

absorbance was measured at the indicated wave length (μ): toluidine (*o*-, 13.43; *m*-, 13.02; *p*-, 12.37); N-methyl-toluidine (*o*-, 13.44; *m*-, 13.05; *p*-, 12.43). Comparison

with known mixtures showed a deviation of no more than $\pm 1\%$ for any isomer. Infrared spectra were obtained with a Perkin-Elmer model 21 infrared spectrophotometer.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WESTERN MICHIGAN UNIVERSITY, KALAMAZOO, MICH.]

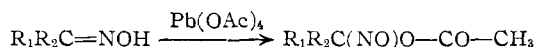
The Preparation and Structure of Azoacetates, a New Class of Compounds¹

BY DON C. IFFLAND, LYNN SALISBURY AND WM. R. SCHAFER

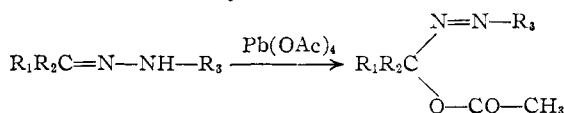
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Lead tetraacetate is shown to react with ketohydrazone to form azoacetates. The structure for these compounds, $R_1R_2C(OAc)N=NR_3$, is established from analysis of the ultraviolet spectra; a mechanism is proposed for the reaction.

In an earlier report² it was shown that lead tetraacetate reacts with ketoximes to form nitrosoacetates



An apparently similar reaction of lead tetraacetate with cyclohexanone phenylhydrazone that formed an unidentified high boiling oil was also described. This reaction of lead tetraacetate has now been examined in detail and found to be general for the preparation of a new class of compounds, the azoacetates,³ from ketohydrazone.



The properties of fourteen compounds prepared in this way from hydrazones are collected in Table I. The reactions producing these compounds are marked by simplicity, generally high yields and freedom from reaction by-products which might interfere with easy isolation of the azoacetates. As indicated by the yields in Table I, the course of the reaction is not affected by variation of alkyl, cycloalkyl or phenyl substituents at the carbonyl carbon in the hydrazone or by variation of the aryl or alkyl substituent at the hydrazone nitrogen. In addition to the reactions of lead tetraacetate, lead tetrabenzoate with benzophenone phenylhydrazone gave an azobenzoate in 86% yield.

Generally, these reactions have been carried out in methylene chloride solution at 0 to 10°. Benzene and acetic acid solvents have also been used with no change in the nature of the reaction. However, the latter solvents are much less convenient because of lower solvent capacity for both reactants and result in greater difficulty in isolation of the reaction product.

The structure of the azoacetates obtained from hydrazones in the lead tetraacetate reaction is similar to the autoxidation product described by Pausaker. It has been concluded that the autoxidation of hydrazones, such as benzaldehyde phenyl-

hydrazone, with oxygen form azohydroperoxides,^{4a} $C_6H_5CH(O-OH)N=NC_6H_5$, while peracids (perphthalic acid) gave azoxy compounds.^{4b,5} The structure for the azoacetates is established conclusively by the ultraviolet spectra. As shown in Table II, the azoacetates derived from ketoalkylhydrazones show only a weak absorption band at 350-357 $m\mu$. This absorption is clearly the R-band characteristic of azoalkanes as shown by azomethane.⁶ In contrast, those azoacetates prepared from arylhydrazones are characterized by an intense absorption at 266-277 $m\mu$ with a weak absorption at 395-404 $m\mu$. These values are independent of the alkyl or aryl structure of R_1 and R_2 as well as a change from acetate to benzoate. This absorption resembles the spectra of alkylazobenzenes.^{6a} The intensive band is undoubtedly due to the azo conjugation with the benzene ring (K-band) while the weak absorption shows the characteristic bathochromic shift of the R-band. These values are also similar to the spectra of the recently described azonitriles.⁷ α -(Phenylazo)-isobutyronitrile for example has maxima at 270 and 390 $m\mu$ ($\log \epsilon$ 3.81 and 2.30, respectively). Thus, the observed spectra indicate that the azoacetate structure rather than the unrearranged structure, $R_1R_2C=NN(OAc)R_3$, is correct for these compounds.

The rate of the reaction of lead tetraacetate with hydrazones was followed in a few instances by measuring the amount of unchanged lead tetraacetate. The reaction in an aliquot sample was halted immediately by adding water and converting the unreacted lead tetraacetate to lead dioxide. This brown precipitate was washed, dried and weighed. The determination was completed entirely in a centrifuge tube and a precision of 96 to 98% was realized with known amounts of pure lead tetraacetate.

With acetone phenylhydrazone and acetone *p*-nitrophenylhydrazone reactions were 90 to 95% complete at 30 sec. when the first aliquot was ob-

(1) Presented in part at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960. This work was supported in part by the National Science Foundation under Grant NSF-G 5789.

(2) D. C. Iffland and G. X. Criner, *Chemistry & Industry*, 176 (1956).

(3) For convenience the designation azoacetate is suggested for the general structure shown. In the experimental section the systematic acetoxyarylaazoalkane or acetoxyalkylazoalkane name is used.

(4) (a) K. A. Pausaker, *J. Chem. Soc.*, 3478 (1950); (b) B. M. Lynch and K. A. Pausaker, *ibid.*, 2517 (1950), and following papers.

(5) Dr. Bernard Gillis, Duquesne University (private communication), has indicated that peracetic acid oxidation of phenylhydrazones also leads to azoacetates as described in this paper; he will publish details of his procedure.

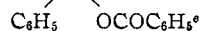
(6) (a) A. Burawoy, *J. Chem. Soc.*, 1865 (1937); (b) for a review of correlation between structure and absorption, see E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, Chap. 4.

(7) M. C. Ford and R. A. Rust, *ibid.*, 1297 (1958).

TABLE I
YIELDS AND PROPERTIES OF AZOACETATES

$$\begin{array}{c} R_1 \\ \diagup \\ CN=NR_3 \\ \diagdown \\ R_2 \\ \diagup \\ OCOCH_3 \end{array}$$

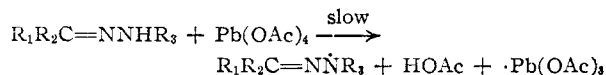
	R ₁	R ₂	R ₃	Yield, %	[B.p. or m.p.] °C.	n _D ²⁰	d ₄ ²⁵	[Nitrogen, %]	
					mm.			Found	Theory
I	CH ₃ -	CH ₃ -	C ₆ H ₅ -	83	89	1	1.5152	13.65	13.50
II	CH ₃ -	CH ₃ -	<i>p</i> -BrC ₆ H ₄ -	80	113	1	1.5480	9.94	9.83
III	CH ₃ -	CH ₃ -	<i>p</i> -NO ₂ C ₆ H ₄ -	78	141	0.5	1.5398	16.76	16.73
IV	CH ₃ -	CH ₃ -	2,4-(NO ₂) ₂ C ₆ H ₃ -	89	M.p. 87-88			19.06	18.91
V	CH ₃ -	CH ₃ -	β-C ₆ H ₅ Et-	55	147	8	1.4967 ^a	11.66	11.96
VI	CH ₃ -	CH ₃ -	1-Phenyl-2-propyl	77	96	1	1.4948 ^b	11.42	11.28
VII	CH ₃ -	C ₂ H ₅ -	C ₆ H ₅ -	81	100	1	1.5141	12.87	12.72
VIII	-(CH ₂) ₅ -	CH ₃ -	C ₆ H ₅ -	75	78	5	1.4560 ^c	15.24	15.21
IX	-(CH ₂) ₅ -	CH ₃ -	C ₆ H ₅ -	76	137	1	1.5361	11.18	11.38
X	-(CH ₂) ₅ -	2,4-(NO ₂) ₂ C ₆ H ₃ -		80	M.p. 102-103			16.60	16.66
XI	C ₆ H ₅ -	C ₆ H ₅ -	C ₆ H ₅ -	90	M.p. 101-103			8.54	8.48
XII	C ₆ H ₅ -	C ₆ H ₅ -	CH ₃ -	^d	M.p. 125-126 ^d			10.54	10.44
XIII	C ₆ H ₅ -	C ₆ H ₅ -	<i>t</i> -C ₄ H ₉ -	65	M.p. 61-63			9.19	9.03
XIV	C ₆ H ₅ -	C ₆ H ₅ -	C ₆ H ₅ -	86	M.p. 159-161			7.18	7.14



^a *t* = 23°. ^b *t* = 20°. ^c *t* = 27°. ^d 42 g. of impure hydrazone gave 21 g. of pure azoacetate recrystd. from 60-90° petr. ether; minimum yield 40%. ^e An azobenzoate.

tained. A more amendable compound was acetone 2,4-dinitrophenylhydrazone which provided a half-reaction time of 25 min. (average *k*, 0.19 l. mole⁻¹ min.⁻¹) when 0.02 mole of reactants were mixed in 125 ml. of methylene chloride at 25°. The data obtained fitted the second-order rate equation.⁸ Acetone *o*-nitrophenylhydrazone gave a comparable rate. The rate-retarding effect of the *o*-nitro group is most likely a consequence of strong intramolecular association between the *o*-nitro group and the amino hydrogen atom.⁹ A steric factor is shown to be insignificant since the rate of the reaction of acetone *o*-bromophenylhydrazone was as fast as the unsubstituted acetone phenylhydrazone. Finally, in acetic acid solution, rather than methylene chloride, the reaction of 0.004 mole of each acetone 2,4-dinitrophenylhydrazone and lead tetraacetate in acetic acid gave a rate constant of 0.51 l. mole⁻¹ min.⁻¹ at 25°.

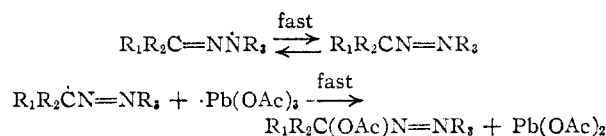
This reaction of hydrazones with lead tetraacetate, although much faster, appears similar to the lead tetraacetate oxidation of enolizable ketones to yield the α-acetoxy ketone studied by Cavill and Solomon.¹⁰ The following mechanism sequence, related to that described by Cavill and Solomon, is proposed for this new reaction of hydrazones



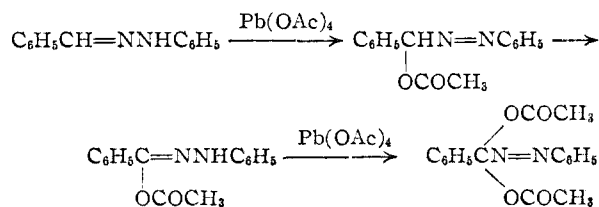
(8) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 13, 17.

(9) The dependence of this reaction upon the reactivity of the amino hydrogen atom also points up another similarity to the reaction of oximes with lead tetraacetate. Thus, replacement of the structurally equivalent hydroxyl hydrogen atom by a methyl group has lead to an 89% recovery of cyclohexanone oxime *O*-methyl after 4.5 hr. reaction with lead tetraacetate under conditions which converted cyclohexanone oxime to the nitrosoacetate in 35% yield in only 0.25 hr.

(10) G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 4426 (1955).



Finally, the reaction of lead tetraacetate with one aldehyde hydrazone, benzaldehyde phenylhydrazone, has been examined. Here, a dark red oil was produced; b.p. 158-163° (1.5 mm.), *n*_D²⁵ 1.5953, λ_{max} 283 mμ, log ε_{max} 3.61. This material has not been obtained in pure form for analysis but is believed to be an azodiaceate formed by the sequence of reactions



The chemical properties of the azoacetates prepared from hydrazones are currently being investigated.

Experimental¹¹

Except as indicated below, the hydrazones were prepared from the necessary ketones and substituted hydrazines by adapting general procedures.¹² The boiling points and refractive indices or the melting points were in agreement with literature values.

Benzophenone *t*-butylhydrazone was prepared from diphenyldiazomethane and *t*-butylmagnesium chloride.¹³ β-

(11) Microanalyses are by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected. All ultraviolet spectra were determined using a Beckman model DU spectrophotometer. The solvent was 95% ethanol in every case.

(12) (a) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 131, 219; (b) R. Adams and J. R. Johnson, "Laboratory Experiments in Organic Chemistry," The Macmillan Co., New York, N. Y., 1949, p. 257.

(13) P. A. S. Smith, J. M. Clegg and J. Lakritz, *J. Org. Chem.*, **23**, 1598 (1958).

TABLE II
 SPECTRA OF AZOACETATES AND RELATED AZO COMPOUNDS

Compound	λ_{\max} , m μ	log ϵ	λ_{\max} , m μ	log ϵ
I	267	3.97	400	2.28
VII	266	4.05	400	2.33
IX	266	3.97	.. ^a	
XI	269	4.14	.. ^a	
XIV	270	4.07	404	2.37
II	277	4.96	.. ^a	
III	270 ^b	4.03	395	4.46
VIII			357	1.39
XII			352	1.58
V			355	1.56
VI			356	1.49
XIII			350 ^c	2.11
CH ₃ N=NCH ₃ ^d			347	>1
CH ₃ N=NCH ₂ H ₅ ^d	260	3.89	403	1.94
(C ₆ H ₅) ₂ CHN=NC ₆ H ₅ ^e	275	4.08	341	4.68

^a Not measured. ^b Inflection point; maximum at 252 m μ , log ϵ 4.19, corresponds to K-band in nitrobenzene (λ_{\max} 252, log ϵ 4.00); ref. 6b, p. 153. ^c No maxima above 210 m μ ; value is for shoulder. ^d Ref. 6a. ^e Observed in this work; Prepared according to S. E. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 3628 (1955), who report only maxima at 345 m μ .

Phenylethylhydrazine was obtained by alkylation of hydrazine.¹⁴

1-Phenyl-2-hydrazinopropane was prepared from 1-phenyl-2-propylamine via the sydnone synthesis¹⁵; b.p. 126 to 130° (12 mm.), n_D^{20} 1.5395, d_4^{20} 0.995.

Anal. Calcd. for C₉H₁₄N₂: N, 18.64. Found: N, 18.52.

Benzophenone methylhydrazine decomposed slowly at room temperature with evolution of gas. Freshly distilled material with the following properties was used: b.p. 140 to 141° (0.5–1 mm.), n_D^{20} 1.6228 to 1.6248.

Acetone *o*-bromophenylhydrazine was prepared from *o*-bromophenylhydrazine¹⁶; b.p. 115–117° (2 mm.), n_D^{20} 1.6019. This hydrazine was used only in the rate experiments and the azoacetate was not isolated.

Lead tetraacetate (90%) was procured from Arapahoe Chemicals, Inc. This product, wet with acetic acid, was used in all except the rate reactions. For the latter use the 90% material was washed free of acetic acid with 20–40° petroleum ether and vacuum dried. Lead tetrabenzoate was prepared according to the procedure of Hey, Sterling and Williams.^{17,18}

Generally, 0.1 mole of each hydrazine was treated with the lead salt in a common procedure with the only variation being in the amount of solvent needed to attain solution of the reagents. The following description is typical:

Preparation of 2-Acetoxy-2-phenylazopropane.—A solution of 14.8 g. (0.10 mole) of acetone phenylhydrazine dis-

solved in 25 ml. of methylene chloride was added in the course of 15 minutes to a stirred solution of 49 g. (0.11 mole) of lead tetraacetate dissolved in 200 ml. of methylene chloride. The slightly exothermic reaction was maintained at 0 to 10° with an ice-bath during the addition of the hydrazine, then warmed to 20 to 25° and stirred an additional 15 minutes. The solution quickly developed a yellow color and a white precipitate of lead diacetate formed. The reaction mixture was next stirred with 200 ml. of water. Any lead dioxide formed was removed by filtration and the methylene chloride layer was separated and washed successively with water and dilute sodium bicarbonate solution until free of acetic acid. After drying over anhyd. sodium sulfate, the solvent was removed by vacuum evaporation and the residue vacuum distilled to produce 17.0 g. (83%) of 2-acetoxy-2-phenylazopropane having the properties indicated in Table I.

The addition of 0.02 mole of acetone phenylhydrazine dissolved in 30 ml. of dry benzene to 0.022 mole of lead tetraacetate dissolved in 250 ml. of dry benzene gave a 91% yield of the azoacetate isolated as described in the methylene chloride procedure.

Determination of Rate of Reaction of Lead Tetraacetate with Acetone 2,4-Dinitrophenylhydrazine.—A solution of 4.76 g. (0.02 mole) of acetone 2,4-dinitrophenylhydrazine was prepared in methylene chloride at 25° and diluted to exactly 30 ml. A second solution of 9.74 g. (0.022 mole) of acetic acid-free lead tetraacetate was prepared in methylene chloride at 25° and diluted to exactly 80 ml. A reaction flask with a motor driven stirrer was placed in a constant temperature water-bath and maintained at 25.0 ± 0.1°. The two solutions were added simultaneously and as rapidly as possible to the reaction flask. At the desired sampling time, a 2-ml. aliquot was withdrawn and pipetted into a mixture of 5 ml. of ether and 5 ml. of water contained in a tared 15-ml. centrifuge tube. The tube was stoppered and shaken vigorously. Lead dioxide was collected by centrifugation and washed successively with 5-ml. portions of water, 95% ethanol and absolute ether. The tube and contents were dried 30 min. at 105°. Table III contains a summary of weights of lead dioxide obtained in a series of samples from the reaction described above along with values for the reactions of 0.02 mole of acetone *o*-nitrophenylhydrazine (reactants equimolar) in 125 ml. of methylene chloride.

TABLE III

Min.	Wt. PbO ₂ , g.	k , l. moles ⁻¹ min. ⁻¹	Min.	Wt. PbO ₂ , g.	k , l. moles ⁻¹ min. ⁻¹
Acetone 2,4-dinitrophenylhydrazine			Acetone <i>o</i> -nitrophenylhydrazine		
15	0.0579	0.25	8	0.0372	0.59
45	.0362	.22	15	.0272	.63
90	.0272	.18	27	.0202	.57
176	.0211	.14	45	.0142	.57
270	.0153	.15	65	.0107	.56

The reaction of 0.04-mole amounts of acetone 2,4-dinitrophenylhydrazine and lead tetraacetate in 125 ml. of methylene chloride at 25° gave values of k between 0.32 and 0.67. When acetone phenylhydrazine, acetone *p*-nitrophenylhydrazine and acetone *o*-bromophenylhydrazine were substituted for acetone *o*-nitrophenylhydrazine in the above procedure, no lead dioxide was obtained in samples removed after 60 sec.

(19) A 0.0831-g. sample of lead tetraacetate dissolved in 2 ml. of methylene chloride yielded 0.0431 g. (96.2%) of lead dioxide in this procedure.

(14) E. Votocek and O. Leminger, *Coll. Czech. Chem. Comm.*, **4**, 273 (1932).

(15) J. Fugger, J. M. Tien and I. M. Hunsberger, *J. Am. Chem. Soc.*, **77**, 1843 (1955).

(16) I. M. Hunsberger, E. R. Shaw, J. Fugger, R. Ketcham and D. Lednicher, *J. Org. Chem.*, **21**, 394 (1956).

(17) D. H. Hey, C. J. M. Sterling and G. H. Williams, *J. Chem. Soc.*, 2747 (1954).

(18) We are indebted to Mr. Gerald Martin for assistance in the preparation of lead tetrabenzoate and for its reaction with benzophenone phenylhydrazine.