this reagent in liquid ammonia, followed by two equivalents of benzyl chloride, gave a better yield (30%) of alkylation product. Moreover, this product consisted exclusively of the monobenzylated ester which was isolated as the corresponding acid (III).

Since *tert*-butyl acetate not only undergoes relatively more α-hydrogen ionization with an alkali amide than ethyl acetate but also exhibits less tendency to self-condense, the *tert*-butyl ester should be more suitable for alkylation. In agreement with this, the benzylation of *tert*-butyl acetate by means of potassium amide was realized in better yield than that of ethyl acetate by means of sodium amide under similar conditions.[4] Thus, the former alkylation produced a 45% yield of acid IV (after hydrolysis) compared to the 16% yield with ethyl acetate. The intermediate potassio *tert*-butyl acetate (V) was first prepared by means of potassium amide in liquid ammonia.

$KCH_2COOC(CH_3)_3$
V

The alkylation of potassio *tert*-butyl acetate (V) with *n*-octyl bromide under similar conditions gave more of the monoalkylated than dialkylated product. The yields of the corresponding acids, which were isolated, were 41% and 12% respectively.

$C_8H_{17}CH_2COOH$
VI

$(C_8H_{17})_2CHCOOH$
VII

EXPERIMENTAL

Benzylation of ethyl acetate. (*A*) *By sodium amide.* To a stirred suspension of 0.3 mole of sodium amide in 250 ml. of liquid ammonia[5] was added during one minute 26.4 g. (0.3

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(1) Supported by the National Science Foundation.

(2) B. E. Hudson and C. R. Hauser, *J. Am. Chem. Soc.*, **62**, 2457 (1940).

(3) C. R. Hauser and J. K. Lindsay, *J. Am. Chem. Soc.*, **77**, 1050 (1955).

(4) Both potassium amide and sodium amide gave the same results in the butylation of *tert*-butyl diethylacetate; see C. R. Hauser and W. J. Chambers, *J. Am. Chem. Soc.*, **78**, 3837 (1956).

(5) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8**, 122 (1954).