taminants. Since no elemental analyses (see Table I) were obtained for known compounds I, V, and VI, a sample NMR spectrum was obtained for the lowest molecular weight compound (I). This spectrum (60 mc.) revealed two sharp singlets at 2.29 and 3.13 p.p.m., which upon integration gave the expected 2 to 1 ratio of acyl to *N*-alkyl protons.

EXPERIMENTAL

***N*-*n*-Propyldiacetimide (IX).** A mixture of 164 grams (1.61 moles) of acetic anhydride and 35.0 grams (0.37 mole) of *N*-*n*-propylamine hydrochloride was stirred for 6 hours with heating by means of an oil bath maintained at 160° C. A slow stream of dry nitrogen was passed through the mixture for 1 hour to expel hydrogen chloride. The excess anhydride was removed under reduced pressure and the residue was distilled to obtain 37.5 grams of a liquid (b.p. 116° C. at 40 mm. of Hg). A gas chromatogram indicated that this distillate contained a small amount of a less volatile component. Redistillation of the material through a 30.5-cm. Scanco semimicro concentric tube column gave 29.3 grams of a liquid (b.p. 96.5–100° C. at 19 mm. of Hg) which still contained some of the second component. This material was dissolved in 300 ml. of *n*-hexane and passed through a 2 × 50 cm. column of Florisil. An additional 300 ml. of *n*-hexane was used to elute the imide from the column. Concentration of the eluate and distillation of the residue gave 18.0 grams (34.4%) of a colorless liquid [b.p. 106–07° C. at 26 mm. of Hg, $\lambda_{max}^{liquid\ film}$ 1670 to 1710 cm.$^{-1}$ (imide C=O)].

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Infrared Spectra and Synthesis of Some Acetophenone Derivatives

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The acetophenone derivatives were synthesized by the Friedel-Crafts acylation of the symmetrical trialkylbenzenes. The nitroacetophenones were prepared by nitration of the ketone in acetic acid–acetic anhydride solution. Nine organic compounds heretofore unreported were prepared: 2,4,6-triisopropyl-α-methylbenzyl acetate (m.p., 62.5–63.5); 2,4,6-triisopropyl-α-methylbenzyl alcohol (m.p., 92–93); 2′,4′,6′-triisopropyl-3′-aminoacetophenone (m.p., 109–10); 2′,4′,6′-triisopropyl-2-bromoacetophenone (m.p., 53–54); 2′,4′,6′-triisopropyl-3′-nitroacetophenone (m.p., 110–12); 2′,4′,6′-triisopropylbutyrophenone (m.p., 41–42); 2′,4′,6′-triisopropyl-3′-nitrobutyrophenone (m.p., 101.5–2.5); 2′,4′,6′-triisopropylpropiophenone (m.p., 87–88); and 2′,4′,6′-triisopropyl-3′-nitropropiophenone (m.p., 113–14). The effect of ring substituent groups upon the infrared absorption frequency assigned to the carbonyl group of the acetophenones is discussed.

THE ACETOPHENONE derivatives were synthesized by the Friedel-Crafts acylation of the symmetrical trialkylbenzenes. The nitroacetophenones were prepared by nitration of the ketone in acetic acid–acetic anhydride solution. Nine organic compounds heretofore unreported were prepared: 2,4,6-triisopropyl-α-methylbenzyl acetate, 2,4,6-triisopropyl-α-methylbenzyl alcohol, 2′,4′,6′-triisopropyl-3′-aminoacetophenone, 2′,4′,6′-triisopropyl-2-bromoacetophenone, 2′,4′,6′-triisopropyl-3′-nitroacetophenone, 2′,4′,6′-triisopropylbutyrophenone, 2′,4′,6′-triisopropyl-3′-nitrobutyrophenone, 2′,4′,6′-triisopropylpropiophenone, and 2′,4′,6′-triisopropyl-3′-nitropropiophenone.

In addition, three known compounds were prepared. The effect of ring substituent groups upon the infrared absorption frequency assigned to the carbonyl group of the acetophenones was studied. The observed absorption frequencies assigned to the carbonyl group of the acetophenones indicated that this group was not in the plane of the aromatic ring.

SYNTHESIS

The best general method found for the synthesis of the acetophenones was a Friedel-Crafts acylation (*16*) of the symmetrical trialkylbenzenes. The melting point and analytical data of the compounds described in this article may be found in Table I. The differential thermal analysis curves for the three nitro compounds are shown in Figures 1, 2, and 3. All attempts to substitute 1,3,5-tri-*tert*-butylbenzene and 1,2,4,6-tetraisopropylbenzene by this method failed, only rearranged or dealkylated products being obtained.

The nitro group was introduced by nitration with concentrated nitric acid in acetic acid and acetic anhydride (*5*). Excellent yields of the desired products were obtained. Nitration with other nitration reagents, red fuming nitric acid (*9*), mixtures of concentrated nitric acid and concentrated sulfuric acid (*11*), and potassium nitrate and concentrated sulfuric acid (*17*), resulted in rearranged, oxidized, or dealkylated products. CAUTION! Nitration of organic

Table I. Analytical and Physical Data for Acetophenone Derivatives

Name	Melting Point, °C.	Formula	C Calcd.	C Found	H Calcd.	H Found	N Calcd.	N Found	Br Calcd.	Br Found	Infrared Absorption Bands, Cm.$^{-1}$ Infrared carbonyl	Infrared Absorption Bands, Cm.$^{-1}$ Sym. stretch nitro
2′,4′,6′-Triisopropylacetophenone (*9*)(I)	87–8	$C_{17}H_{26}O$	82.80	83.11	10.64	10.26					1699.7	
2,4,6-Triisopropyl-α-methylbenzyl alcohol (II)	92–3	$C_{17}H_{28}O$	82.19	82.17	11.36	11.38						
2,4,6-Triisopropyl-α-methylbenzyl acetate (III)	62.5–63.5	$C_{19}H_{30}O_2$	78.58	78.66	10.41	10.56						
2′,4′,6′-Triisopropyl-2-bromoacetophenone (IV)	53–4	$C_{17}H_{25}OBr$	62.76	62.84	7.75	7.62			24.56	24.98	1698.1 and 1721.5	
2′,4′,6′-Triisopropyl-3′-nitroacetophenone (V)	110–12	$C_{17}H_{25}O_3N$	70.07	70.04	8.65	8.30	4.81	5.15			1706.5	1376
2′,4′,6′-Triisopropyl-3′-aminoacetophenone (VI)	109–10	$C_{17}H_{27}N$					5.36	5.10			1701.5	
2′,4′,6′-Triisopropylbutyrophenone (VII)	41–2	$C_{19}H_{30}O$	83.16	83.46	11.02	10.86					1702.6	
2′,4′,6′-Triisopropyl-3′-nitrobutyrophenone (VIII)	101.5–02.5	$C_{19}H_{29}O_3N$	71.44	71.07	9.15	9.13	4.39	4.71			1705.3	1375
2′,4′,6′-Triisopropylpropiophenone (IX)	87–8	$C_{18}H_{28}O$	83.01	83.46	10.84	11.22					1699.3	
2′,4′,6′-Triisopropyl-3′-nitropropiophenone (X)	113–14	$C_{18}H_{27}O_3N$	70.79	70.48	8.91	9.10	4.59	4.88			1705.4	1378
2′,4′,6′-Trimethylacetophenone (*14*) (XI)											1701.8	
2′,4′,6′-Triethylacetophenone (*8*) (XII)											1700.3	

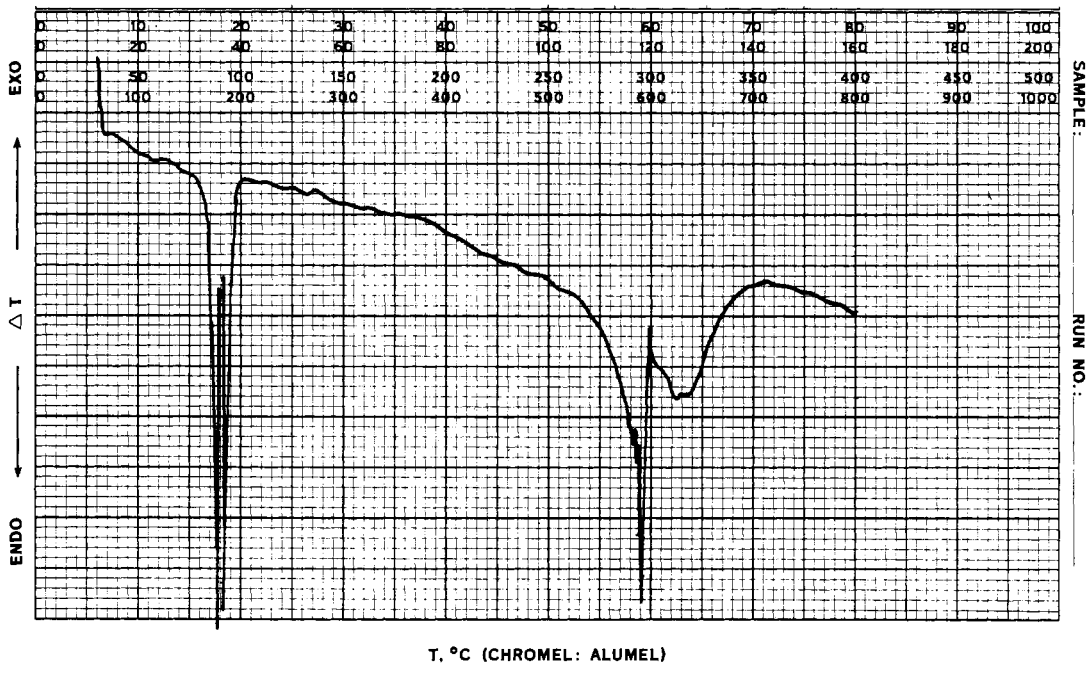

Figure 1. Differential thermal analysis of 3′-nitro-2′,4′,6′-triisopropylacetophenone

compounds with red fuming nitric acid may be hazardous. Reactions should be carried out on a small scale with adequate shielding. Attempts to prepare 2′,4′,6′-triisopropyl-3′,5′-dinitroacetophenone (for infrared absorption studies) by the method reported in the literature (*9*) failed.

The chemical reduction of the 2′,4′,6′-triisopropylacetophenone to the benzyl alcohol proceeded smoothly with lithium aluminum hydride in ether (*4*). Chemical reduction of the nitro group of 2′,4′,6′-triisopropyl-3′-nitroacetophenone was moderately successful when concentrated hydrochloric acid and stannous chloride (*15*) were used. Refluxing hydriodic acid (*10*), iron and glacial acetic acid (*2*), iron and hydrochloric acid (*13*), and hydrazine and Raney nickel (*1*) failed to convert the nitro compound to the amine derivative.

The 2′,4′,6′-triisopropyl-2-bromoacetophenone was prepared by bromination of the acetophenone derivative in chloroform (*6*). This product, a mild lachrymator, failed to react when treated with cyclohexylamine or morpholine in attempts to prepare the α-amino derivatives (*7*).

These compounds are the subject matter of a patent listing them as active herbicides (*12*).

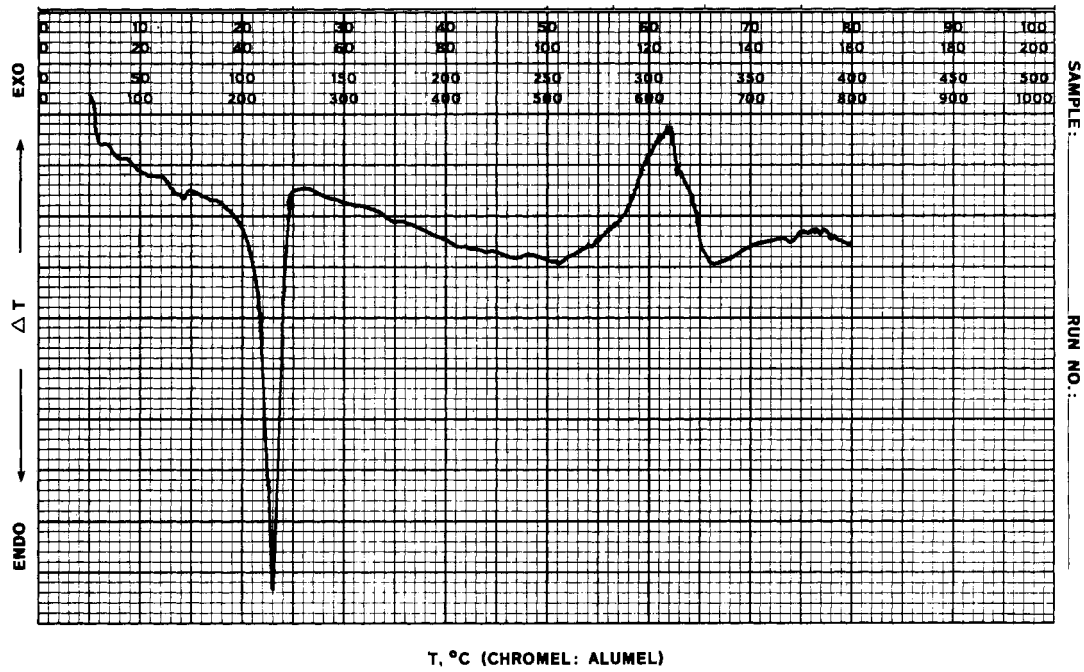

Figure 2. Differential thermal analysis of 3'-nitro-2',4',6'-triisopropylpropiophenone

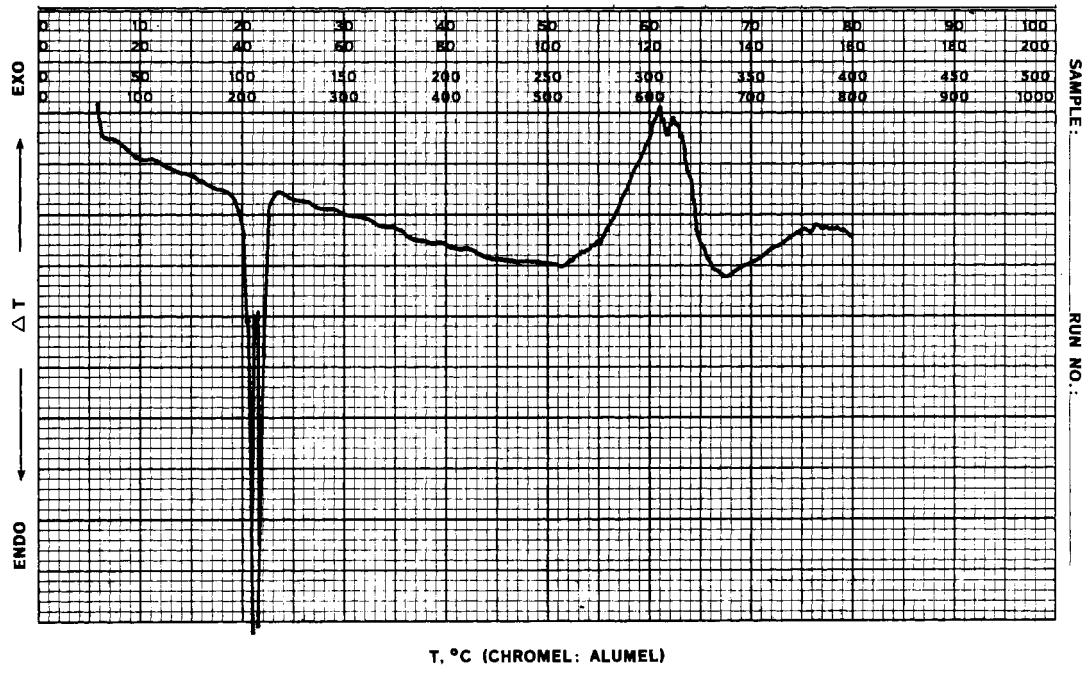

Figure 3. Differential thermal analysis of 3'-nitro-2',4',6'-triisopropylbutyrophenone

INFRARED CORRELATIONS

The infrared absorption frequency assigned to the carbonyl group has been reported by Bellamy (*3*). In general, the infrared absorption frequency of the carbonyl group of aryl-alkyl ketones ranges between 1685 and 1695 cm.$^{-1}$. Substituents on the aromatic ring or the alkyl group may cause a shift in the carbonyl group absorption frequency of 1692 cm.$^{-1}$ (*3*), whereas acetone gives a value of 1718 cm.$^{-1}$ (*3*). The insertion of other substituent groups in the phenyl ring, especially at the 2- and 6- positions, will cause some steric crowding. This crowding forces the carbonyl group out of the plane of the phenyl ring and results in higher carbonyl absorption frequencies (*3*). This has been demonstrated with methyl-, ethyl-, and isopropyl-substituent groups (Table I). The absorption frequencies assigned to the carbonyl groups of the trialkylacetophenone derivatives are intermediate between those of acetophenone (1692 cm.$^{-1}$) and acetone (1718 cm.$^{-1}$). The observed shifts were of the magnitude of 6 to 10 cm.$^{-1}$. The insertion of a nitro group, meta to the carbonyl, into the trialkylacetophenone derivatives causes a further shift to higher absorption frequencies (approximately 13 to 14 cm.$^{-1}$). However, a *m*-amino group causes only a slight shift above that of the trialkylacetophenone.

The nitro compounds all showed an absorption frequency for the nitro group at 1535 cm.$^{-1}$. This suggests that the nitro group is coplanar with the aromatic ring.

The bromo group substituted in the alpha position to the carbonyl group caused the expected shift to higher absorption frequencies (*3*).

EXPERIMENTAL

Purity of the samples was determined by sharpness of the melting point (uncorrected) and elemental analysis. The infrared spectra were recorded with a Beckman IR-9 potassium bromide, foreprism-grating spectrophotometer. Samples were scanned from 3800 to 1333 wave numbers in carbon tetrachloride solutions and from 1333 to 400 wave numbers in carbon disulfide solution.

The succeeding acetophenones were prepared by methods described in the literature: 2′,4′,6′-trimethylacetophenone (*14*), 2′,4′,6′-triethylacetophenone (*8*), and 2′,4′,6′-triisopropylacetophenone (*9*). The 2′,4′,6′-triisopropylacetophenone was also prepared by the reverse addition of the alkylbenzene to the catalyst and acylating reagent in carbon tetrachloride. Extreme care must be exercised when nitrating organic compounds with nitric acid in acetic anhydride. The formation of acetyl nitrate is possible and is therefore a potential hazard. These reactions should be run slowly at cold temperatures with adequate shielding.

2′,4′,6′-Triisopropyl-3′-nitroacetophenone (V). To an agitated and efficiently cooled solution of 246 grams of I in 670 ml. of acetic anhydride and 285 ml. of glacial acetic acid was added a solution of 80 ml. of concentrated nitric acid in 285 ml. of glacial acetic acid at such a rate (approximately 3 hours) that the temperature did not exceed 5° C. The mixture was stirred an additional 2 hours at 0° to 5° C. and allowed to warm to room temperature overnight. The reaction mixture was poured cautiously into 3 gallons of ice and ice water with vigorous agitation. The precipitate was collected by filtration, washed with distilled water, and air-dried. Yield was 274 grams (94%). A small sample recrystallized from ethanol gave pale yellow needle-like crystals.

2′-4′-6′-Triisopropyl-3′-nitrobutyrophenone (VIII). To an agitated and efficiently cooled solution of 137 grams of VII in 500 ml. of acetic anhydride and 325 ml. of glacial acetic acid was added a solution of 40 ml. of concentrated nitric acid in 325 ml. of glacial acetic acid at such a rate (approximately 3 hours) that the temperature did not exceed 5° C. The mixture was stirred an additional 2 hours at 0° to 5° C. and allowed to warm to room temperature overnight. The reaction mixture was poured cautiously into 3 gallons of ice and ice water with vigorous agitation. The precipitate was collected by filtration, washed with distilled water, and air-dried. Yield was 125 grams (78%). A small sample recrystallized from ethanol gave pale yellow needle-like crystals.

2′,4′,6′-Triisopropyl-3′-nitropropiophenone (X). To an agitated and efficiently cooled solution of 130 grams of IX in 500 ml. of acetic anhydride and 300 ml. of glacial acetic acid was added a solution of 40 ml. of concentrated nitric acid in 300 ml. of glacial acetic acid at such a rate (approximately 3 hours) that the temperature did not exceed 5° C. The mixture was stirred an additional 2 hours at 0° to 5° C. and allowed to warm to room temperature overnight. The reaction mixture was poured cautiously into 3 gallons of ice and ice water with vigorous agitation. The precipitate was collected by filtration, washed with distilled water, and air-dried. Yield was 112 grams (73%). A small sample recrystallized from ethanol gave pale yellow crystals.

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