retained each time. No differences could be observed in the heats of neutralization of samples taken after one and two crystallizations.

Solid solutions were prepared by several methods to test the reproducibility of the preparations. For all the results reported here, samples were prepared by dissolving known amounts of the two acids in ether and evaporating to dryness, as these samples gave the fastest rates of solution and more reproducible heats. No differences in the heats of neutralization could be detected with samples crystallized at different rates, or between the first and last fractions of the crystallization. Some samples were prepared by fusion of known amounts of the acids and slow crystallization at the melting point, while others were fused at temperatures above the melting point and quickly crystallized by pouring the liquid on a cold glass plate. These samples gave heats in excellent agreement with those recrystallized from ether, though less reproducible because of lower rates of solution and possibly some changes in composition through sublimation. Fusion at temperature greater than 150° C. produced samples with lower heats of neutralization. The causes of this effect were not investigated.

RESULTS

The calorimetric reaction scheme is given by reactions 1 and 2, where X_B is mole fraction of benzoic acid and the symbol (*) is used to indicate that the preceding species is dissolved in the solvent mixture, 50% (volume) methanol-water.

$$[X_B\,\mathrm{BH} + (1 - X_B)m\mathrm{FBH}]\,(\mathrm{solid}) + \mathrm{OH}^-\,(^*) = X_B\,\mathrm{B}^-\,(^*) + (1 - X_B)m\mathrm{FB}^-\,(^*) + \mathrm{H_2O}\,(^*) \quad (1)$$

$$\mathrm{BH(s)} + \mathrm{OH}^-\,(^*) = \mathrm{B}^-\,(^*) + \mathrm{H_2O}\,(^*) \quad (1a)$$

$$m\mathrm{FBH(s)} + \mathrm{OH}^-\,(^*) = m\mathrm{FB}^-\,(^*) + \mathrm{H_2O}\,(^*) \quad (1b)$$

$$X_B\,\mathrm{BH(s)} + (1 - X_B)m\mathrm{FBH(s)} = [X_B\,\mathrm{BH} + (1 - X_B)m\mathrm{FBH}]\,(\mathrm{solid}) \quad (2)$$

$$\Delta H_2 = X_B \Delta H_{1a} + (1 - X_B)\,\Delta H_{1b} - \Delta H_1 = \Delta H^{\mathrm{mix}}$$

Reactions 1a and 1b are recognized as special cases of Reaction 1 when X_B has the values 1 and 0. The measured heats of neutralization and the calculated heats of mixing are given in Table I. Each listed value is the average of at least two independent measurements, and the uncertainties are the maximum deviation from the mean. Figure 1 shows that the heat of mixing reaches a maximum value of about 350 cal. per mole around $X_B = 0.4$.

Similar studies on the partially miscible systems of benzoic acid and *o*- and *p*-fluorobenzoic acids are now in progress.

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Trinitromethane Adducts of α,β-Unsaturated Aldehydes and Acylals

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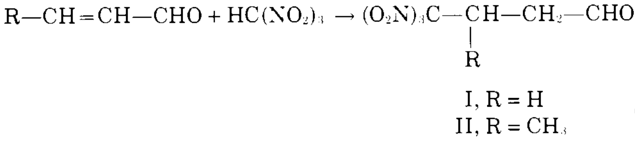
The Michael addition of trinitromethane to α,β-unsaturated aldehydes and acylals yielded the corresponding trinitroaldehydes and trinitroacylals in good yield. Physical properties of the compounds are given. A facile synthesis for 4,4,4-trinitrobutyraldehyde is reported.

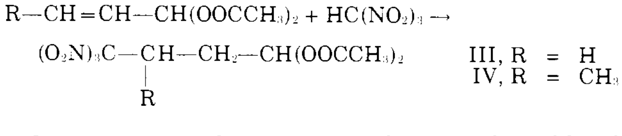
ALTHOUGH the Michael addition of trinitromethane to α,β-unsaturated compounds has been studied extensively (*1*, *5-7*), there have been no reports of polynitroaliphatic aldehyde derivatives prepared by this method. Ostensibly, Schimmelschmidt (*7*) obtained 3-methyl-4,4,4-trinitrobutyraldehyde by trinitromethane addition to the ethylenic and carbonyl groups of crotonaldehyde, followed by regeneration of the aldehyde group by sodium bicarbonate; however, no experimental details or physical properties were given. Since the authors were interested in polynitroaliphatic aldehyde derivatives, the Michael addition of trinitromethane to unsaturated aldehydes and acylals was investigated, and the previously unreported 4,4,4-trinitrobutyraldehyde and similar compounds were successfully prepared by facile syntheses.

Trinitromethane underwent Michael addition to acrolein and crotonaldehyde in aqueous and chloroform solvent, Equation 1, to give good yields of 4,4,4-trinitrobutyraldehyde, I, and 3-methyl-4,4,4-trinitrobutyraldehyde, II.



$$\mathrm{R{-}CH{=}CH{-}CHO + HC(NO_2)_3 \rightarrow (O_2N)_3C{-}\underset{\displaystyle R}{CH}{-}CH_2{-}CHO} \qquad \begin{matrix}\mathrm{I,\ R = H}\\ \mathrm{II,\ R = CH_3}\end{matrix} \quad (1)$$

The addition of trinitromethane to 1,1-diacetoxy-2-propene and to 1,1-diacetoxy-2-butene was also successful, Equation 2, and gave the Michael adducts, 1,1-diacetoxy-4,4,4-trinitrobutane, III, and 1,1-diacetoxy-3-methyl-4,4,4-trinitrobutane, IV.



$$\mathrm{R{-}CH{=}CH{-}CH(OOCCH_3)_2 + HC(NO_2)_3 \rightarrow} \\ \mathrm{(O_2N)_3C{-}\underset{\displaystyle R}{CH}{-}CH_2{-}CH(OOCCH_3)_2} \qquad \begin{matrix}\mathrm{III,\ R = H}\\ \mathrm{IV,\ R = CH_3}\end{matrix} \quad (2)$$

Both aqueous and nonaqueous solvents such as chloroform have been used as media for addition reactions of tri-

Table I. Trinitromethane Adducts of α,β-Unsaturated Aldehydes and Acylals

Compound	Yield, %	M.P./B.P. Mm. Hg., ° C.	n_D^{25}	Empirical Formula	Carbon, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found
4,4,4-Trinitrobutyraldehye	68[a] 64[b]	.../87–89 (0.35)	1.4731	$C_4H_5N_3O_7$	23.20	23.73	20.29	20.40
2,4-Dinitrophenylhydrazone	...	157–158 dec./...	...	$C_{10}H_9N_7O_{10}$	31.02	31.35	25.33	25.28
3-Methyl-4,4,4-trinitrobutyraldehyde	44[a] 57[b]	.../85–87 (0.45)	1.4675	$C_5H_7N_3O_7$	27.16	27.80	19.00	18.90
2,4-Dinitrophenylhydrazone	...	157–158 dec./...	...	$C_{11}H_{11}N_7O_{10}$	32.92	33.18	24.44	24.49
1,1-Diacetoxy-4,4,4-trinitrobutane	32[c] 97[d]	69–70/...	...	$C_8H_{11}N_3O_{10}$	31.07	31.00	13.59	13.36
1,1-Diacetoxy-3-methyl-4,4,4-trinitrobutane	73[c] 51[d]	[e]	1.4658	$C_9H_{13}N_3O_{10}$	33.44	33.22	13.00	12.80

[a] Reaction solvent: water. [b] Reaction solvent: chloroform. [c] Method A. [d] Method B. [e] Nondistillable oil.

nitromethane; optimum yields are obtained in aqueous systems (*4*) at pH <7; nonaqueous systems do not require the usual alkaline catalyst for Michael addition (*1*). To obtain the best possible yields of polynitroaldehydes, the authors studied the addition of trinitromethane to acrolein and crotonaldehyde in water solution at ambient temperature and in refluxing chloroform solution (Table I). Although there seems to be little difference in yield of I from the two solvents, it is more advantageous to use the aqueous system, since relatively pure product can be obtained by simple extraction and washing of the extract several times with water. Heating of the chloroform reaction mixture produced undesirable by-products and oxides of nitrogen, thereby making purification of the product more difficult. The addition of trinitromethane to crotonaldehyde gave unexpectedly lower yields (44%) in the aqueous system than in refluxing chloroform (57% yield). This is probably because of the lower water solubility of crotonaldehyde compared with that of acrolein. However, the aqueous system was preferred because of the ease of product purification. Some difficulty was encountered in obtaining satisfactory elemental analyses for I and II since these compounds tended to decompose slowly at ambient temperature. Therefore, using a known procedure (*2*), these aldehydes were converted to their 2,4-dinitrophenylhydrazone derivatives, which gave satisfactory elemental analyses. In addition, the structures of I and II were confirmed by NMR analysis.

The addition of trinitromethane to the aldehyde acylals was briefly investigated to determine if it was advantageous to block the free aldehyde group. The aldehyde acylals, 1,1-diacetoxy-2-propene and 1,1-diacetoxy-2-butene, were allowed to react with trinitromethane in ether solution with 1 mole equivalent of boron trifluoride etherate at ambient temperature to give III and IV. III was obtained as a white crystalline material, and IV was obtained as an oil which could not be crystallized or distilled; III and IV were characterized by elemental and infrared analyses and NMR spectra as 1,1-diacetoxy-4,4,4-trinitrobutane and 1,1-diacetoxy-3-methyl-4,4,4-trinitrobutane, respectively. The trinitromethane addition to acylals in chloroform or ether at ambient or reflux temperature without boron trifluoride gave inconsistent yields of III and IV.

To confirm further the structures of III and IV, they were also prepared by a previously reported procedure for the synthesis of acylals (*3*). The aldehydes, I and II, were treated with acetic anhydride and a catalytic amount of sulfuric acid to give products identical to III and IV when compared by infrared and NMR analysis.

EXPERIMENTAL

Proton NMR spectra were run on a Varian HA-100 spectrometer, and infrared spectra were run on a Perkin-Elmer 137 spectrophotometer. All temperatures are reported in degrees Centigrade. Melting points were determined on a Fischer-Johns melting point apparatus. Elemental analyses were determined by Stanford University Microanalytical Laboratory, Stanford, Calif.

CAUTION. *Because of their explosive nature, reasonable care and precautions should be taken when handling or distilling polynitro compounds.* The distillation of I resulted in an explosion on one occasion.

4,4,4-Trinitrobutyraldehyde, I. To a cold (0° to 5° C.) stirred solution of 6.0 grams (0.04 mole) of trinitromethane in 25 ml. of water, there was added dropwise a solution of 2.2 grams (0.04 mole) of acrolein in 15 ml. of water. A clear, yellow oil separated immediately, and the reaction mixture was stirred at ambient temperature for 15 hours. The yellow oil was extracted into 25 ml. of methylene chloride, and this solution was washed with three 25-ml. portions of water followed by two 25-ml. portions of 5% aqueous sodium bicarbonate solution. The organic phase was dried with anhydrous magnesium sulfate, filtered, and evaporated to a clear, pale yellow oil which was distilled under reduced pressure, b.p. 87–9° C. (0.35 mm.), to give 5.5 grams (68% yield) of I, n_D^{25} 1.4731. Distillation of the product was not necessary when the methylene chloride solution had been washed thoroughly with water, dried, and evaporated, since material obtained in this way was identical with distilled product.

NMR spectrum in deuterochloroform with tetramethylsilane (TMS) reference: C_1 proton at 0.28τ (singlet), C_2 protons at 7.04τ (triplet of doublets, J = 4 cps., 2 cps.), C_3 protons at 6.64τ (triplet, AB pattern, J = 4 cps.). The integral was consistent with the assignment of protons. Infrared spectrum (neat): 3.35(w), 3.45(w) C—H; 5.79(s) C=O; 6.25(s), 7.68(m), 12.40μ(m) NO_2.

2,4-Dinitrophenylhydrazone of I. Using a known procedure (*2*), the 2,4-dinitrophenylhydrazone derivative of I was prepared. A solution of 0.62 gram (0.003 mole) of I in 60 ml. of ethyl alcohol was added in one portion to 35 ml. of a 0.1 molar solution of 2,4-dinitrophenylhydrazine in ethanolic phosphoric acid (equal amounts of 85% phosphoric acid and ethyl alcohol). The resulting cloudy mixture was warmed to 60° C. for 10 minutes and then cooled in an ice bath. The precipitated yellow solid was filtered, washed with water, and recrystallized from ethyl alcohol to give a near quantitative yield of product, m.p. 157–8° C. dec.

3-Methyl-4,4,4-trinitrobutyraldehyde, II. This compound was prepared in 44% yield in a manner similar to I.

NMR spectrum in deuterochloroform with TMS reference: C_1 proton at 0.30τ (singlet), C_2 protons centered at 7.18τ (triplet of doublets, AB pattern, $J \sim 8$ cps), C_3 proton at 6.03τ (pentet, $J \sim 8$ cps), 3-methyl protons at 8.64τ (doublet, J = 6 cps). The integral was consistent with the assignment of protons. Infrared spectrum (neat): 3.45(w) C—H; 5.79(m) C=O; 6.25(s), 7.70(m), 12.48 microns (s) NO_2.

2,4-Dinitrophenylhydrazone of II. The same procedure described for I was used to prepare the 2,4-dinitrophenylhydrazone of II which was recrystallized from ethyl acetate-hexane, m.p. 157–8° C. dec.

1,1-Diacetoxy-4,4,4-trinitrobutane, II. METHOD A. A solution containing 10 ml. of anhydrous ether, 3.0 grams (0.019 mole) of 1,1-diacetoxy-2-propene, 2.9 grams (0.019 mole) of trinitromethane and 2.7 grams (0.019 mole) of boron trifluoride etherate was stirred at ambient temperature for 8 hours. The dark brown reaction mixture was dissolved in 25 ml. of ether and was washed with four 25-ml. portions of water. The ether solution was dried with anhydrous magnesium sulfate, filtered, and evaporated to a dark red, viscous sirup which was extracted with two 25-ml. portions of boiling hexane. The hexane solution was cooled overnight in the refrigerator to yield 1.85 grams of orange crystals (32% yield). The product was decolorized with activated charcoal in ether solution and was crystallized by adding hexane to give white crystals melting at 60° to 70° C.

NMR spectrum in deuterochloroform with TMS reference: C_1 proton at 3.18τ (triplet, J = 45 cps), C_2 protons at 7.76τ (quartet, J = 4.5 cps), C_3 protons at 6.80τ (triplet, J = 8.4 cps), and acetyl protons at 7.96τ (singlet). The integral was consistent with the assignment of protons. Infrared spectrum (KBr): 3.40(3) C—H; 5.72(s) C=O; 6.30(3), 7.72(m), 12.48(s) NO_2; 8.05(s), 8.32(s) ester C—O; 9.92 microns (m).

METHOD B. Compound III was prepared by a previously reported procedure (*3*) for the synthesis of acylals. To a solution containing 2.0 grams (0.010 mole) of I in 10 ml. of acetic anhydride was added 2 drops of 96% sulfuric acid. The mixture was stirred at ambient temperature for 15 hours, then poured into 100 ml. of water, and stirred for 15 minutes. The pale yellow oily lower organic phase was extracted with 25 ml. of ether, and the ether phase was washed with two 100-ml. portions of 5% sodium bicarbonate solution. The organic phase was dried with anhydrous magnesium sulfate, filtered, and evaporated to give 2.9 grams (97% of theory) of III which was recrystallized from ether-hexane to give white needle crystals, m.p. 69–70° C. The infrared and NMR spectra of III prepared by this method were identical to those of III prepared by method A.

1,1-Diacetoxy-3-methyl-4,4,4-trinitrobutane, IV. METHOD A. This compound was prepared by the procedure used for III, but the product could not be crystallized. The yellow oil which was obtained (4.0 grams, 73%) was identified as IV by elemental analysis, and infrared and NMR spectra.

NMR spectrum in deuterochloroform with TMS reference: C proton at 3.14θ (doublet of doublets, J = 6 cps, 4 cps), C_2 protons at 7.80θ (multiplet), C_3 proton at 6.62τ (quintet, J = 6 cps), 3-methyl protons at 8.52τ (doublet, J = 6 cps), acetyl protons at 7.93τ (two singlets separated by 3 cps). The integral was consistent with the assignment of protons. The acetyl protons appeared as two distinct signals each integrating for three protons. The two signals probably arise from rotational conformations present in this compound, whereas they are not evident in III. Infrared spectrum (neat): 3.35(w), 3.40(w) C—H; 5.65(s) C=O; 6.25(s), 7.70(m), 12.50(m) NO_2; 8.80(s), 8.32(s) ester C—O; 9.90μ(m).

METHOD B. The same procedure described for the synthesis of III by method B was used for the synthesis of IV by this method. IV was obtained in 51% yield, and the infrared and NMR spectra were identical to IV prepared by method A.

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Synthesis of Substituted 7-(1-Naphthyl)benz[*a*]anthracenes

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By known procedures, three new ketones and two new benz[*a*]anthracene derivatives were prepared and characterized. Per cent yields, boiling and/or melting points, and elemental analyses are given.

POLYCYCLIC aromatic compounds are at the forefront of the most exciting chemical research being done today. These compounds provide interesting models for studies in organic synthesis and physical organic chemistry including spectroscopic studies of various sorts, as well as physiological activity-molecular structure correlations. Many of the structures one would like to have are either unavailable or very difficult to prepare with the desired substituent in the proper position in the polycyclic ring system. The synthesis of two new important polycyclic aromatic compounds is reported. One compound, 7-[1-(4-methyl)naphthyl]benz[*a*]anthracene (II), contains an electron repelling methyl group, while the second compound, 7-[1-(4-bromo)naphthyl]benz[*a*]anthracene (IV), contains an electron attracting bromine atom. The position of the substituent in each case is known, and most importantly, it