used. In this fashion 85–93% yields of esters of a variety of acids were obtained from phenacyl bromides in acetone after one hour at room temperature. With the less reactive *p*-nitrobenzyl chloride, it was necessary to add a catalytic amount of sodium iodide and to reflux for two hours in order to obtain 50–70% yields of esters. The results from these simple halides are shown in Table I. In the steroid series, similar conditions were used to prepare 3,21-dihydroxy-Δ^5-pregnene-20-one 21-acetate in 88.5% yield from the corresponding 21-iodo derivative.

The results from a study of variations in reaction conditions as applied to the preparation of phenacyl benzoate from phenacyl bromide, benzoic acid, and triethylamine are shown in Table II. Equally good results were obtained in solvents other than acetone, although the reaction appeared to be somewhat slower. In each case, however, the reaction mixture was homogeneous until the crystallization of triethylammonium bromide began. It is noteworthy that a large excess of the salt is not required (compare Runs 1 and 2) and that a large excess of triethylamine over the acid apparently is not deleterious (Run 3).

TABLE II

PHENACYL BENZOATE FROM PHENACYL BROMIDE AND TRIETHYLAMMONIUM BENZOATE

Phenacyl bromide, 0.02 mole; reaction time, one hour

Run	C_6H_5COOH Moles	$(C_2H_5)_3N$ Moles	Ml. of Solvent[a]	Temp., °C.	Yield, %[b]
1	0.175	0.109	50A	25	85
2	.0216	.0202	25A	25	92
3	.0216	.109	25A	25	90
4	.0216	.0202	25B	80[c]	85
5	.0216	.0202	25M	64[c]	94
6	.0216	.0202	25E	78[c]	94
7	.0216	.0202	25P	82[c]	92

[a] A, acetone; B, benzene; M, methanol; E, ethanol; P, 2-propanol. [b] Based on phenacyl bromide. [c] Reaction carried out under reflux.

EXPERIMENTAL[9]

3,21-Dihydroxy-Δ^5-pregnene-20-one 21-acetate. To a solution of 47 g. (0.78 mole) of glacial acetic acid and 49 g. (0.49 mole) of triethylamine in 130 ml. of acetone was added 13.2 g. (0.03 mole) of 3-hydroxy-21-iodo-Δ^5-pregnene-20-one.[5] The clear solution was refluxed for 45 minutes, cooled to room temperature and diluted slowly with 225 ml. of water. The product was filtered, washed thoroughly with water, and dried to constant weight *in vacuo.* The resulting 3,21-dihydroxy-Δ^5-pregnene-20-one 21-acetate was obtained as nearly white crystalline material weighing 9.9 g. (88.5%), m.p. 182–183°, $[\alpha]_D^{28}$ +43° (*c*, 1.0 in ethanol). An analytically pure sample prepared by recrystallization from acetone melted at 185–186°, $[\alpha]_D^{25}$ +45° (*c*, 1.0 in ethanol).

Preparation of esters (Table I). To a solution of 0.175 mole of the acid and 0.109 mole of triethylamine in 50 ml. of acetone was added 0.02 mole of the halogen compound. With the phenacyl bromides, precipitation of triethylammonium bromide from the clear solution usually started within a few minutes. After one hour at room temperature the mixture was slowly diluted with 100 ml. of water which first dissolved the amine salt, then caused separation of the water-insoluble product. The solid material was filtered, washed thoroughly with aqueous 5% sodium bicarbonate followed by water, and dried to constant weight *in vacuo.* The yields and melting points of the products so obtained are shown in Table I.

When the conditions described above for the phenacyl bromides were used with *p*-nitrobenzyl chloride, there was no apparent reaction. There was no precipitation of triethylammonium chloride, and 75–90 per cent of the starting halide could be recovered. While no attempt was made to determine the optimum conditions, it was found that refluxing the acetone solution for two hours in the presence of 0.2 g. of sodium iodide was sufficient to bring about at least partial conversion. The products were isolated as above, and the results are shown in Table I.

Preparation of phenacyl benzoate (Table II). The general procedure and isolation (except in Run 4) were as described above for the phenacyl bromides except for changes in solvent and quantities of reagents as indicated in Table II. The reactions in acetone were carried out at room temperature. Incomplete reaction after one hour at room temperature in the other solvents was indicated by the strong lachrymatory odor of phenacyl bromide. One hour at reflux temperature was apparently sufficient for complete reaction in these cases.

In Run 4, the benzene solution was cooled, washed with aqueous 5% sodium bicarbonate and water, and evaporated to dryness under reduced pressure. Trituration of the residue with the *n*-pentane gave the crystalline product as shown in Table II.

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[9] Melting points are uncorrected.

The Proton Magnetic Resonance and Structure of the Diketene-Acetone Adduct[1]

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In previous work there is some question regarding the molecular structure of the adduct obtained from the reaction of diketene with ketones.[2]

The infrared and ultraviolet spectra[2] and the chemical behavior[2,3] of the adduct with acetone have been interpreted as favoring structure I. On the other hand, similar evidence led to the suggestion[4] that the structure is II. We have observed the proton magnetic resonance spectrum[5] of the adduct, and obtained results which show con-

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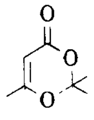
(1) This work was supported by the Office of Naval Research and by a grant-in-aid from E. I. du Pont de Nemours and Co.

(2) M. F. Carroll and A. R. Bader, *J. Am. Chem. Soc.*, **75**, 5400 (1953).

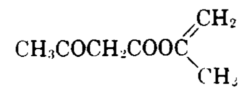
(3) N. G. Gaylord and D. J. Kay, *J. Am. Chem. Soc.*, **77**, 6641 (1955).

(4) Kh. V. Bal'yan and A. L. Shtangeev, *Zhur. Obshchei Khim.*, **24**, 238 (1954); *Chem. Abstr.*, **49**, 4525 (1955).

(5) L. H. Meyer, A. Saika, and H. S. Gutowsky, *J. Am. Chem. Soc.*, **75**, 4567 (1953).

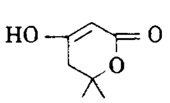


I



$$CH_3COCH_2COOC\begin{matrix}\diagup CH_2 \\ \diagdown CH_3\end{matrix}$$

II



III

clusively that the structure is I, the 2,2-dimethyl-4-methyl-6-keto-1,3-dioxene.

The proton spectrum of the liquid adduct at room temperature under conditions of moderate resolution is given in Fig. 1A. Three absorption lines are present, with relative intensities of approximately 6:3:1 suggesting immediately that they arise respectively from the $C(CH_3)_2$, CH_3—C=C and C=CH—C groups of structure I. Structure II would be expected to have four lines with relative intensities of 3:3:2:2 and structure III, which has also been considered,[2] four lines, 6:2:1:1. The δ-values, referred to H_2O, of the three lines observed are −0.335, −0.305, and +0.025, which agree very well with the characteristic absorption regions of CH_3—C, CH_3—C=C, and C=CH—C groups in compounds of known structure.[5] The enolic form of II is eliminated by similar arguments.

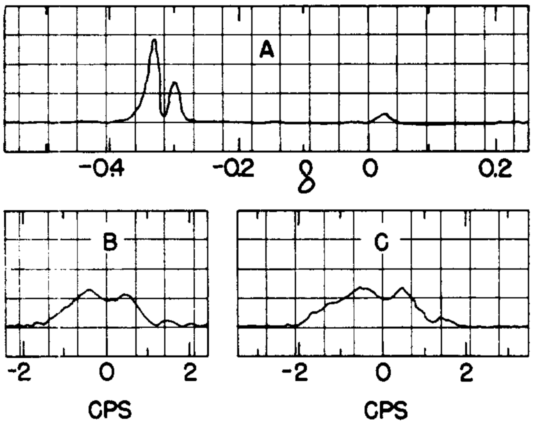


FIG. 1. THE PROTON MAGNETIC RESONANCE ABSORPTION spectrum of the liquid diketene-acetone adduct at room temperature, using a spinning sample with an effective volume of 0.02 ml. A. The entire spectrum under conditions of moderate resolution; the total sweep in magnetic field is 34 milligauss; sweep time, 10 sec. B and C. The line at a δ of −0.305 and the line at a δ of +0.025, respectively, under higher resolution. The intensity scale for C is one-fourth that for B.

Conclusive support of structure I is afforded by the multiplet structure,[6] shown in Fig. 1B and 1C, exhibited under higher resolution by the lines assigned to the CH_3—C=CH—C protons. The CH_3 group resonance is a doublet while that of the C=CH—C group is a 1:3:3:1 quartet, as expected for a 3-proton system coupled to a single proton with a chemically shifted resonance.[6] Structure I is the only one in which such an interaction can occur. Moreover, the protons in the CH_3—C=CH=C group are "insulated" by six chemical bonds from the $C(CH_3)_2$ protons so there should be no splitting of the latter, again agreeing with experiment.

EXPERIMENTAL

Sample. The commercially available diketone acetone adduct (Aldrich Chemical Company, Inc.) was carefully redistilled (b.p. 66.0–66.5°/2 mm.; n_D^{20} 1.464) a few days before the spectrum was observed. The spectra of samples several months old exhibited absorption in addition to that shown in Fig. 1, indicating a small amount of decomposition. There was no evidence in the spectrum of the newly distilled sample of other than the one component.

Procedure. The apparatus and experimental procedure were similar to those used earlier,[5] with some modifications described elsewhere.[7] The spectra were recorded at a fixed frequency of 17.735 Mc using the permanent magnet with a field of about 4165 gauss. The standard deviations of the measured δ-values are no more than ±0.01.

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[6] H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

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Phenazine Syntheses. VI.[1]
N-Methylphenazinium Methyl Sulfates

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In the course of investigating the activity of different classes of phenazines against Sarcoma 37, a number of water-soluble quaternaries were prepared by the action of dimethyl sulfate on various phenazines in nitrobenzene, following Kehrmann and Havas.[2]

In general, the base was dissolved in dry nitrobenzene in the proportion of 5 cc. of the solvent per gram of phenazine. Freshly-distilled dimethyl sulfate (1.5 cc. per gram of phenazine) was added to the solution when it had been heated slightly above 110° by means of an oil-bath at about 120°. The mixture was maintained at 105–110° for 5 minutes with stirring, then removed from the bath. The spontaneous precipitate was filtered off when the solution had cooled to room temperature, and was

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[1] Paper V, *J. Org. Chem.*, **21**, 565 (1956).

[2] Kehrmann and Havas, *Ber.*, **46**, 343 (1913); *Cf.* Hillemann, *Ber.*, **71**, 37 (1938).