Methyl 2,2,3,3-Tetramethylcyclopropanecarboxylate (1).—2,2,3,3-Tetramethylcyclopropanecarboxylic acid,[2] m.p. 117–118°, was esterified with a distilled solution of ethereal diazomethane. Work-up, followed by distillation at 25 mm., yielded analytically pure ester, $n^{25}\text{D}$ 1.4382, showing a single peak on vapor phase chromatography; n.m.r. chemical shifts (CCl_4) at τ 6.43 (3H, singlet), 8.78 (6H, singlet), 8.82 (6H, singlet), and 8.90 (1H, singlet).

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.23; H, 10.26. Found: 69.43; H, 10.33.

2,2,3,3-Tetramethyl-1-hydroxymethylcyclopropane (4).—A solution of 4.0 g. (25.6 mmoles) of **1** in 25 ml. of ether was added to a stirred, cooled solution of 3.8 g. (100 mmoles) of lithium aluminum hydride in 100 ml. of ether. The solution was refluxed for 30 min. and then cooled. A solution of 27 g. of ammonium chloride in 100 ml. of water was added cautiously with stirring and cooling, and the resulting mixture was stirred for 18 hr. Separation of the ether layer and extraction of the aqueous layer with ether, followed by further work-up yielded 3.5 g. of a slightly yellow residue. Distillation at 20 mm. yielded 2.48 g. (76%) of analytically pure alcohol, $n^{25}\text{D}$ 1.4483, showing a single peak on vapor phase chromatography; n.m.r. chemical shifts (CCl_4) at τ 6.46 (2H, doublet, $J = 7.5$ c.p.s.), 8.25 (1H, broad), 8.91 (6H, singlet), 9.00 (6H, singlet), and 9.53 (1H, triplet, $J = 7.5$ c.p.s.).

Anal. Calcd. for $C_8H_{16}O$: C, 75.00; H, 12.50. Found: C, 75.05; H, 12.45.

Alcohol **4** was further characterized by preparation of the *p*-nitrobenzoate, m.p. 104.5–106° from alcohol; n.m.r. chemical shifts (CCl_4) at τ *ca.* 1.8 (4H), 5.63 (2H, doublet, $J = 8$ c.p.s.), 8.84 (6H, singlet), 8.90 (6H, singlet), and 9.27 (1H, triplet, $J = 8$ c.p.s.).

Anal. Calcd. for $C_{15}H_{19}NO_4$: C, 64.98; H, 6.86. Found: C, 64.87; H, 6.82.

α,α,2,2,3,3-Hexamethyl-1-hydroxymethylcyclopropane (7).—The reported preparation[19] involves the addition of methyl Grignard to ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate. We found it convenient to prepare **7** from the reaction of excess ethereal methyllithium on 2,2,3,3-tetramethylcyclopropanecarboxylic acid, the mixture being allowed to stand at room temperature for 2 days. Work-up, followed by distillation at 30 mm., yielded analytically pure **7**, in 70% yield, $n^{25}\text{D}$ 1.4368, showing a single peak on vapor phase chromatography; n.m.r. chemical shifts (CCl_4) at τ 8.73 (6H, singlet), 8.78 (6H, singlet), 8.94 (6H, singlet), 9.32 (1H, singlet), and 9.90 (1H, singlet).

Methyl 2,2,3-Trimethylcyclopropanecarboxylate (Mixtures Enriched in *cis* and *trans* Isomers).—A solution of 25 g. (0.357 mole) of 2-methyl-2-butene[20] and 31.4 g. of ethyl diazoacetate[21] (92% by volumetric assay or 0.253 mole) was added *via* a dilution head, over a period of 12 hr., to a stirred and vigorously refluxing mixture of 25 g. (0.357 mole) of 2-methyl-2-butene, 20 g. of diethyl maleate, and 3 g. of powdered copper. (The reaction flask was heated with an oil bath maintained at 125 to 135°.) After nitrogen evolution had ceased (0.265 mole as measured by a wet-test meter, Precision Scientific Co.), the mixture was cooled and filtered. Distillation yielded initially 24 g. of recovered 2-methyl-2-butene and then 19 g. (32% based on unrecovered olefin) of product, b.p. 105–115° (65 mm.).

The ethyl ester was saponified and the resulting acid was esterified with distilled ethereal diazomethane, 11.2 g. of ethyl ester yielding 8.06 g. (78%) of methyl ester, b.p. 63–64° (24 mm.), showing a single peak by vapor phase chromatography; n.m.r. chemical shifts (CCl_4) at τ 6.42 (1.7H, singlet), 6.44 (1.3H, singlet), and 8.83–8.94 (11.0H) corresponding to a 43:57 mixture of *cis* and *trans* isomers. Partial saponification of this *ca.* 1:1 mixture (56 mmoles) of methyl esters by refluxing overnight in a solution of 1.57 g. (24 mmoles) of 85% potassium hydroxide in 75 ml. of methanol–water (2:1 v./v.) yielded, after work-up and distillation, 4.21 g. of recovered ester; n.m.r. chemical shifts at τ 6.42 and 6.44 corresponding to a 37:63 mixture of *cis* and *trans* isomers. Work-up of the acid formed in the saponification, followed by esterification with diazomethane and subsequent distillation, yielded 2.05 g. of ester; n.m.r. chemical shifts (CCl_4) at τ 6.42 and 6.44 corresponding to a 10:90 mixture of *cis* and *trans* isomers.

Partial saponification of another batch of methyl ester, under slightly different conditions, led to the recovery of *cis*-enriched ester. Thus, saponification of 8.24 g. (58 mmoles) of a *ca.* 1:1 mixture of isomers with a solution of 1.65 g. (25 mmoles) of 85% potassium hydroxide in 52 ml. of methanol–water (3.3:1 v./v.) by warming on a steam bath for 12 hr. yielded, after work-up and distillation, 3.38 g. of recovered ester; n.m.r. chemical shifts (CCl_4) at τ 6.42 and 6.44 corresponding to a 70:30 mixture of *cis* and *trans* isomers. (Recovered acid yielded a 37:63 mixture of *cis* and *trans* isomers.) Another partial saponification of the 3.38 g. (24 mmoles) of recovered ester with a solution of 0.66 g. (10 mmoles) of 85% potassium hydroxide in 19 ml. of methanol–water (3.75:1 v./v.) by warming for several days yielded 1.33 g. of recovered ester which was not further enriched in *cis* isomer (*cis–trans* 70:30).

2,2,3-Trimethyl-1-hydroxymethylcyclopropane (Mixtures Enriched in *cis* and *trans* Isomers).—Following the procedure given for the preparation of **2**, 500 mg. (3.52 mmoles) of a mixture of **2** and **3** (70% *cis*) was reduced with lithium aluminum hydride. After work-up, distillation at 25 mm. yielded 249 mg. (62%) of a mixture of *cis* and *trans* primary alcohols **5** and **6**; n.m.r. chemical shifts (CCl_4) at τ *ca.* 6.5 (2.0H, predominantly as an A_2X pattern), 7.4 (1H, broad singlet), and 8.94–9.63 (11.0H).

Similarly, 500 mg. (3.52 mmoles) of a mixture of **2** and **3** (90% *trans*) was reduced, yielding 283 mg. (71%) of a mixture of **5** and **6**; n.m.r. chemical shifts at τ *ca.* 6.5 (2.0H, predominantly as an ABX pattern), 7.1 (1H, broad singlet), and 8.93–9.85 (11.0H).

α,α,2,2,3-Pentamethyl-1-hydroxymethylcyclopropane (Mixtures Enriched in *cis* and *trans* Isomers).—To 500 mg. (3.52 mmoles) of a mixture of **2** and **3** (70% *cis*) in 30 ml. of ether was added a solution of methyllithium (*ca.* 20 mmoles) in 50 ml. of ether. The solution was refluxed for 4 hr. and then allowed to stand at room temperature for 12 hr. Work-up (no acid treatment!), followed by distillation at 25 mm., gave 265 mg. (53%) of a mixture of *cis* and *trans* tertiary alcohols **8** and **9** which showed only one peak (unresolved) on vapor phase chromatography; n.m.r. chemical shifts (CCl_4) at τ *ca.* 9.9 (0.8H, predominantly half of an AB pattern, $J = 9.5$ c.p.s.) and 8.72–9.66 (17.0H).

Similarly, 160 mg. (1.1 mmole) of a mixture of **2** and **3** (90% *trans*) was converted to 90 mg. (56%) of a mixture of **8** and **9** which showed only one peak (unresolved) on vapor phase chromatography; n.m.r. chemical shifts (CCl_4) at τ *ca.* 9.7 (1.2H, predominantly half of an AB pattern, $J = 6.0$ c.p.s.) and 8.7–9.6 (17.0H).

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[19] A. P. Meschcheryakov and I. E. Dolgii, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk.*, 496 (1961).

[20] Aldrich Chemical Co., distilled.

[21] N. E. Searle, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 424.

The Boron Trifluoride Catalyzed Reaction of Acetophenone with Acetic Anhydride

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That the acid-catalyzed reaction of acetophenone with acetic anhydride yields a methyldiphenylpyrylium salt has been known for 50 years.[2–8] Dypnone has been used as the ketonic reactant in place of acetophenone.[5,7] The use of boron trifluoride in this regard has not been reported.

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[1] To whom communication should be addressed.

[2] W. Dilthey, *J. prakt. Chem.*, **94**, 72 (1916).

[3] W. Schneider and A. Rose, *Ber.*, **55**, 2775 (1922).

[4] R. J. W. LeFevre and J. Pearson, *J. Chem. Soc.*, 1197 (1933).

[5] P. P. Hopford and R. J. W. LeFevre, *ibid.*, 1989 (1938).

[6] K. Dimroth, *et al.*, *Ann.*, **604**, 221 (1957).

[7] O. Diels and K. Alder, *Ber.*, **60**, 716 (1927).

[8] W. Schroth and G. Fischer, *Z. Chem.*, **4**, 281 (1964).

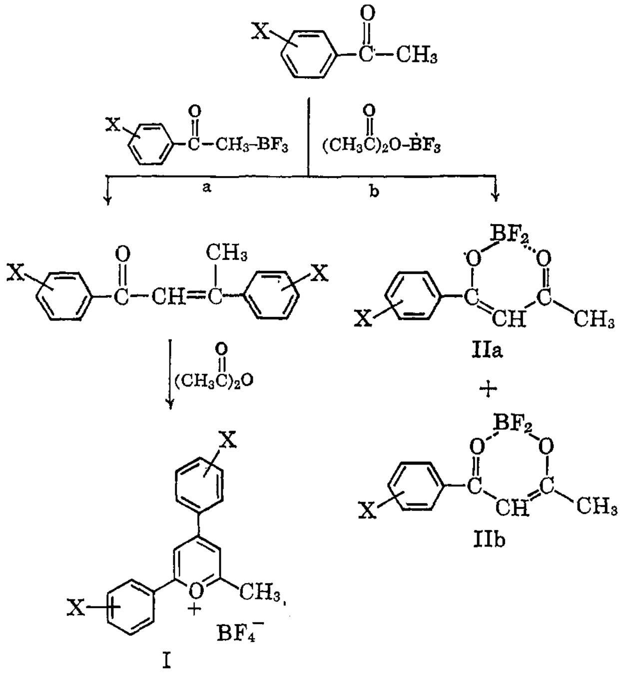
On the other hand, previous workers have shown that the boron trifluoride catalyzed reaction of alkanoic acid anhydrides and acetophenone result in good yields of 1,3-diketones.[9,10] In each of these cases the reaction was carried out at ice-bath temperature, using an anhydride–ketone ratio of 2:1 with boron trifluoride gas. In no case, however, was the isolation of any pyrylium salt analogous to I reported.[11]

It has now been found that when this reaction was run at room temperature using boron trifluoride etherate as the acid catalyst there was obtained a mixture of 2,4-diphenyl-6-methylpyrylium fluoborate (I, X = H) and the boron difluoride complex of benzoylacetone (II, X = H). Changes in order of addition, reactant ratios, or use of boron trifluoride gas made only quantitative differences in the products obtained.

Attempts to acylate benzoylacetone using boron trifluoride catalysis have given only II.[12] Apparently this same lack of reactivity carries over to reactions of II with acetophenone.

When dypnone was substituted for the acetophenone in the above procedures involving boron trifluoride etherate, no product II was isolated; I was isolated in 33% yield.[12] Based on these observations the reaction path in Scheme I is indicated.

SCHEME I



I

The relative importance of paths a and b may be influenced by reaction temperature or by the presence or absence of ether (Table I). It would appear also that ketone structure may influence the reaction path to some extent.

TABLE I

FACTORS AFFECTING YIELD OF I AND II

Acetophenone, moles	Anhydride, moles	BF_3, moles[a]	Temperature	% yield I[b]	% yield II[b]
0.5	1.13	1.1 (E)	Ambient	19	17
0.5	1.8	0.54 (E)	Ambient	14	19
0.4	0.4	0.66 (E)	Ambient–135°	31	c
0.5	0.9	1.07	Exotherm	11	45
1	2	0.5	Ice bath	..	83

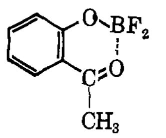
[a] E designates boron trifluoride etherate, otherwise gaseous. [b] Yields are based on moles of ketone employed. The stoichiometry relative to boron trifluoride is not certain. [c] Occurrence of II was not observed. This does not conclusively prove its absence because of method of work-up.

The structural proof of I (X = H) was based on infrared studies, ultimate analyses, and conversion to 2,4-diphenyl-6-methylpyridine with subsequent spectral studies on this material. All other I analogs or homologs were so designated on the basis of ultimate analyses and infrared spectral studies which demonstrated their similarity to I (X = H).

The by-product II was identified on the basis of the similarity of its melting point to that of a material reported by Morgan and Tunstall, obtained by reaction of boron trifluoride with benzoylacetone.[13] The identity of II was further substantiated by infrared spectral studies and by conversion to β-iminobutyrophenone (V) upon treatment with ammonia.[14] Compound V was converted to benzoylacetone by treatment with dilute acid and slight warming. The structures of the other II analogs prepared in the work were assigned on the basis of elemental analyses and infrared similarities to II (X = H).

The actual structure of II, a or b, has not been determined, although the IIa may be considered implicit in the mechanism of the formation of this complex.[15] The lack of reactivity of II could be explained if it were considered a resonance hybrid of a and b although no real evidence exists supporting this.

The reaction with acetic anhydride has been extended to other acetophenone derivatives. In the case of 4-hydroxyacetophenone only the compound analogous to I (X = 4-OH) was isolated in 70% yield. The sole product isolated from 3-nitroacetophenone was an 8% yield of II (X = 3-NO_2), while both I, 17% yield, and II, 9% yield (X = 4-Cl), were isolated from 4-chloroacetophenone. In the case of 2-hydroxyacetophenone no products related to I or II (X = 2-OH) were observed. Instead, there was isolated a material whose properties, infrared spectrum, and elemental analysis are in agreement with structure III. Apparently, the chelate of this ketone is formed primarily and further reaction, under the present conditions, does not occur as was found to be the case with benzoylacetone. The formal similarities of II and III are obvious. Attempts to



III

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[9] J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **67**, 284 (1945).

[10] H. Meerwein and D. Vossen, *J. prakt. Chem.*, **141**, 149 (1934).

[11] W. C. Dovey and R. Robinson [*J. Chem. Soc.*, 1389 (1935)] reported the isolation of 2,4,6-triphenylpyrylium fluoborate (IV) from the reaction of acetophenone with boron trifluoride. The proximity of the melting points of I (X = H) and IV made a comparison of these two materials desirable (see Experimental).

[12] D. F. Tavares, W. I. O'Sullivan, and C. R. Hauser, *J. Org. Chem.*, **27**, 1251 (1962), ref. 5 therein.

[13] G. T. Morgan and R. B. Tunstall, *J. Chem. Soc.*, **125**, 1963 (1924).

[14] C. Beyer and L. Claisen, *Ber.*, **20**, 2180 (1887); F. K. Beilstein, "Handbuch der organischen Chemie," Vol. 7, 4th Ed., 1919, p. 683.

[15] C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8**, 100 (1954).

extend the reaction to propiophenone and phenacyl chloride were unsuccessful.

When the reaction was applied to acetophenone and propionic anhydride at ambient temperature, a 46% yield of the pyrylium homologous to I (X = H) was obtained. No material homologous to II (X = H) was observed. When 4-chloroacetophenone was reacted with propionic anhydride, the material homologous to I (X = 4-Cl) was obtained in 25% yield while a trace of material homologous to II (X = 4-Cl) was isolated.

Experimental

Melting points and boiling points are uncorrected. The n.m.r. data were collected using a Varian A-60 n.m.r. spectrometer with chloroform-*d* as solvent and tetramethylsilane as the internal standard. The infrared spectra were obtained on a Perkin-Elmer Model 21 infrared spectrometer using KBr plaques 1% in concentration. In all cases the 47% boron trifluoride etherate employed was redistilled, b.p. 124°. The elemental analyses were carried out by the Galbraith Laboratories, Knoxville, Tenn.

The Reaction of Acetophenone, Acetic Anhydride, and Boron Trifluoride. A. Involving Boron Trifluoride Etherate at Elevated Temperature.—A mixture of 48 g. (0.4 mole) of acetophenone, 42 g. (0.4 mole) of acetic anhydride, and 120 g. (0.82 mole) of 47% boron trifluoride etherate in a round-bottom flask fitted with a small column and a distilling head was heated slowly to a kettle temperature of 135° while the head temperature rose from 50 to 120° over a period of 75 min. A total of 70 ml. of distillate was collected. The hot reaction mixture was then poured into 300 ml. of ethyl acetate with stirring and the yellow solid which formed was collected on the filter and air dried. Recrystallization from 300 ml. of acetic acid gave 21 g. (31% yield based on acetophenone) of I (X = H), m.p. 248.5–250°.

B. Involving Boron Trifluoride Etherate at Room Temperature.—A mixture of 60 g. (0.5 mole) of acetophenone and 187 g. (1.8 mole) of acetic anhydride was treated with 80 g. (0.54 mole) of 47% boron trifluoride etherate at room temperature. About a 10° rise in temperature was noted.

After 24 hr. the solid was collected on a filter, washed with ether, and air dried to give 31 g. of yellow solid. This solid was extracted with 300 ml. of ethyl acetate to give two solid fractions, one insoluble, I (X = H), and the other ethyl acetate soluble, II (X = H). The product I, recrystallized from acetic acid, m.p. 249.5–252.5°, was isolated in 14% yield based on acetophenone while II, m.p. 158–159°, was isolated in 19% yield based on acetophenone.

C. Involving Boron Trifluoride Gas.—A mixture of 60 g. (0.5 mole) of acetophenone and 92 g. (0.9 mole) of acetic anhydride was mixed at room temperature and then with stirring 73 g. (1.07 mole) of boron trifluoride gas was added as follows by means of a tube at the bottom of the flask: 30 g. at room temperature when a rapid temperature increase occurred with subsequent solidification, 30 g. while the reaction mixture was being cooled in ice–water, and 23 g. following addition of 120 ml. of ether. The mixture was left at room temperature for 3 days after which it was diluted with 200 ml. of ether and filtered to give, when dried, 77 g. of crude product. The total product was extracted with 500 ml. of ethyl acetate to give 9 g. (11% yield) of I (X = H), m.p. 250–252°, and 47.5 g. (45% yield) of II (X = H), m.p. 156.5–158.5°.

The Reaction of Dypnone with Acetic Anhydride Catalyzed by Boron Trifluoride Etherate.—A mixture of 11 g. (0.05 mole) of dypnone and 11 g. (0.1 mole) of acetic anhydride was treated dropwise with stirring with 30 g. (0.15 mole) of 47% boron trifluoride. The addition was carried out at such a rate that, with cooling, the temperature remained at about 10°. When the first drop of boron trifluoride etherate was added, the reaction mixture turned green and progressively darkened throughout the addition. Toward the end of the addition solid began to separate. When addition was complete, the reaction mixture was stirred at 10° for 1 hr. and the solid was collected on a filter, washed three times with alcohol, and air dried to give 7 g. of crude product. The crude material was extracted with ethyl acetate; no soluble material was noted. The product was then crystallized from acetic acid to give 5.5 g. (33% yield) of I (X = H).

Proof of Structure of Compound I (X = H). A. Ultimate Analysis.—A sample was recrystallized from ethanol to give a yellow solid, m.p. 248–249°.

Anal. Calcd. for $C_{18}H_{15}BF_4O$: C, 64.70; H, 4.53. Found: C, 64.48; H, 4.48.

B.—The infrared spectrum showed phenyl absorption at 6.35 and 6.7, strong pyrylium bands at 6.2 and 6.67, and monosubstituted phenyl absorption at 12.95 and 14.8 μ. A broad strong band centered at 9.5 μ indicated BF_4^-. A weak band at 3.4 and a shoulder at 7.5 μ indicated $-CH_3$.

C. Conversion to 2,4-Diphenyl-6-methylpyridine.—To 35 ml. of methanolic ammonia (saturated at 0°) was added 3 g. of I (X = H) to give a dark amber solution. This solution was heated at boiling on the steam bath until all ammonia was discharged. The hot reaction mixture was then poured into 350 ml. of cold water with stirring, and the solid which separated was subsequently collected on the filter. This material was crystallized from petroleum ether (b.p. 60–75°) to give about 1 g. of a solid m.p. 75–76.5° (lit.[2] m.p. 72–73°).

The infrared spectrum showed a band at 3.4 and a shoulder at 7.25 μ characteristic of a $-CH_3$ group together with the expected aryl bonds, and n.m.r. studies showed, in addition to aromatic H bonds, a slightly broadened singlet at 2.67 p.p.m. characteristic of tolyl $-CH_3$.

Proof of Structure of Compound II (X = H). A. Ultimate Analysis.—A sample was recrystallized from ethyl acetate to give a white solid, m.p. 158–160° (lit.[13] m.p. 155°).

Anal. Calcd. for $C_{10}H_9BF_2O$: C, 57.19; H, 4.32; B, 5.15. Found: C, 57.59, 57.47; H, 4.42, 4.37; B, 5.47, 5.57.

The infrared spectrum showed aromatic bands at 6.25 and 6.7, a chelated carbonyl band at 6.49, a CH_3 band (relatively strong) at 7.3, BF_2 bands at 9.2 and 9.45, and monosubstituted aromatic bands at 12.85 and 14.15 μ.

B. Reaction with Ammonia. β-Iminobutyrophenone (V).—About 3 g. of II was treated with about 50 ml. of ammonium hydroxide and the mixture was heated and treated with ethanol until complete solution took place. The mixture was allowed to cool and pieces of ice were added while a pink solid separated. The solid was air dried and then crystallized from 30 ml. of toluene to give a white solid, m.p. 143–144.5° (lit.[14] m.p. 143°).

Anal. Calcd. for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69; mol. wt., 161. Found: C, 74.44, 74.36; H, 6.85, 6.92; N, 8.92, 8.94; mol. wt. (ebullioscopic), 155 ± 1.5.

The infrared spectrum showed bands at 6.2 and 7.2 μ indicative of $O{=}\overset{|}{C}{-}CH{=}\overset{|}{C}{-}NH_2 \rightleftharpoons O{=}\overset{|}{C}{-}CH_2{-}\overset{|}{C}{=}NH$ and also monosubstituted phenyl bands.

C. Hydrolysis of V. Benzoylacetone.—A small portion of V was dissolved in 6 *N* HCl and warmed slightly. An oil separated which crystallized on standing. It was collected on the filter, washed with water, and air dried. The material (m.p. 59–60°) was identical in its infrared spectrum with authentic benzoylacetone (m.p. 59–60°).

Nonidentity of I with 2,4,6-Triphenylpyrylium Fluoborate (IV).[11] A.—The synthesis of IV was carried out by the reaction of acetophenone with benzaldehyde in the presence of BF_3.[16] The product possessed m.p. 252–254° (ethanol).[17] Infrared studies showed no bands characteristic of CH_3 in the 3- or 7-μ region.

B. Conversion of IV to 2,4,6-Triphenylpyridine.—Using the method for 2,4-diphenyl-6-methylpyridine, 3 g. of IV gave 1 g. of 2,4,6-triphenylpyridine: m.p. 134–135° (ethanol), lit.[17] m.p. 137° (ethanol). An infrared spectrum showed only aromatic absorption and n.m.r. studies showed only aromatic hydrogen.

2-Ethyl-4,6-diphenylpyrylium Fluoborate.—In a 500-ml. erlenmeyer flask was placed a mixture of 12 g. (0.1 mole) of acetophenone, 25 ml. of propionic anhydride, and 40 g. (0.28 mole) of 47% boron trifluoride etherate. After a period of time a rise in temperature was noted and solid began to separate. After 2 days the mixture was diluted with 450 ml. of ether and the solid which separated was collected and, after washing with ether and air drying, weighed 9 g. This solid was extracted with 150 ml. of boiling ethyl acetate to remove any material analogous to

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[16] R. Lombard and J. P. Stephen, *Compt. rend.*, **237**, 333 (1955); *Chem. Abstr.*, **48**, 11404*a* (1954).

[17] R. C. Elderfield and T. P. King, *J. Am. Chem. Soc.*, **76**, 5437 (1954).

II. The insoluble material was crystallized from acetic acid to give 8 g. of product (46% yield), m.p. 261–262°.

Anal. Calcd. for $C_{19}H_{17}BF_4O$: C, 65.54; H, 4.92. Found: C, 65.5; H, 4.04.

2-Ethyl-4,6-di(4-chlorophenyl)pyrylium Fluoborate.—This material was prepared in a manner analogous to the preceding compound using the same proportion of reactants. From the reaction mixture there was isolated 9 g. of crude product, which gave 8.5 g. of ethyl acetate insoluble material. Recrystallization from acetic acid gave 5 g. (25% yield) of pyrylium salt product, m.p. 245–247° dec.

Anal. Calcd. for $C_{19}H_{15}BCl_2F_4O$: C, 54.17; H, 3.63. Found: C, 54.25; H, 3.56.

The ethyl acetate extract was evaporated to dryness and the residue was recrystallized from ethyl acetate to give a few milligrams of material, m.p. 156–157.5°. Infrared showed it to be analogous to II.

Anal. Calcd. for $C_{11}H_{10}BClF_2O_2$: C, 51.06; H, 3.87. Found: C, 50.92; H, 3.94.

Reaction of Substituted Acetophenones with Acetic Anhydride in the Presence of Boron Trifluoride Etherate.—These materials were prepared by a procedure similar to that employed in the two preceding sections involving 0.1 mole of ketone in 25 ml. of acetic anhydride with 40 g. (0.28 mole) of boron trifluoride etherate. In the case of 4-chloroacetophenone five times these amounts were used. The crude reaction products were washed with ether and extracted with hot ethyl acetate to separate type-I from type-II products. Yields are based on moles of ketone employed. The physical constants and other data are recorded as follows.

4-Hydroxyacetophenone: I (X = 4-OH), m.p. 215–217°, 70% yield; no type-II product observed.

Anal. Calcd. for $C_{18}H_{15}BF_4O_3$: C, 58.70; H, 4.25. Found: C, 58.34; H, 4.33.

3-Nitroacetophenone: no type-I product; II (X = 3-NO_2), m.p. 174–175.5°, 8% yield.

Anal. Calcd. for $C_{10}H_7BF_2NO_4$: C, 47.10; H, 3.16; N, 5.49. Found: C, 47.20; H, 2.87; N, 5.70.

4-Chloroacetophenone: I (X = 4-Cl), m.p. 267–268°, 17% yield.

Anal. Calcd. for $C_{18}H_{13}BCl_2F_4O$: C, 53.64; H, 3.25. Found: C, 53.65; H, 3.26.

II (X = 4-Cl), m.p. 226.5–228°, 9% yield.

Anal. Calcd. for $C_{10}H_7BClF_2O_2$: C, 49.08; H, 3.27. Found: C, 49.23; H, 3.41.

2-Hydroxyacetophenone.—No product analogous to I or II was isolated. There was instead isolated a 52% yield of III, m.p. 142.5–145°.

Anal. Calcd. for $C_8H_7BF_2O_2$: C, 52.17; H, 3.80. Found: C, 51.78; H, 4.19.

Acknowledgment.—Appreciation is expressed to Mr. H. L. Joyce and Mr. C. B. Strow for their aid in obtaining and interpreting the infrared and n.m.r. spectra.

The Nuclear Magnetic Resonance Spectra of *aci*-Nitro Anions

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The advent of n.m.r. spectroscopy allows the chemist to observe many phenomena that were previously undiscernible except by interpretive methods such as infrared and ultraviolet data, kinetics, characteristic reactions, etc. One of the most interesting fields lies in the area of reactive intermediates. This paper reports the observation of such an intermediate, i.e., the nitronate anion, by n.m.r. spectroscopy.

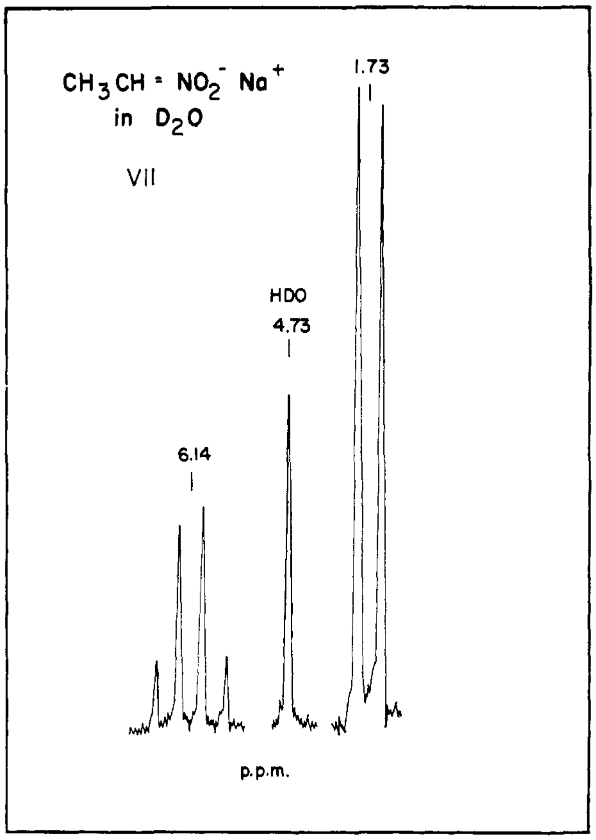
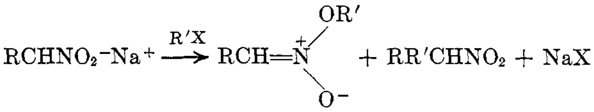


Figure 1.—The 60-Mc. n.m.r. spectrum of the sodium salt of nitroethane (VII) in deuterium oxide at room temperature.

It has been general knowledge for many years that aliphatic nitro compounds dissolve in aqueous base. Using this principle, Holleman[1] (1895), as well as Hantzsch and Schultze[2] (1896), isolated a nitronic acid (eq. 1) by careful acidification of an alkaline solution of the nitro compound. This constituted the first example of the tautomerism of the nitro group.

$$\mathrm{ArCH_2NO_2} \xrightarrow[\mathrm{ROH}]{\mathrm{NaOH}} \mathrm{ArCHNO_2^-Na^+} \xrightarrow{\mathrm{H_3O^+}} \mathrm{ArCHNO_2H} \qquad (1)$$

Structural proof for the nitronate anion, as well as for the nitronic acid, has been derived from chemical evidence. The alkylation[3] of the *aci*-nitro anion provides O-alkylation products (I, a nitronic ester) as well as the C-alkylation products (II). More recently Kornblum and Brown[4] have shown that the *aci*-nitro anion can be completely O-alkylated to the nitronic ester (III).



$$\mathrm{RCHNO_2^-Na^+} \xrightarrow{\mathrm{R'X}} \mathrm{RCH{=}\overset{+}{N}(OR')(O^-)} + \mathrm{RR'CHNO_2} + \mathrm{NaX} \qquad (2)$$

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[1] A. F. Holleman, *Rec. trav. chim.*, **14**, 121 (1895).

[2] A. Hantzsch and O. W. Schultze, *Ber.*, **29**, 2251 (1896).

[3] A concise review of early alkylation reactions is given by J. T. Thurston and R. L. Shriner, *J. Org. Chem.*, **2**, 183 (1937).

[4] N. Kornblum and R. A. Brown, *J. Am. Chem. Soc.*, **86**, 2681 (1964).