also supports structure 2,4-dimesitoyl-3,5-dibenzylcyclohexene; it has a shoulder at 242 mμ (ε 16,200).

Reduction of 2,4-Dimesitoyl-3,5-dibenzylcyclohexene with Lithium Aluminum Hydride.—A solution of 4 g. (0.0043 mole) of the diketone in 50 ml. of dry tetrahydrofuran was added slowly with stirring to a suspension of 0.42 g. (0.013 mole) of lithium aluminum hydride in 50 ml. of dry tetrahydrofuran. The reaction mixture was stirred at room temperature for 1.5 hr., and the excess hydride decomposed by cautious addition of ice chips with the flask immersed in an ice bath. The product, isolated by conventional procedures, was recrystallized from ethanol–chloroform; m.p. 193–193.7°; yield, 2.15 g. (53.4%). Further recrystallization from ethanol gave long white needles melting at 200–200.5°.

Anal. Calcd. for $C_{40}H_{46}O_2$: C, 85.97; H, 8.30. Found: C, 85.62; H, 8.41.

The infrared spectrum (Nujol, hexachlorobutadiene) has bands at 3460, 1680 (broad), and 857 cm.$^{-1}$, which are to be expected for 3-mesitoyl-2,6-dibenzylcyclohexylmesitylcarbinol.

Acetylation of 0.2 g. of the carbinol gave the acetate, which crystallized from ethanol; m.p. 135–136°; yield, 59%. The infrared spectrum (Nujol, hexachlorobutadiene) has bands for acetate (1730), ketone (1694), and mesityl (855 cm.$^{-1}$) groups.

Oxidation of the carbinol with chromium trioxide in pyridine[10] gave 2,4-dibenzyl-1,3-dimesitoylcyclohexane, which crystallized from ethanol–chloroform as white prisms, m.p. 152.5–154°. The infrared spectrum (Nujol, hexachlorobutadiene) is consistent with the structure 2,4-dibenzyl-1,3-dimesitoylcyclohexane (ν_{max} 1689, 1680, 857 cm.$^{-1}$; no band is found in the O–H stretching region).

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[10] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarrett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

2,4-Dinitrophenylhydrazones. IV.[1] The Reactions of Vinyl Ketones and β-Alkoxy Ketones. The Formation of Substituted 6-Nitrobenzotriazole Oxides

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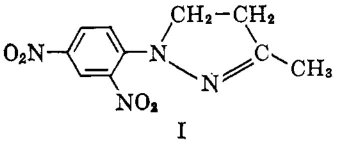
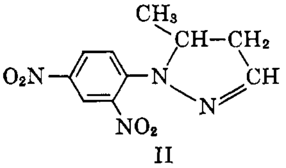
The compound described by Matsoyan and Vartanyan as 3-methyl-1-(2,4-dinitrophenyl)pyrazoline has been prepared in several ways. The ethyl analog also has been prepared. These compounds are shown not to be the pyrazolines. It is proposed that they are 3-(3′-oxobutyl)-6-nitrobenzotriazole 1-oxide and 3-(3′-oxopentyl)-6-nitrobenzotriazole 1-oxide, respectively. The 2,4-dinitrophenylhydrazones of four 4-alkoxybutanones have been made. It is shown that the derivatives recorded by Matsoyan and Vartanyan are not the 2,4-dinitrophenylhydrazones. Data in the literature concerning ethyl vinyl ketone 2,4-dinitrophenylhydrazone and 3-ethyl-1-(2,4-dinitrophenyl)pyrazoline are corrected.

Some years ago one of us showed[1] that the newly reported[2] technique for preparing 2,4-dinitrophenylhydrazones could be used with acid-sensitive carbonyl compounds and gave as an illustration the preparation of the derivative of methyl vinyl ketone. Although this ketone has been known for many years its 2,4-dinitrophenylhydrazone had not, as we thought, been reported. Actually, we found later that Martin had reported the derivative also in 1959.[3] We had pointed out[2] that unless care were exercised in preparing the derivative of this ketone one might obtain instead, for example, the derivative of a 4-alkoxybutanone. We also had noted Nazarov's[4] report that treatment of methyl vinyl ketone with 2,4-dinitrophenylhydrazine in acidic ethanol–dioxane solution gave a solid with a melting point of 217° and a carbon analysis 2.3% low for the expected derivative.

We were interested in Nazarov's compound and our interest led us in the direction of the derivatives of 4-alkoxybutanones and the formation of pyrazolines. As a result we found some conflicting observations in the literature, the attempted clarification of which has resulted in the present work.

In a paper by Matsoyan[5] on 4-alkoxybutanones and pyrazolines, two observations aroused our interest. The first was that by boiling a mixture of 4-alkoxybutanones in strongly acidic, ethanolic 2,4-dinitrophenylhydrazine a compound was obtained having a melting point of 160–161°, and this was described as 3-methyl-1-(2,4-dinitrophenyl)pyrazoline (I). Now it happened that we had had occasion earlier to prepare this pyrazoline and its 5-methyl isomer (II). Our melting points were close to those already reported by Mousseron[6]; namely, 131–132° for the 3-methyl (lit.[6] 129–130°) and 117.5–119° for the 5-methyl (lit.[6] 114–115°) isomer.


I


II

The second was in the list of 2,4-dinitrophenylhydrazones of twelve 4-alkoxybutanones.[5] When we examined this list we were struck by the fact that six of the derivatives had melting points covered by the range 211 to 221°. An identical list of derivatives, except for the omission of the last two, is given by Nazarov.[7] The coincidence in melting points of the six derivatives with that of Nazarov's[4] unknown compound was obvious.

Thus, it appeared that Matsoyan's pyrazoline was not I or II and that some interesting chemistry linked methyl vinyl ketone and the 4-alkoxybutanone deriva-

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[1] (a) For paper III see H. J. Shine, *J. Org. Chem.*, **24**, 1790 (1959); (b) taken in part from the M.S. thesis of Li-Tzu Fang, Texas Technological College, August, 1962; (c) the financial support for this work was obtained in the form of a grant (no. 1603AD) from Texas Technological College, for which we express our gratitude.

[2] H. J. Shine, *J. Org. Chem.*, **24**, 252 (1959).

[3] G. Martin, *Ann. chim.*, **13** (4), 541 (1959).

[4] I. N. Nazarov, L. A. Kasitsyna, and I. I. Zaretskaya, *Zh. Obshch. Khim.*, **27**, 606 (1957).

[5] S. G. Matsoyan and S. A. Vartanyan, *Izv. Akad. Nauk Arm. SSR, Ser. Fiz. Mat., Estestven. Tekh. Nauk.*, **8**, 31 (1955).

[6] M. Mousseron, R. Jacquier, and J. Brun, *Compt. rend.*, **247**, 617 (1958).

[7] I. N. Nazarov, S. A. Vartanyan, S. G. Matsoyan, and V. N. Zhamagortsyan, *Zh. Obshch. Khim.*, **23**, 1986 (1953).

tives with the unknown structures of Matsoyan's pyrazoline and Nazarov's compound.

We have, therefore, made the 2,4-dinitrophenylhydrazones of four of the 4-alkoxybutanones and investigated the reaction described by Matsoyan.

Results and Discussion

The So-Called Pyrazoline.—The Russian authors[5] record the melting point of their compound as 160–161°. They made the compound by boiling under reflux a mixture of the ethoxy-, isopropoxy-, and cyclohexyloxybutanones with 2,4-dinitrophenylhydrazine in strongly acidic ethanol. It would be interesting to conjecture why the mixture of the three ketones was used. We have prepared what we believe is the same compound in a variety of ways. We first made the compound by treating a mixture of the *n*-butoxy- and cyclohexyloxybutanones by the procedure described[5] and later by using the *n*-butoxy ketone alone or, much more conveniently, by using commercially available 4-hydroxybutanone. The same compound was obtained also, but in poorer yield, by using methyl vinyl ketone in the same way. All of the analytical work was carried out on the product made from a mixture of the *n*-butoxy and cyclohexyloxybutanones.

The melting point of this compound is nearer 182° than 160°. The compound will melt at 159–160° if it is heated at this temperature long enough. Actually, the compound will melt and decompose over any range of temperatures between 155–182°, but the melting is sharp only near 180°. Our best result, obtained by lowering the compound in capillary tubes into a preheated bath, was 182–182.5°.

Elemental analysis corresponded with $C_{10}H_{10}N_4O_4$, which describes methyl vinyl ketone 2,4-dinitrophenylhydrazone, and the 3-methyl- and 5-methyl-1-(2-4-dinitrophenyl)pyrazolines. These compounds were available in our laboratory and, furthermore, the pyrazolines were recorded in the literature[6] (but later than the Russian publication). That the Russian compound could not be a pyrazoline was also immediately evident to us when we attempted to recrystallize it. The compound does not dissolve in carbon tetrachloride, is not sufficiently soluble in chloroform (or deuterochloroform) for n.m.r. work, but is recrystallizable from hot water. These characteristics are entirely the opposite of those of the two isomeric pyrazolines and are indicative of a polar compound.

The infrared spectrum of the compound showed a sharp, strong carbonyl peak at 1736 cm.$^{-1}$. Later work with the compound made in several other ways showed (Fig. 1) that the position of the peak varied, slightly, over the range 1727–1736 cm.$^{-1}$. However, since the instrument used was not designed for high resolution, this range in frequency is not considered to be significant.

The n.m.r. spectra of the unknown compound and of three pyrazolines were obtained. The n.m.r. spectra of 5-methyl-1-(2,4-dinitrophenyl)-2-pyrazoline, 1,5-diphenyl-2-pyrazoline, and 3-methyl-1-(2,4-dinitrophenyl)-2-pyrazoline are shown in Fig. 2, 3, and 4, respectively. The observed chemical shifts, relative intensities, multiplicities, and coupling constants are in agreement with the proposed structures. The A_2B_2-type spectrum of the methylene resonances in 3-methyl-1-(2,4-dinitrophenyl)-2-pyrazoline is attributed to rapid inversion about the 1-nitrogen atom. Under this condition the two hydrogens in each of the two methylene groups have the same chemical shifts. The other pyrazolines are probably also undergoing rapid inversion, but the methylene hydrogens are, nevertheless, nonequivalent, because of the asymmetry introduced by the C-5-substituent.[8]

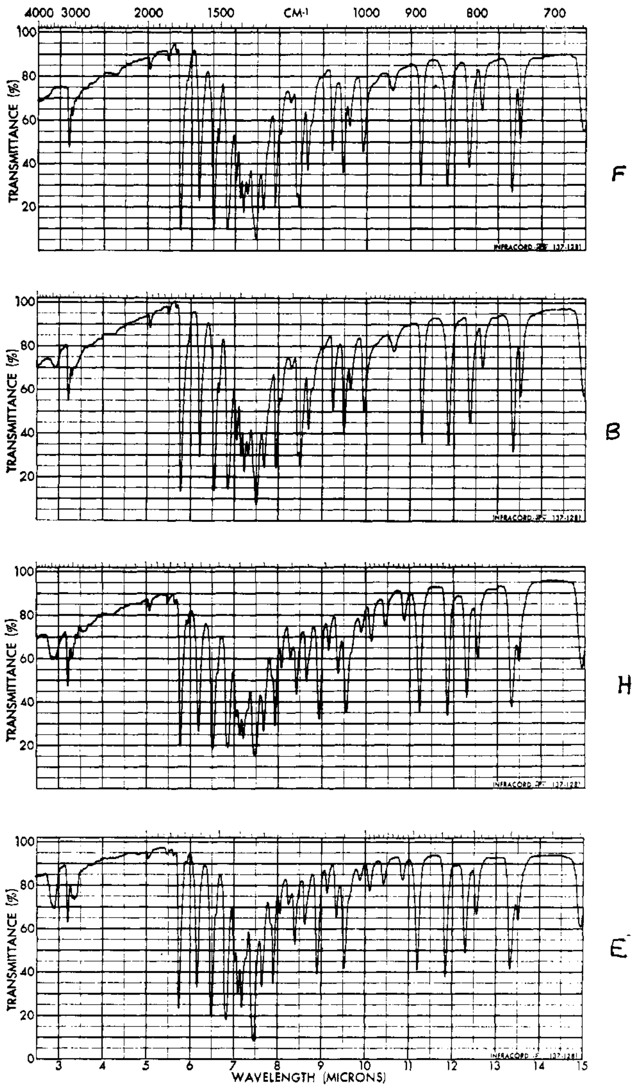

Fig. 1.—Infrared spectra of 3-(3′-oxobutyl)- (B, F) and 3-(3′-oxopentyl)-6-nitrobenzotriazole 1-oxide (E, H). Key to the letters is in the Experimental.

Because of its low solubility in carbon tetrachloride, carbon disulfide, and deuteriochloroform, the n.m.r. spectrum of the unknown compound was obtained by using perdeuteriopyridine as the solvent. The spectrum is shown in Fig. 5. Although the pattern of the aromatic ring hydrogens is typical of 1,2,4-trisubstituted benzenes, the chemical shifts of the aromatic hydrogens are distinctly different from those of the two 2,4-dinitrophenylpyrazolines discussed before. This indicated that this compound was not a pyrazoline. In the spectra of 2,4-dinitrophenylhydrazones it has been found that the hydrogen on the nitrogen atom which is alpha to the aromatic ring resonates at about 10 p.p.m.[9] The absence of a comparable band in the spectrum of the unknown compound showed that it was not a

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(8) W. D. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958).

(9) N. F. Chamberlain, unpublished work.

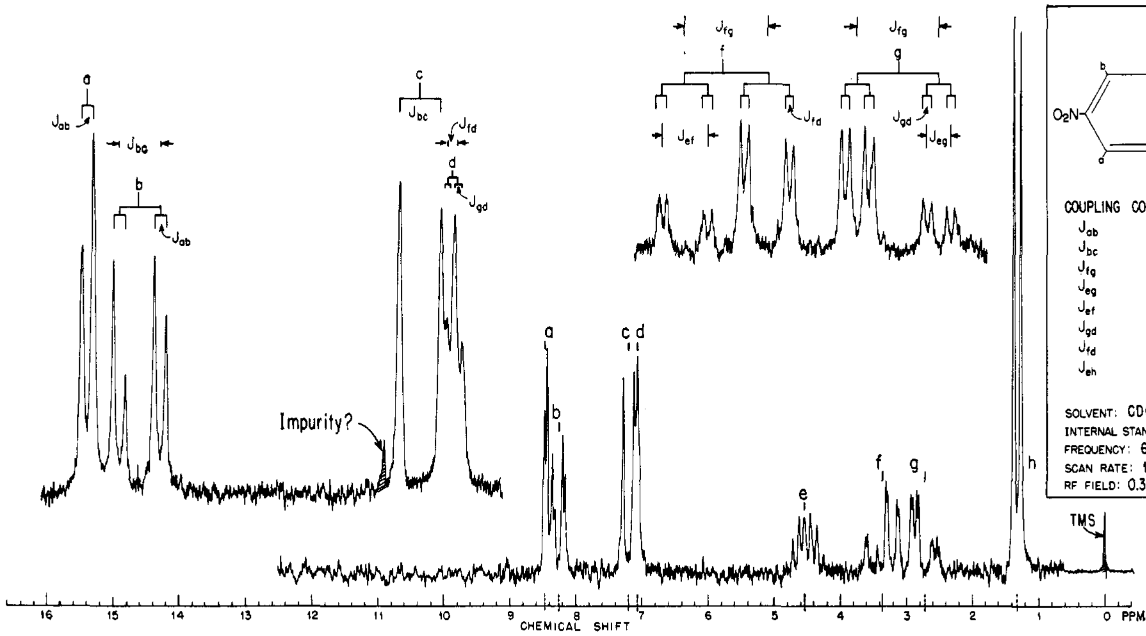


Fig. 2.—Hydrogen n.m.r. spectrum of 5-methyl-1-(2,4-dinitrophenyl)-2-pyrazoline.

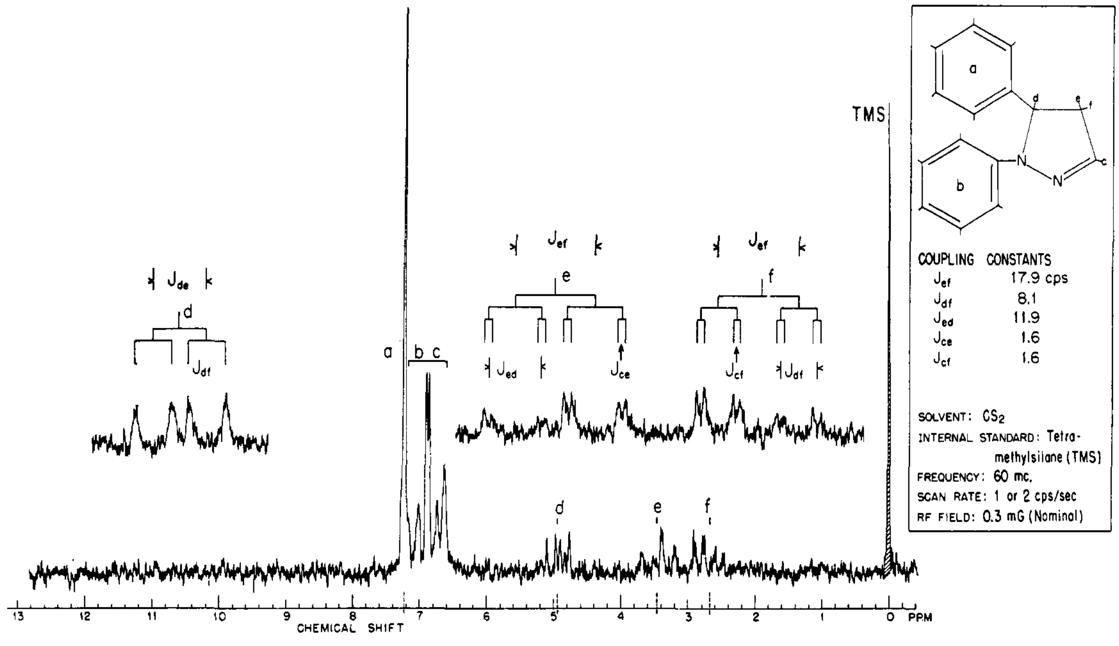


Fig. 3.—Hydrogen n.m.r. spectrum of 1,5-diphenyl-2-pyrazoline.

2,4-dinitrophenylhydrazone. The nonaromatic portions of the spectrum of Fig. 5 exhibit the two triplet patterns characteristic of an A_2B_2 group and a singlet which is attributed to an isolated methyl group. The AB coupling constant in this A_2B_2 pattern is typical of aliphatic chains. These results, together with the infrared carbonyl band and the solubility characteristics of this compound, led us to propose that it was a ketoalkyl-substituted 6-nitro-1-oxy-1,2,3-benzotriazole. This was confirmed by making the same compound from reactions of 6-nitro-1-hydroxy-1,2,3-benzotriazole with 4-*n*-butoxybutanone and methyl vinyl ketone. The products obtained were the same as those obtained from treating 4-hydroxybutanone, methyl vinyl ketone, and the mixture of 4-alkoxybutanones by the Russian procedure.

The reactions described before that lead to a substituted 6-nitro-1-oxy-1,2,3-benzotriazole are not restricted to the butanones. Identical results were obtained from the analogous ethyl vinyl ketone and 1-ethoxypentan-3-one. In this series, the sodium salt of 6-nitro-1-hydroxy-1,2,3-benzotriazole reacted with 1-chloropentan-3-one to give the same product.

The necessary feature in the carbonyl compound seems, at this time, to be that the substituent and carbonyl group be in the 1,3-positions. Our attempts to carry out similar reactions with 3-hydroxybutanone and 5-hydroxypentan-2-one failed.

We propose that the Russian reaction and our reactions lead to 6-nitro-1-oxy-1,2,3-benzotriazolyl ketones. Each of the 1,2,3-positions is a contender for the ketoalkyl substituent (see p. 2329, col. 1).

The ultraviolet spectra of the compounds IV indicate that the substituent is on the 3-position. The ultraviolet spectra of alkyl substituted 6-nitro-1-oxy-1,2,3-benzotriazoles are described in detail by Macbeth and

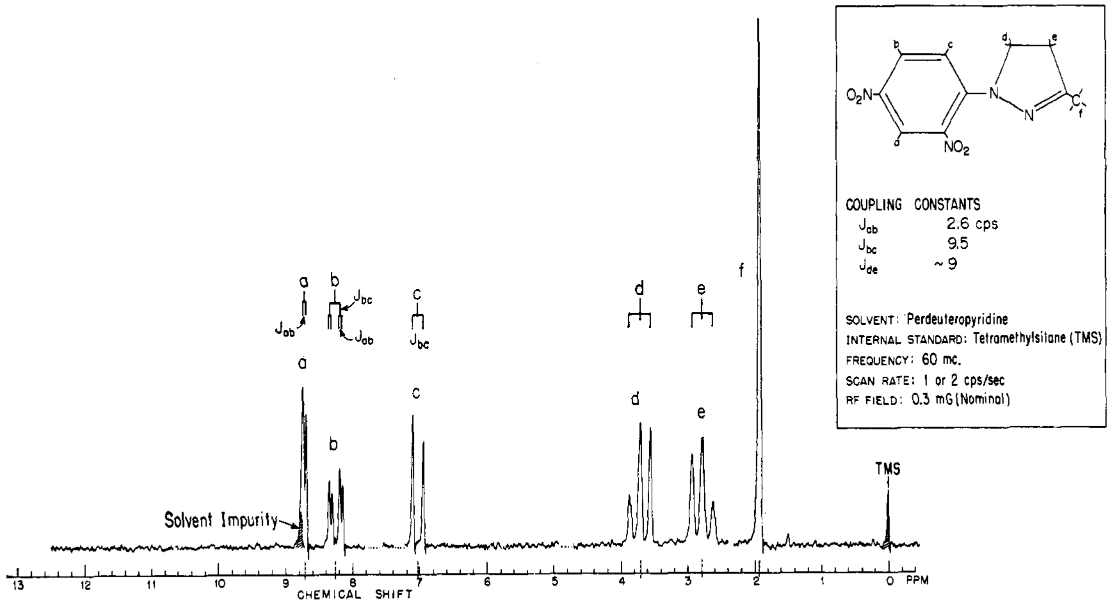


Fig. 4.—Hydrogen n.m.r. spectrum of 3-methyl-1-(2,4-dinitrophenyl)-2-pyrazoline. The dotted portions of the base line indicate where signals from solvent hydrogens occurred and have been removed.

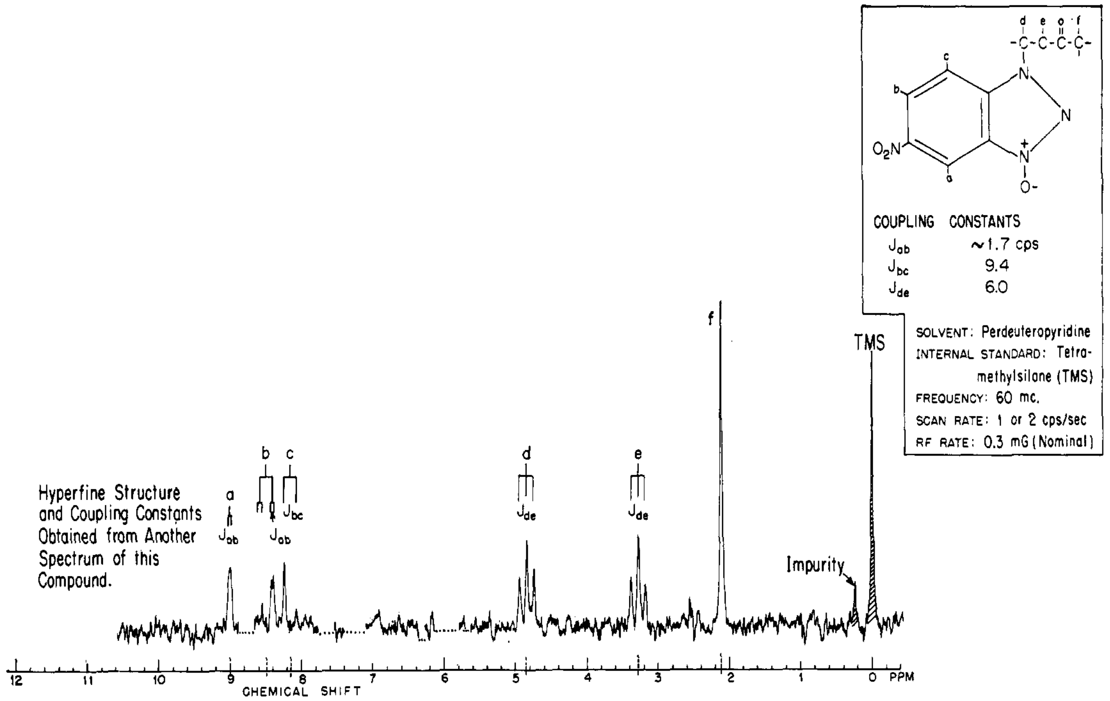
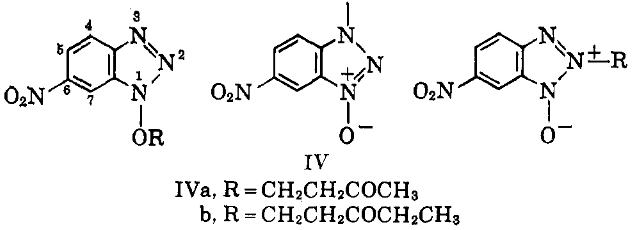


Fig. 5.—Hydrogen n.m.r. spectrum of 3-(3′-oxobutyl)-6-nitrobenzotriazole 1-oxide. The dotted portions of the base line indicated where signals from solvent hydrogens occurred and have been removed.



IV

IVa, R = $CH_2CH_2COCH_3$
b, R = $CH_2CH_2COCH_2CH_3$

Price.[10] Our ultraviolet data are compared with the 3-methyl and 1-methoxy compounds (IV, R = CH_3) in Table I. The coincidence with the 3-methyl-6-nitro-1,2,3-benzotriazole oxide data is striking. This is particularly so since one of the ways in which IVb was prepared was by the reaction of the sodium salt of the parent 6-nitro-1-hydroxy-1,2,3-benzotriazole with 1-chloropentan-3-one. When we carried out the reaction of ethyl iodide with this sodium salt as described by Curtius and Mayer,[11] the 1-ethoxy compound (IV, R = Et) was obtained; the ultraviolet spectrum in ethanol corresponded with that given for the 1-methoxy compound.[10] Alkylation of hydroxybenzotriazoles can give a mixture of N-alkyl and O-alkyl substituted products.[12,13] The apparent selectivity of the keto-alkyl substitution is rather unusual.

(10) A. K. Macbeth and J. R. Price, *J. Chem. Soc.*, 111 (1936).

(11) T. Curtius and M. Mayer, *J. prakt. Chem.*, **76**, 369 (1907).

(12) O. L. Brady and C. V. Reynolds, *J. Chem. Soc.*, 1273 (1931).

(13) O. L. Brady and J. Jakobvits, *ibid.*, 767 (1950).

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA (mμ) OF SUBSTITUTED 6-NITROBENZOTRIAZOLES (IV)

Solvent	1-MeO-[a]	1-Oxy-3-Me-[a]	IVa and IVb
Ethanol	241.5	263	263–264[b]
	273	349	349–350[b]
Water	244	262	262–263[b]
	280	338	337–338[b]

[a] Data from ref. 10. [b] The maxima occurred within these limits regardless of how IVa and IVb were prepared.

We cannot rule out the possibility that the ketoalkyl substituent in IV may be on the 2-position. 2-Substituted benzotriazoles show only a single maximum in the ultraviolet[14–16] in the region 275 mμ for an alkyl substituent and 310 mμ for a phenyl substituent. 3-Methyl-6-nitrobenzotriazole has two maxima in the ultraviolet (244.5 and 295 mμ in ethanol)[10] and so does 3-methyl-6-nitrobenzotriazole 1-oxide.[10] In deciding against a 2-substituent in our IVa and IVb we are assuming that, like 2-substituted benzotriazoles, the 2-substituted nitrobenzotriazole oxides also may show only one maximum. This assumption may be wrong.

The mechanism of the formation of IVa and IVb by the Russian procedure is obscure. Boiling 2,4-dinitrophenylhydrazine in acidic ethanol does not give 6-nitro-1-hydroxy-1,2,3-benzotriazole. This compound is made from 2,4-dinitrophenylhydrazine in basic solutions.[11,17,18] It is surprising that a keto group in IVa,b should survive the reaction with 2,4-dinitrophenylhydrazine. One might expect that IVa and IVb would arise from the initial formation of either the 2,4-dinitrophenylhydrazone or the pyrazoline and, if this were the case, one might anticipate a 3-position substituent in the IV. However, so far, we have been unable to convert either the 2,4-dinitrophenylhydrazones of methyl vinyl ketone and 4-*n*-butoxybutanone or the pyrazoline I to IVa. Another point of interest are the reports[19–21] that methylol ketones in general give pyrazolines when treated with 2,4-dinitrophenylhydrazine.

These are points which we are now trying to clarify. Further work is in progress on the nature of Nazarov's compound, m.p. 217°.

2,4-Dinitrophenylhydrazones of 4-Alkoxybutanones.—The derivatives of the four ketones which we prepared had low melting points, as one might anticipate for 2,4-dinitrophenylhydrazones of this class. The melting points were: 4-isopropoxy-, 58–59° (220–221°); 4-*n*-butoxy-, 74.5–75.5° (211–212°); 4-isobutoxy-, 74–75° (214–215°); and 4-cyclohexyloxy-, 79.5–80.5° (217–219°); the values in parentheses are those reported by Matsoyan and Vartanyan.[5] These derivatives were prepared by Shine's method.[2] In experiments with 4-isopropoxybutanone it was found that a customary method of preparing 2,4-dinitrophenylhydrazones, the use of ethanol and hydrochloric acid to dissolve the 2,4-dinitrophenylhydrazone, gave a product melting over the range 156–210°. It is apparent that this result illustrates what the Russian workers[5] were recording; that is, a reaction that is acid-catalyzed but does not give the 2,4-dinitrophenylhydrazone.

Experimental[22]

4-Alkoxybutanones.—The isopropoxy, *n*-butoxy, isobutoxy, and cyclohexyloxy ketones were made by the method used by Killian[23] for the methoxybutanone. The alcohols needed for the addition to methyl vinyl ketone were dried prior to use. Isopropyl alcohol was dried by boiling with aluminum foil and mercuric chloride. The other alcohols were dried over anhydrous potassium carbonate. Each of the alcohols was then fractionally distilled. Addition of the alcohols across the double bond was catalyzed by boron trifluoride etherate and mercuric oxide; trifluoroacetic acid[23] was not used. The crude alkoxybutanone solutions were washed with saturated potassium carbonate solution, dried over potassium carbonate, and fractionally distilled. The physical constants were: isopropoxy, b.p. 74.5–75° (35 mm.), $n^{25}\text{D}$ 1.4069; *n*-butoxy, b.p. 99–100° (35 mm.), $n^{25}\text{D}$ 1.4050; isobutoxy, b.p. 94.5–95.5° (35 mm.), $n^{25}\text{D}$ 1.4095; cyclohexyloxy, b.p. 135–136° (35 mm.), $n^{25}\text{D}$ 1.4505.

2,4-Dinitrophenylhydrazones of the 4-Alkoxybutanones.—These were somewhat troublesome to isolate. Thus, with the isopropoxy ketone the use of ethanolic hydrochloric acid gave a product melting over the range 156–210°. The method finally adopted was to dissolve the ketone in the corresponding alcohol and add the solution to a solution of 2,4-dinitrophenylhydrazine in diglyme[2] (dimethyl ether of diethylene glycol). The solution was then acidified with a drop or two of concentrated hydrochloric acid and this was followed by water, which precipitated the derivative. Recrystallization was also a problem, because of the low melting points of the derivatives. The following results were obtained.

4-Isopropoxybutanone 2,4-dinitrophenylhydrazone, m.p. 58–59° (aqueous isopropyl alcohol) (lit.[5] m.p. 220–221°).

Anal. Calcd. for $C_{13}H_{18}N_4O_5$: C, 50.31; H, 5.85; N, 18.06. Found: C, 50.32; H, 6.15; N, 17.99.

4-*n*-Butoxybutanone 2,4-dinitrophenylhydrazone, m.p. 74.5–75.5° (aqueous diglyme) (lit.[5] m.p. 211–212°).

Anal. Calcd. for $C_{14}H_{20}N_4O_5$: C, 51.86; H, 6.17; N, 17.28. Found: C, 52.03; H, 6.21; N, 17.16.

4-Isobutoxybutanone 2,4-dinitrophenylhydrazone, m.p. 74–75° (ligroin) (lit.[5] m.p. 214–215°).

Anal. Calcd. for $C_{14}H_{20}N_4O_5$: C, 51.86; H, 6.17; N, 17.28. Found: C, 52.12; H, 6.35; N, 17.36.

4-Cyclohexyloxybutanone 2,4-dinitrophenylhydrazone, m.p. 79.5–80.5° (aqueous diglyme) (lit.[5] m.p. 217–219°).

Anal. Calcd. for $C_{16}H_{22}N_4O_5$: C, 54.84; H, 6.33; N, 15.9. Found: C, 55.21; H, 6.04; N, 16.16.

Ethyl Vinyl Ketone.—1-Chloro-3-pentanone was made from ethylene and propionyl chloride following the procedure of Woodward[24] and this ketone was dehydrohalogenated with sodium benzoate.[25] The wet ketone was separated from the codistilled water and used without further treatment to prepare the 2,4-dinitrophenylhydrazone; Shine's method[2] was used. The derivative crystallized in two forms, either red or light orange needles. The red crystals had m.p. 127.9–128.8°, λ_{max} ($CHCl_3$) 371 mμ; the orange needles had m.p. 129.7–130.8°, λ_{max} ($CHCl_3$) 371 mμ. The product was obtained finally wholly in the orange form by crystallizing from a large volume of ethanol and seeding with an orange crystal; lit. m.p. 138.5°,[3] 129–129.5°.[26]

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.00; H, 4.58; N, 21.20. Found: C, 49.75; H, 4.43; N, 21.50.

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(14) H. Specker and H. Gawrosch, *Ber.*, **75**, 1338 (1942).

(15) F. Krollpfeiffer, H. Pötz, and A. Rosenberg, *ibid.*, **71**, 596 (1938).

(16) R. H. Wiley, K. H. Hussung, and J. Moffat, *J. Am. Chem. Soc.*, **77**, 5105 (1955).

(17) O. L. Brady and J. N. E. Day, *J. Chem. Soc.*, **123**, 2258 (1923).

(18) O. M. Shemyakina, B. M. Bogoslovsky, and M. M. Shemyakin, *J. Gen. Chem.*, *USSR*, **26**, 2165 (1956).

(19) A. S. Spriggs, C. M. Hill, and G. W. Senter, *J. Am. Chem. Soc.*, **74**, 1555 (1952).

(20) R. L. Wear, *ibid.*, **73**, 2390 (1951).

(21) G. T. Morgan and E. L. Holmes, *J. Chem. Soc.*, 2667 (1932).

(22) Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points are uncorrected.

(23) D. B. Killian, G. F. Hennion, and J. A. Nieuwland, *J. Am. Chem. Soc.*, **58**, 892 (1936).

(24) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLamore, *ibid.*, **74**, 4223 (1952).

(25) S. Archer, W. B. Dickinson, and M. J. Unser, *J. Org. Chem.*, **22**, 92 (1957).

(26) Private communication from Dr. E. H. Ramshaw, CSIRO, Dairy Research Section, Highett, Victoria, Australia.

The reaction of 2,4-dinitrophenylhydrazine with ethyl vinyl ketone is reported by McMahon.[27] Two products were obtained. One with m.p. 128.8–129° was described as probably the product of addition to the olefinic linkage, because of the N analysis (19.44%). The other, m.p. 166–166.5°, was described as probably the 2,4-dinitrophenylhydrazone or the isomeric pyrazoline. It appears now that the first product was the 2,4-dinitrophenylhydrazone and that the second was neither this nor the 3-ethyl-1-(2,4-dinitrophenyl)pyrazoline (see later).

1-Ethoxypentan-3-one.—Anhydrous ethanol and dried, redistilled ethyl vinyl ketone were treated by the boron trifluoride method.[23] Fractional distillation gave a 44% yield of the ethoxypentanone, b.p. 33–36° (2 mm.), n^{25}D 1.4111.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.68; H, 10.93.

The 2,4-dinitrophenylhydrazone was prepared by Shine's method[2] and had m.p. 80.5–81.5° (ethanol), λ_{max} ($CHCl_3$) 369 mμ.

Anal. Calcd. for $C_{13}H_{18}N_4O_5$: C, 50.32; H, 5.85; N, 18.05. Found: C, 50.46; H, 6.06; N, 18.20.

1-(2,4-Dinitrophenyl)-2-pyrazolines.—The 3-methyl-, 5-methyl-, and 3-ethylpyrazolines were made by treating methyl vinyl ketone, crotonaldehyde, and ethyl vinyl ketone with 95% hydrazine hydrate by a modification of the procedure of Beech, Turnbull, and Wilson.[28] The carbonyl compound (20 ml.) was dissolved in 40 ml. of methanol and the hydrazine hydrate (20 ml.) was added while cooling the mixture in an ice bath. A vigorous reaction ensued. The mixture was boiled under reflux for 20 min., all operations being in a nitrogen atmosphere. The methanol was distilled and the residue was taken up in ether. After drying the ether solution over potassium carbonate, the product was distilled under reduced pressure. The products were collected at 50–55° (15 mm.) (3-methyl), 60–65° (15 mm.) (5-methyl), and 60–65° (3 mm.) (3-ethyl).

The 1-(2,4-dinitrophenyl)pyrazolines were prepared by the method of Chambers and Willard,[29] using 2,4-dinitrobromobenzene. The 3-methyl- and 3-ethylpyrazolines were treated in ether solution, but this method failed with the 5-methylpyrazoline. In this case it was necessary to boil in ethanol solution containing fused sodium acetate.[29] The following products were obtained.

1-(2,4-Dinitrophenyl)-3-methyl-2-pyrazoline, m.p. 131–132° (acetic acid) (lit.[6] m.p. 129–130°).

Anal. Calcd. for $C_{10}H_{10}N_4O_4$: C, 48.00; H, 4.03; N, 22.38. Found: C, 48.27; H, 4.04; N, 22.30.

1-(2,4-Dinitrophenyl)-5-methyl-2-pyrazoline, m.p. 117.5–119° (ethanol) (lit.[6] m.p. 114–115°).

Anal. Calcd. for $C_{10}H_{10}N_4O_4$: C, 48.00; H, 4.03; N, 22.38. Found: C, 48.28; H, 3.88; N, 22.20.

1-(2,4-Dinitrophenyl)-3-ethyl-2-pyrazoline, m.p. 115–117° (ethyl acetate).

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.00; H, 4.58; N, 21.20. Found: C, 50.02; H, 4.52; N, 21.00.

Reactions of 6-Nitro-1-hydroxy-1,2,3-benzotriazole (III).—6-Nitro-1-hydroxy-1,2,3-benzotriazole was prepared by both the method of Brady and Day[17] and of Curtius and Mayer.[11] In each case the product was recrystallized from hot water. The Brady product decomposed rapidly at 205° (lit. 194°) while the Curtius product decomposed rapidly at 194° (lit. 205–206°, 199–200°, and 190–192°).

With Ethyl Iodide.—The sodium salt of III and ethyl iodide were used as described by Curtius and Mayer.[11] The 1-ethoxy-6-nitro-1,2,3-benzotriazole obtained had m.p. 79–81° (aqueous ethanol), λ_{max} (ethanol) 242 and 277 mμ, with an inflection at 315 mμ; λ_{max} ($CHCl_3$) 280 and 320 mμ.

With 4-*n*-Butoxybutanone.—To a solution of 0.75 g. of 4-*n*-butoxybutanone and 0.8 g. of III in 10 ml. of ethanol was added 1 ml. of concentrated hydrochloric acid. The solution was boiled under reflux for 16 hr. On cooling to room temperature bright yellow crystals deposited. These were recrystallized from hot water and had m.p. 179–179.5° dec. determined by introducing capillary into the bath at 179°. This is labeled product A.

With Methyl Vinyl Ketone.—(a) A solution of 0.5 g. of methyl vinyl ketone in 7.5 ml. of ethanol was shaken overnight with 0.5 g. of solid III. The III slowly disappeared and was replaced by yellow plate-like crystals. (b) A similar experiment with the addition of 5 drops of concentrated hydrochloric acid gave a similar result.

The products from experiments a and b were combined and recrystallized from hot water, giving m.p. 169.5–170.5° dec. (see previous). This is labeled product B.

With 1-Ethoxypentan-3-one.—A solution of 3 g. of 1-ethoxypentan-3-one, 4 ml. of concentrated hydrochloric acid, and 3.5 g. of III in 20 ml. of ethanol was stirred and boiled under reflux for 12 hr. On cooling yellow, plate-like crystals deposited. The ethanol-washed and dried product weighed 4.3 g. (97.7% yield). Recrystallization from hot water gave m.p. 151.5–153° dec. by introducing the capillary into the bath at 150°. When the bath was heated from room temperature the m.p. was 148–152° dec. This is labeled product C.

With Ethyl Vinyl Ketone.—Experiments a and b were performed as with methyl vinyl ketone. In these cases similar observations were made. The combined products were crystallized from hot water and gave m.p. 151.5–153° dec. This is labeled product D.

With 1-Chloropentan-3-one.—The following solution was boiled under reflux for 4 hr.: 3 g. of the sodium salt of III and 3 g. of 1-chloropentan-3-one in 60 ml. of absolute ethanol. The product obtained on cooling was recrystallized from hot water and had m.p. 151–153° dec. (see preceeding). This is labeled product E.

Reactions with 2,4-Dinitrophenylhydrazine.—The following reactions were designed to follow as closely as possible the conditions used by Matsoyan and Vartanyan.[5]

With a Mixture of 4-Alkoxybutanones.—(a) To a mixture of 5.3 g. of *n*-butoxybutanone, 3.5 g. of cyclohexyloxy butanone and 8 g. of 2,4-dinitrophenylhydrazine in 40 ml. of ethanol was added 10 ml. of concentrated hydrochloric acid. The mixture was stirred under reflux for 11 hr. On cooling the solution a voluminous deposit formed. This was filtered and washed with cold ethanol and dried giving 5.0 g., m.p. 160–163.5° dec. The recrystallization of portions of this product from hot water gave yellow hexagonal plates whose melting point varied with the sample. That is, melting points of 162.5–163.5°, 159–162°, 164.5–165.5°, 166–167° were recorded, all with decomposition. Some of the product was recrystallized from aqueous dimethyl sulfoxide, and the melting point was determined by plunging capillaries into a preheated bath. With the bath at 162° the product remained unaffected for several minutes and then slowly melted and decomposed over the range 165–165.5°. By gradually raising the bath temperature and repeating this process with fresh material it was found that the product melted rapidly and decomposed at 182–182.5°. This product was labeled F.

Anal. Calcd. for $C_{10}H_{10}N_4O_4$: C, 48.00; H, 4.03; N, 22.38. Found: C, 48.28; H, 3.97; N, 21.88.

(b) On one occasion, when repeating this experiment, an oil separated after the first few minutes of boiling. Cooling caused the oil to solidify, and the yellow solid had m.p. 195–200°. Recrystallization from chloroform gave m.p. 212–214°. Cooling the original alcoholic filtrate in ice gave yellow plates, m.p. 165–167° dec.

With 4-Hydroxybutanone.—A solution of 3.8 g. of 4-hydroxybutanone and 5 ml. of concentrated hydrochloric acid in 20 ml. of ethanol was stirred under reflux for 17 hr. On cooling a black viscous deposit formed and this was filtered off. The filtrate deposited a brown-yellow solid which was washed with ethanol and dried, giving 2.3 g. (26%). The product was recrystallized from aqueous dimethyl sulfoxide and had m.p. 179–179.5° dec., the bath temperature starting at 178°. This product is labeled G.

With 1-Ethoxypentan-3-one.—The solution contained 3.8 g. of the ketone and 5 ml. of concentrated hydrochloric acid in 20 ml. of ethanol, and was stirred under reflux for 21 hr. with 4 g. of 2,4-dinitrophenylhydrazine. Cooling gave 2.6 g. of yellow solid, which after crystallization from chloroform had m.p. 150.5–151.5°. This is product H.

Anal. Calcd. for $C_{11}H_{12}N_4O_4$: C, 50.00; H, 4.58; N, 21.20. Found: C, 49.95; H, 4.82; N, 21.07.

With 3-Hydroxybutanone and 5-Hydroxypentan-2-one.—The 5-hydroxypentan-2-one was made from 2-methylfuran by the

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(27) E. M. McMahon, J. N. Roper, Jr., W. P. Untermohlen, Jr., R. H. Hasek, R. C. Harris, and J. H. Brant, *J. Am. Chem. Soc.*, **70**, 2971 (1948).

(28) S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952).

(29) W. L. Chambers and M. L. Willard, *J. Am. Chem. Soc.*, **82**, 3373 (1960).

method of Londergan.[30] The 3-hydroxybutanone was from Distillation Products. The only recognizable product obtained from treating 3-hydroxybutanone in the manner described in the previous cases was recovered 2,4-dinitrophenylhydrazine. Treating 5-hydroxypentan-2-one in the same way gave a black viscous fluid which resisted attempts at working up.

The Products A, B, F, and G.—These were shown to be identical by their infrared spectra. These spectra had a strong, sharp carbonyl band in the region 1727–1736 cm.^{-1}. The ultraviolet spectra were also identical and had maxima at 263–264 and 349–350 $m\mu$ in ethanol; maxima at 267 and 361 $m\mu$ and a shoulder at 340 $m\mu$ in chloroform.

The Products C, E, D, and H.—These were shown to be identical by their infrared spectra. A strong carbonyl band appeared in the region 1727–1730 cm.^{-1}. The ultraviolet spectra had the same characteristics as those of the products A, B, F, and G.

Spectra.—The infrared spectra were obtained in potassium bromide pellets on a Perkin-Elmer Infracord, Model 137. The ultraviolet spectra were obtained with a Beckman Model DK-2 recording spectrophotometer. The n.m.r. spectra were obtained with a Varian Associates Model A-60 spectrometer. The solvents, internal standard, and instrumental conditions are noted on the spectra.

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Hydrogenolyses of Aromatic Halides with Triaryltin Hydrides[1]

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Electronic and solvent effects have been evaluated for the hydrogenolysis of aromatic halides with triaryltin hydrides. For the aromatic halides, electron-releasing groups inhibit the reaction while electron-attracting groups accelerate the reaction. Hydroxylic solvents speed the reaction and triphenylboron accelerates the reaction more in hydroxylic solvents than in hydrocarbon solvents. Consistent with these data is a heterolytic reaction mechanism, but not necessarily SN1 or SN2. New triaryltin hydrides described are tris(*p*-tolyl)tin, tris(*p*-fluorophenyl)tin, and trimesityltin hydrides.

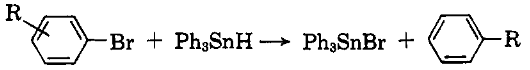
A number of workers have recently reported on the hydrogenolyses of alkyl,[5-9,11] aryl,[5,7,10] and acyl[12] halides with organotin hydrides. It has been shown that triphenyltin hydride is an effective hydrogenolysis agent[5-8,10] and that the ease of replacement of the halogens[7,10] is iodine > bromine > chlorine. It has also been demonstrated that aromatic hydrogenolysis is decreased by electron-donating groups in the *para* position.[10] We would now like to report on a more detailed study of the effect of substituents and solvents on the hydrogenolysis of aromatic halides.

A series of substituted bromobenzenes and halonaphthalenes was treated with triaryltin hydrides and in each case the bromine was removed from the benzene ring or the halogen from the halonaphthalene and triaryltin halide was formed. The extent of hydrogenolysis was determined by titration of the triaryltin halide formed with base (Tables I, II, III, and IV). Tables I and II show that the reaction of triphenyltin hydride and tri(*p*-tolyl)tin hydride with the substituted bromobenzenes at 154° proceeded nearly to completion, affording yields between 85–100%.

At 124°, the reaction showed a greater selectivity, giving lower yields with compounds substituted with electron-donating groups in the *ortho* and *para* positions and increased yields with compounds substituted with electron-withdrawing groups. The increased yields of the *o*- and *m*-anisyl bromides may be due to the inductive effect of the methoxyl group. The increased reactivity of the phenyl substituted bromobenzenes cannot be explained on the basis of their electron-withdrawing ability. On the basis of electron withdrawal of the nitrile group a much higher yield

TABLE I

HYDROGENOLYSES OF AROMATIC HALIDES



R			% Yield		
ortho	*meta*	*para*	Temp., °C.: 94	124	154
CH_3	. . .	. . .	10	52	. . .
. . .	CH_3	. . .	9	34	. . .
. . .	. . .	CH_3	10	50	91
OCH_3	. . .	. . .	12	60	. . .
. . .	OCH_3	. . .	5	43	. . .
. . .	. . .	OCH_3	7	34	90
H	H	H	12	55	90
F	. . .	. . .	14	78	. . .
. . .	F	. . .	17	85	. . .
. . .	. . .	F	9	71	. . .
Cl	. . .	. . .	39	96	. . .
. . .	Cl	. . .	38	88	100.5
. . .	. . .	Cl	16	82	97
Ph	. . .	. . .	16	94	. . .
. . .	Ph	. . .	8	80	. . .
. . .	. . .	Ph	22	90	95
CF_3	. . .	. . .	61	98	. . .
. . .	CF_3	. . .	21	80	. . .
. . .	. . .	CF_3	13	79	. . .
. . .	. . .	CN	20	59	
Iodobenzene			84	90	100

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[3] Taken from part of the thesis submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Bachelor of Science (Chemistry), 1962.

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