of ether. The combined ether extracts were dried over sodium sulfate and concentrated by distillation. The residue was distilled at reduced pressure to give three fractions of (−)-α-chloropropionic acid weighing a total of 1.1 g. (22%) and all with b.p. 69.5° (1.2 mm.). The third fraction had α_D^{25} −1.73 ± 0.02° (neat, l 1.0) and neutral equivalent 110.5 (calcd.: 108.5). The neutral equivalent solution after titration with standard base was dextrorotatory.

The other half of the ozonide hydrolysis solution was treated with 5 g. of 30% hydrogen peroxide. The α-chloropropionic acid obtained after extraction and distillation amounted to about 1 g. (20%) and had α_D^{25} −1.46 ± 0.02° (neat, l 1.0) but appeared to be quite impure.

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The Structure of the Dimer of 1-Phenyl-4-methyl-2-penten-1-one

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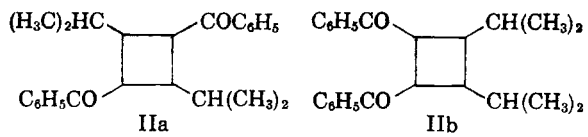
Kulka, *et al.* recently reported[1] that treatment of 1-phenyl-4-methyl-2-penten-1-one (I), (the condensation product of acetophenone with isobutyraldehyde), with aqueous methanolic alkali gave a dimer (II), m.p. 144.5–145°. Vacuum distillation of II in presence of catalytic amounts of sodium acetate gave back I. As attempts to detect an ethylenic linkage (catalytic hydrogenation, formation of a dibromide) failed, a 1,2,3,4-tetrasubstituted cyclobutane structure, IIa or IIb, was assigned to II. The formation of a dioxime and an infrared absorption band at 880 cm.$^{-1}$ were cited as evidence supporting such an assignment.



IIa IIb

As the formation of such cyclobutane structures under alkaline conditions seemed surprising to us,[2] the structure of II was reinvestigated.

The NMR spectrum[3] of II, prepared according to Kulka, *et al.*, was determined in a deuterochloroform solution using tetramethylsilane as an internal standard,[4] and is shown in Fig. 1.

The spectrum rules out structures IIa and IIb and can only be interpreted on the basis of the structure given below.

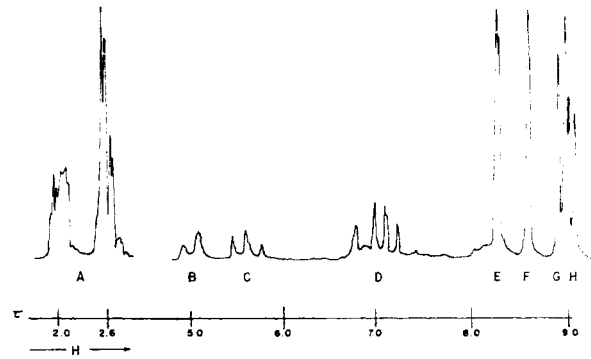
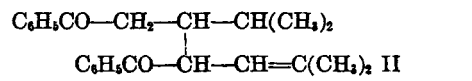


Fig. 1. The NMR spectrum of II in deuterochloroform (60 Mc/s)



This structure is compatible in every detail with the NMR spectrum and is in fact the Michael addition[5] product of the conjugate anion $C_6H_5—C(=O)—C^-H—CH=C(CH_3)_2$ of II to the α,β-unsaturated ketone I itself. The alkali-catalyzed dimerzation of the α,β-unsaturated ketones piperitone[6] and 3-methyl-cyclohex-2-en-1-one[7] has indeed been shown to occur *via* an initial Michael addition followed by further reactions.

The NMR spectrum clearly shows the presence of one isopropyl group. The bands G and H at highest field[8] (τ, 8.9, 9.0) are due to the two methyl groups split by a single hydrogen (J = 7.2 c.p.s.). The nonequivalence of the two methyl groups is due to the presence of an asymmetric center in the molecule, an observation made in the case of the alkaloid lunacrine.[9] The other two methyl groups (bands E and F) are not part of an isopropyl group, thus ruling out[10] structures IIa and IIb. Their position at low field (τ, 8.34, 8.60) corresponds to methyl groups attached to a doubly bonded carbon.[8] The magnitude of the splitting (1.3–1.5 c.p.s.) is too small for 1:2 coupling but is consistent with 1:3 coupling observed in olefinic compounds.[11]

(1) K. Kulka, R. J. Eiserle, J. A. Rogers, Jr., and F. W. Richter, *J. Org. Chem.*, **25**, 270 (1960).

(2) Cyclobutane compounds are well known in the photodimerization of ethylenic compounds, *cf.* A. Schönberg, *Präparative Organische Photochemie*, Springer-Verlag, Berlin, 1958.

(3) Varian V-4302 60 mc/s instrument.

(4) G. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(5) E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179, (1959).

(6) W. I. Taylor, *Chem. and Ind.*, 252 (1954). W. A. Ayer and W. I. Taylor, *J. Chem. Soc.*, 2227 (1955).

(7) G. Buchi, J. H. Hansen, D. Knutson, and E. Koller, *J. Am. Chem. Soc.*, **80**, 5517 (1958).

(8) G. D. Tiers, *Tables of τ-values for a variety of Organic Compounds*, Part I, Minnesota Mining and Manufacturing Company, St. Paul, Minn., 1958.

(9) S. Goodwin, J. N. Shoolery, and L. F. Johnson, *J. Am. Chem. Soc.*, **81**, 3065 (1959).

(10) One or two isopropyl groups should be observed in the spectrum of IIa or IIb depending on the exact stereochemistry of the cyclobutane ring. In the analogous case of substituted truxillic and truxinic acids, the nonequivalence of substituents has been used to determine their stereochemistry. R. Anet, *Chem. and Ind.*, 897 (1960).

(11) L. M. Jackman, *Application of N.M.R. Spectroscopy in Organic Chemistry*, Pergamon Press, New York, 1959.

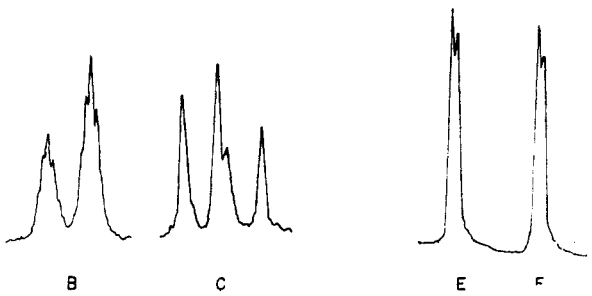


Fig. 2. Fine splitting in NMR spectrum of II

Confirmation of the double bond is obtained in band B (τ, 4.97) corresponding in position to an olefinic proton.[8] This is coupled to one adjacent hydrogen (10 c.p.s.) and shows further fine splitting (see Fig. 2) of the same magnitude as the methyl bands E and F. The unequal coupling with two methyl groups (1.5 for E and 1.3 c.p.s. for F) is due to the difference in the 1:3-*cis* and 1:3-*trans* coupling[12] and is consistent with the poorly resolved septets in band B. Band C can then be assigned to the proton coupled with the olefinic proton, as it shows the same spacing (10 c.p.s.) as in band B and is also at low field (τ, 5.6), being α to the carbonyl and β to the double bond.[11] If this deduction is correct then the fact that band C is a quartet is most simply explained by having the proton giving rise to band C coupled both to the olefinic proton (J = 10 c.p.s.) and to another proton (J = 8.75 c.p.s.).

The spectrum of the remaining protons is in bands A, D and under band E. The former is due to the aromatic protons which are similar to those of acetophenone and corresponds to ten protons. The spectrum of the tertiary hydrogen of the isopropyl group is only partially visible under band E as it is extensively split by the six hydrogens on the two methyl groups and also by adjacent hydrogen. Intensity measurements on band D show that it corresponds to three protons as compared with one each for B and C. The detailed analysis of this is not feasible by first-order treatment as the chemical shift is of the same order as the coupling constant resulting in an ABC system.[13]

The properties of the dimer II can be rationalized on the basis of the structure proposed. Although the double bond is only trisubstituted, models show considerable steric hindrance. The latter has been shown to confer unusual properties even to the disubstituted ethylene, 1,1-dineopentylethylene (III) which can be hydrogenated only at 130 atmospheres at 150° with Raney nickel.[14] The evolution of hydrogen bromide during attempts to brominate II[1] also finds parallel in the properties of III.[14] We have observed that the ethylenic linkage in II is attacked extremely slowly by potassium permanganate as has also been observed with III.

It is interesting that II is a β,γ-unsaturated ketone although it is formed under equilibrating conditions. This may be due to increased steric strain in going from an unconjugated to a conjugated structure. The structure II is consistent with the ultraviolet absorption spectrum which follows that of acetophenone. The formation of the monomer I can be easily visualized as a reverse Michael reaction[5] which needs no further comment.

ADDED IN PROOF: Dr. Kulka (personal communication) has now obtained acetone on ozonolysis of the dimer, in complete agreement with the structure proposed in this paper.

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(12) R. R. Fraser, *Can. J. Chem.*, **38**, 549 (1960).

(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-resolution Nuclear Magnetic Resonance*, McGraw-Hill, New York, 1959.

(14) P. D. Bartlett, G. L. Fraser, and R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 495 (1941).

Cleavage of Ethyl 2,2-Diphenyl-4-pentenoylglycinate by Oxidants and Acids

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The participation of amide groups in intramolecular displacement reactions has been utilized as a principle for the elaboration of selective methods to cleave peptide bonds next to γ,δ-unsaturated acids such as tryptophan[1,2] and tyrosine.[3] These degradative reactions may be used to advantage not only for analytical studies but also for the development of blocking groups in peptide synthesis. Indole-3-propionic[1] and phloretic acids[3] in principle are acceptable blocking groups for the synthesis of peptides that contain no functional groups whose rate of reaction with *N*-bromosuccinimide or *N*-bromoacetamide is faster than with that of the blocking groups. This note shows that by comparison observations on the use of a straightforward γ,δ-unsaturated acid such as 2,2-diphenyl-4-pentenoic acid (I) as a blocking group, though offering no immediate advantages with regard to yield, may serve as a guide for the development of groups removable not only by positive bromine but also by the controlled action of acid.

Bromination of acid I under anhydrous conditions has been found to lead to a bromolactone formulated as IV,[4] which has now also been obtained

(1) A. Patchornik, W. B. Lawson, E. Gross, and B. Witkop, *J. Am. Chem. Soc.*, **81**, 5923 (1960).

(2) L. K. Ramachandran and B. Witkop, *J. Am. Chem. Soc.*, **81**, 4028 (1959).

(3) G. L. Schmir, L. A. Cohen, and B. Witkop, *J. Am. Chem. Soc.*, **81**, 2228 (1959).

(4) P. N. Craig and I. H. Witt, *J. Am. Chem. Soc.*, **72**, 4925 (1950). *Cf.* M. de Moura Campos and N. Petragnani, *Ber.*, **93**, 317 (1960).