179. *A New Synthesis of Fluoro-ketones.*

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Trifluoroacetic acid, when treated with a Grignard reagent (RMgX; where R = Me, Et, Pr^i, Bu^n, Bu^t, Ph), afforded the corresponding ketone, CF_3·COR. Heptafluorobutyric acid and methylmagnesium iodide gave heptafluoropropyl methyl ketone. The ketones underwent haloform reactions, to give acids, R·CO_2H, identified as *S*-benzylthiuronium salts.

SEVERAL methods have been used hitherto for the synthesis of fluoro-ketones. Ester condensations, followed by hydrolyses of the derived β-keto-esters or β-diketones, have been employed most frequently.[1] For the synthesis of mixed aromatic fluoroalkyl ketones, Friedel–Crafts reactions have been utilised.[2] Fluoroacyl derivatives of reactive aromatic or heterocyclic compounds were made by Hoesch reactions.[3] Grignard-type syntheses involving fluorocarboxylic acid derivatives such as esters, acyl halides, etc., have been used for ketone production, but suffer from certain limitations. The chief of these is the formation, at the same time, of tertiary alcohols and, where the Grignard reagents have β-hydrogen atoms, secondary alcohols by reduction of any carbonyl groups present in the intermediates.[4] Very recently, it was shown by McBee, Pierce, and Meyer [5] that the reaction of Grignard reagents with perfluoro-nitriles proceeds normally, and hence may be used for ketone synthesis.

Experience in this Department has shown that the ester condensation route, though rather laborious, is satisfactory for the preparation of trifluoroacetone. However, when it was applied to the production of ethyl trifluoromethyl ketone, only poor yields of a very impure product were obtained. Accordingly, we considered possible alternative syntheses for fluoro-ketones, and it appeared likely that fluoro-acids themselves might react with Grignard reagents to give carbonyl compounds.

The acidic hydrogen of acids is of course removed by organomagnesium compounds in the well-known Zerewitinoff reaction. Alkanecarboxylic acids have long been known to give tertiary alcohols when treated with excess of organomagnesium halides,[6] but the process does not seem to have been used at all widely. However, ketones were obtained, in yields below 25%, by Salkind and Beburischwili [7] from sodium salts, and by Huston and Bailey [8] from acids themselves, though in the latter case tertiary alcohols were the major products. Highly fluorinated carbonyl compounds can give various quite well-defined compounds in which one carbon atom is linked to two oxygen atoms, *e.g.*, $R{\cdot}CF_2{\cdot}CR'(OR'')_2$. The stabilities of these relative to the hydrocarbon-type analogues are greatly enhanced by the presence of the electronegative fluorine substituents. For a reaction between a fluoro-acid and a Grignard reagent, it seemed possible that, after the former had undergone elimination of the active hydrogen and addition to the carbonyl group, the resulting complex might resist further reaction, in particular any replacement of oxygen-containing functions (such as O·MgX).

This supposition was confirmed experimentally. Anhydrous trifluoroacetic acid reacted readily with a number of Grignard reagents (RMgX; R = Me, Et, Pr^i, Bu^n, Bu^t, Ph) to give, after decomposition of the intermediate complexes in the usual way, the corresponding ketones (CF_3·COR), in reasonable yields (40—60%). Similarly, heptafluorobutyric acid and methylmagnesium iodide afforded heptafluoropropyl methyl ketone.

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[1] *Inter alia*: (*a*) Swarts, *Bull. Acad. roy. Belg.*, 1927, **13**, 175; Darrall, Smith, Stacey, and Tatlow, *J.*, 1951, 2329; (*b*) Henne, Newman, Quill, and Staniforth, *J. Amer. Chem. Soc.*, 1947, **69**, 1819; (*c*) Nes and Burger, *ibid.*, 1950, **72**, 5409; (*d*) Barkley and Levine, *ibid.*, 1953, **75**, 2059; McBee, Pierce, Kilbourne, and Wilson, *ibid.*, p. 3152.

[2] Simons and Ramler, *ibid.*, 1943, **65**, 389; Simons, Black, and Clark, *ibid.*, 1953, **75**, 5621.

[3] Whalley, *J.*, 1951, 665; 1954, 1651.

[4] (*a*) Campbell, Knobloch, and Campbell, *J. Amer. Chem. Soc.*, 1950, **72**, 4380; McBee, Pierce, *et al.*, *ibid.*, 1952, **74**, 1736; 1953, **75**, 2324; 1955, **77**, 83; (*b*) Haszeldine, *J.*, 1953, 1748; 1954, 1273.

[5] McBee, Pierce, and Meyer, *J. Amer. Chem. Soc.*, 1955, **77**, 917.

[6] Grignard, *Compt. rend.*, 1904, **138**, 152.

[7] Salkind and Beburischwili, *Ber.*, 1909, **42**, 4500.

[8] Huston and Bailey, *J. Amer. Chem. Soc.*, 1946, **68**, 1382.

Gas–liquid partition chromatographic examination [9] of the ketones showed that they were either pure or contained only traces of impurities. Preparative-scale gas-chromatographic separation [9] afforded a ready means of removing the contaminants and giving completely pure products, except in the case of *iso*propyl trifluoromethyl ketone. The presence of these very minor constituents in certain cases does not imply that these ketones were particularly impure compared with volatile synthetic products in general. The gas-chromatographic technique, because of its sensitivity, can reveal the presence of very minor components, that would otherwise remain undetected and often do not introduce observable errors in elementary analyses. In relatively large-scale work a second fractional distillation will usually remove such impurities; this was so for some of the ketones. Preparative-scale gas–liquid chromatography, however, is an excellent method for purification of quantities smaller than can be handled in orthodox fractional distillation columns.

The ketonic products were characterised as 2 : 4-dinitrophenylhydrazones. Also, on treatment of the ketones with aqueous alkali, the usual haloform cleavage occurred with the production of carboxylic acids ($R{\cdot}CO_2H$) and presumably the fluorohydrocarbon (CHF_3 or C_3HF_7). The acids were identified mainly as *S*-benzylthiuronium salts (see Berger [10] for observations on the melting points of these salts). On elemental analysis the lower-boiling ketones gave erratic results for carbon, apparently owing to failure of the analytical method in these cases.

Dibutyl ether was used as the solvent in those Grignard syntheses yielding a product which had b.p. <100°, to simplify the isolation.[11] The best yields of ketones were obtained when about 2·5 mol. of Grignard reagent (for 1 mol. of acid) were used in the reaction. No improvement was effected by the addition of the Grignard reagent to the fluoro-acid. Small amounts of material with b. p. greater than that of the ketone were found in each case but we have not as yet identified these by-products.

The mechanism of the addition of Grignard reagents to carbonyl groups is generally considered to involve the formation of a 1 : 1 complex of the organometallic derivative and the carbonyl compound, which is then attacked by a second molecule of the Grignard reagent.[12, 4b] Our results appear to conform with this idea, on the assumption [11, 13] that Grignard reagents are formed from methyl and ethyl iodide in yields of *ca.* 90%. Yields of the methyl and ethyl ketones, from 0·1 mole of trifluoroacetic acid, were 25—30% when 0·18 mole of Grignard reagent was used, 35—40% with 0·2 mole of Grignard reagent, and 50—60% with 0·225—0·30 mole of Grignard reagent. In these reactions, the acid was added to the organometallic compound, *i.e.*, an excess of the latter was present in the early stages. When the Grignard reagent (0·18 mole) was added to the acid (0·1 mole), only 12% of ketone was obtained, though with 0·27 mole of the Grignard reagent *ca.* 50% of ketone was formed. Thus, after allowance for the Grignard reagent (0·1 mole) which reacts with the active hydrogen, more than 0·1 mole seems to be required for the addition.

As mentioned earlier, fluoro-carbonyl compounds are very susceptible to reduction by organomagnesium compounds having β-hydrogen atoms. If ketones can be formed as intermediates in syntheses by using such reagents, the end-products isolated are often secondary alcohols, formed by this reduction.[4a] *iso*Propylmagnesium bromide and other branched-chain Grignard reagents are the most powerful reducing agents in this type of process, and Pierce, Siegle, and McBee [14] have utilised this to provide a useful extension of the general reaction. By treatment of fluoro-esters (*e.g.*, $CF_3{\cdot}CO_2Me$) with a mixture of Grignard reagents (*e.g.*, $MeMgX + Pr^iMgX$) they obtained secondary alcohols (*e.g.*, $CF_3{\cdot}CHMe{\cdot}OH$) from Grignard reagents which contained no β-hydrogen atoms and would normally react further to give tertiary alcohols. The secondary alcohols may of course be oxidised back to ketones, and we have made ethyl trifluoromethyl ketone, identical with the other specimen, in this way. In contrast with the behaviour described above, however, the reactions of trifluoroacetic acid with *iso*propyl- and *tert.*-butyl-magnesium halides have

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[9] Evans and Tatlow, *J.*, 1955, 1184.
[10] Berger, *Acta Chem. Scand.*, 1954, **8**, 427.
[11] Marvell, Blomquist, and Vaughn, *J. Amer. Chem. Soc.*, 1928, **50**, 2910.
[12] (*a*) Swain and Boyles, *ibid.*, 1951, **73**, 870; (*b*) Mosher and Combe, *ibid.*, 1950, **72**, 3994.
[13] Gilman and McCracken, *ibid.*, 1923, **45**, 2462; Gilman and Meyers, *ibid.*, p. 159.
[14] Pierce, Siegle, and McBee, *ibid.*, 1953, **75**, 6324.

given ketones, though in the latter case in yields rather lower than those obtained from straight-chain compounds. The accepted mechanism for the reduction of carbonyl compounds by Grignard reagents involves an internal rearrangement of the 1 : 1 Grignard–carbonyl complex.

In the cases of fluorine-free compounds, if magnesium bromide was used to form a complex with the carbonyl group the amount of reduction was considerably less.[12a] McBee, Pierce, and Meyer,[4a] however, found no evidence that fluoro-carbonyl compounds gave complexes of this type, though the presence of magnesium bromide in a Grignard synthesis did give rise to less reduction. In our reactions, the addition of the magnesium bromide–ether complex seemed to have no effect. The isolation of appreciable yields of ketones from the reactions of branched-chain Grignard reagents with fluoro-acids shows that the groups adjacent to a fluoro-carbonyl function can have profound influences on its behaviour with organomagnesium compounds. It is possible that the known ability of perfluoro-acids to form addition compounds with ethers,[15] which presumably means that the acids are already bound as complexes, is of importance in this aspect of the reaction.

Our general process for ketone synthesis possesses certain advantages; it is simple, it uses the free acids (usually the basic raw materials of each series), and it may be applied to branched-chain compounds. Further investigations, such as the use of other organometallic compounds, may well lead to improvements. Since this work was done, McGrath and Levine [16] have in fact described the preparation of ketones from perfluoro-acids and organolithium compounds. A preliminary report of the present investigation has been published elsewhere.[17]

EXPERIMENTAL

Preparation of 1 : 1 : 1-*Trifluoroacetone*.—Magnesium (7·2 g.) was treated with methyl iodide (42·6 g.) in di-*n*-butyl ether (75 c.c.) to give, in the usual way, methylmagnesium iodide (*ca.* 0·3 mole). The reaction vessel was surrounded by a water-bath at about 10° while trifluoroacetic acid (11·4 g., 0·1 mole) in di-*n*-butyl ether (25 c.c.) was added, dropwise, with continuous stirring. The stirring was continued for a further 90 min. at 10—15°. At 0°, and with a condenser cooled with solid carbon dioxide–alcohol attached to the system, water (25 c.c.) was added, followed by 7N-hydrochloric acid (75 c.c.). The aqueous layer was separated, extracted three times with di-*n*-butyl ether, and the combined ethereal solutions fractionally distilled (1′ column, packed with Dixon gauze spirals), to give 1 : 1 : 1-trifluoroacetone (6·3 g., 56%), b. p. 21·5—22·5°.

Under similar conditions, the following results were obtained by varying the amounts of Grignard reagent used, the figures given being in each case the quantity of methyl iodide used (mole) and the yield of trifluoroacetone (%), respectively : 0·20, 33; 0·22, 37; 0·25, 56; 0·27, 57. When the Grignard reagent (from 0·2 mole of methyl iodide) was added to trifluoroacetic acid (0·1 mole), the ketone was obtained in 12% yield only. When the acid (0·1 mole) was added to the methylmagnesium iodide (from 0·30 mole of methyl iodide) and the mixture stirred at 10—15° for 19 hr., 65% of trifluoroacetone was obtained. From a similar experiment in which the mixture was heated at 75—80° for 2 hr., the ketone was obtained in 62% yield.

The semicarbazone, prepared in the usual way, had m. p. and mixed m. p. 127—128° (Swarts [1a] gave m. p. 127°) (Found : C, 28·5; H, 3·4. Calc. for $C_4H_6ON_3F_3$: C, 28·4; H, 3·6%). The ketone also gave, in the usual manner, the 2 : 4-dinitrophenylhydrazone, m. p. 137·5—138·5° (Found : C, 36·8; H, 2·5; F, 19·1. Calc. for $C_9H_7O_4N_4F_3$: C, 37·0; H, 2·4; F, 19·5%). Henne *et al.*[1b] gave m. p. 139°.

Ethyl Trifluoromethyl Ketone.—Ethylmagnesium iodide (from ethyl iodide, 0·3 mole) was treated with trifluoroacetic acid (0·1 mole) as described above. After the Grignard complex had been decomposed, the ethereal layer was separated, dried ($MgSO_4$), and fractionated (6″ column), and the combined crude products from two such experiments were refractionated (1′ column), to give ethyl trifluoromethyl ketone (52%), b. p. 45—45·5°/741 mm., n^{16} 1·3069 (Found : F, 45·2. Calc. for $C_4H_5OF_3$: F, 45·2%). Barkley and Levine [1d] gave b. p. 44—45°/738 mm.

Under similar conditions, direct addition of trifluoroacetic acid (0·1 mole) to the Grignard

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[15] Hauptschein and Grosse, *J. Amer. Chem. Soc.*, 1951, **73**, 5139.

[16] McGrath and Levine, *ibid.*, 1955, **77**, 3656.

[17] Sykes, Tatlow, and Thomas, *Chem. and Ind.*, 1955, 630.

reagent gave the ketone in yields of 24% (from ethyl iodide, 0·20 mole), 47% (from ethyl iodide, 0·25 mole), and 45% (from ethyl iodide, 0·40 mole). When the acid (0·1 mole) was added to ethylmagnesium iodide (from 0·30 mole of iodide), and the mixture was heated at 80—90° for 2 hr. the yield of ketone was 48%. From a similar experiment in which the reaction mixture was kept at 10—15° for 21 hr., the yield was 54%. Reverse addition of the Grignard reagent to the acid, followed by a reaction time of 90 min., gave yields of ketone of 12% (from 0·20 mole of iodide) and 52% (from 0·3 mole of iodide).

The *semicarbazone*, prepared in the usual manner, had m. p. 128—129° (Found: C, 33·0; H, 4·0; F, 30·8. $C_5H_8ON_3F_3$ requires C, 32·8; H, 4·4; F, 31·1%). The 2 : 4-dinitrophenylhydrazone had m. p. 89·5—91° (Found: C, 39·4; H, 2·8. Calc. for $C_{10}H_9O_4N_4F_3$: C, 39·2; H, 3·0%); Barkley and Levine [1d] gave m. p. 91—92°.

This ketone (2·7 g.) was heated with aqueous 2N-sodium hydroxide (10 c.c.) at 50—60° for 1 hr. After acidification with hydrochloric acid (to pH 4), aqueous *S*-benzylthiuronium hydrochloride was added. The precipitate was recrystallised from water, to give *S*-benzylthiuronium propionate (2·7 g., 53%), m. p. and mixed m. p. 153—154° (Found: C, 55·3; H, 6·9. Calc. for $C_{11}H_{16}O_2N_2S$: C, 55·0; H, 6·7%). Berger [10] gave m. p. 153°.

iso*Propyl Trifluoromethyl Ketone*.—*iso*Propylmagnesium bromide (from 0·6 mole of bromide) reacted with trifluoroacetic acid (0·2 mole) as described earlier. The ethereal solution, obtained as before, was dried ($MgSO_4$) and distilled (1′ column). The combined crude products from two such experiments were refractionated (1′ column), to give the *ketone* (51%), b. p. 58° (Found: F, 39·7. $C_5H_7OF_3$ requires F, 40·7%).

This sample of ketone showed no impurities in an analytical gas-chromatographic tube filled with a dinonyl phthalate–kieselguhr. However, with a polyethylene glycol–kieselguhr packing, a minor impurity (<2%) was detected. This could not be separated on the large-scale chromatographic tube, which has the ester packing (a preparative-scale tube with the polyglycol packing was not available). The impurity may well have been 2 : 3-dimethylbutane (b. p. 58°).

The product afforded in the usual way a 2 : 4-*dinitrophenylhydrazone* (66%), m. p. 80·5—81·5° (Found: C, 41·4; H, 3·5; F, 17·4. $C_{11}H_{11}O_4N_4F_3$ requires C, 41·25; H, 3·5; F, 17·8%).

The ketone was hydrolysed with alkali as described above, to give *iso*butyric acid, which was identified as its *p*-bromophenacyl ester, m. p. and mixed m. p. 75·5° (mixed m. p. with *p*-bromophenacyl *n*-butyrate 46—48°) and as its *S*-benzylthiuronium salt (33%), m. p. and mixed m. p. 145—146° (Found: C, 56·6; H, 6·8. Calc. for $C_{12}H_{18}O_2N_2S$: C, 56·7; H, 7·1%), for which Berger [10] gave m. p. 143°.

n-*Butyl Trifluoromethyl Ketone*.—*n*-Butylmagnesium bromide (from *n*-butyl bromide, 0·3 mole) was treated with trifluoroacetic acid (0·1 mole) as described previously. The ethereal solution was dried ($MgSO_4$) and fractionated (1′ column), to give n-*butyl trifluoromethyl ketone* (63%), b. p. 89·5—90·5°, n^{19} 1·3485 (Found: C, 47·2; H, 6·1. $C_6H_9OF_3$ requires C, 46·8; H, 5·9%). A 2 : 4-*dinitrophenylhydrazone* (76%), prepared in the usual way, had m. p. 48·5—49° (Found: C, 43·1; H, 3·8; F, 16·8. $C_{12}H_{13}O_4N_4F_3$ requires C, 43·1; H, 3·9; F, 17·0%).

Alkaline hydrolysis of the ketone, as previously described, gave *n*-valeric acid, identified, in the usual manner, as its *S*-benzylthiuronium salt (52%), m. p. and mixed m. p. 150—150·5° (Found: C, 58·5; H, 7·4. Calc. for $C_{13}H_{20}O_2N_2S$: C, 58·2; H, 7·5%). Berger [10] gave m. p. 149°.

tert.-*Butyl Trifluoromethyl Ketone*.—*tert*.-Butylmagnesium bromide (from *tert*.-butyl bromide, 0·6 mole) was treated with trifluoroacetic acid (0·2 mole) as described above. By the standard procedure, the ethereal solution was obtained, dried ($MgSO_4$), and fractionated (1′ column), to give the desired compound (28%) which contained a little impurity. Large-scale gas-chromatography afforded pure tert.-*butyl trifluoromethyl ketone* (65% recovery), b. p. 69—70°, n^{20} 1·3515 (Found: F, 36·9. $C_6H_9OF_3$ requires F, 37·0%). An impurity, m. p. 99—100°, isolated from the chromatographic separation appeared to be 2 : 2 : 3 : 3-tetramethylbutane.

In the usual way, a 2 : 4-*dinitrophenylhydrazone*, m. p. 121—122°, was prepared (Found: C, 43·5; H, 3·6%).

Hydrolysis of the ketone, by the standard method, gave pivalic acid, identified as its *S*-benzylthiuronium salt, m. p. and mixed m. p. 146·5—147° (mixed m. p. with *S*-benzylthiuronium *n*-valerate, 133—137°) (Found: C, 58·3; H, 7·3%).

Phenyl Trifluoromethyl Ketone.—Phenylmagnesium bromide (from bromobenzene, 0·3 mole) in diethyl ether (75 c.c.) was treated with trifluoroacetic acid (0·1 mole) in diethyl ether (25 c.c.). The complex was decomposed by the standard procedure. The ethereal solution was dried ($MgSO_4$) and fractionated (6″ column), to give, after removal of the ether and benzene, trifluoroacetophenone (62%), b. p. 152—153°/759 mm., n^{20} 1·4597. The 2 : 4-dinitrophenylhydrazone

(75%) had m. p. 106—107·5° (Found : C, 47·7; H, 2·7; F, 16·3. Calc. for $C_{14}H_9O_4N_4F_3$: C, 47·5; H, 2·6; F, 16·1%). Simons *et al.*[2] gave b. p. 152°/730 mm., n_D^{20} 1·4583, for the ketone and m. p. 94·5—95·5° for the derivative.

The ketone (1·20 g.) was heated with aqueous 2N-sodium hydroxide (10 c.c.) for 30 min. at 80°. Acidification of the solution gave benzoic acid (0·76 g., 95%), m. p. and mixed m. p. 121—122°.

Heptafluoropropyl Methyl Ketone.—Methylmagnesium iodide (from methyl iodide, 0·15 mole) was treated with heptafluorobutyric acid (0·05 mole) as described before. The ethereal solution was dried ($MgSO_4$) and distilled, to give slightly impure heptafluoropropyl methyl ketone (41%), b. p. 63—64°. Large-scale gas-chromatography gave a pure sample (96% recovery) (Found : F, 62·4. Calc. for $C_5H_3OF_7$: F, 62·7%). The 2 : 4-dinitrophenylhydrazone (82%), obtained by the usual method, had m. p. 75·5° (Found : C, 33·8; H, 1·5; F, 34·3. Calc. for $C_{11}H_7O_4N_4F_7$: C, 33·7; H, 1·8; F, 33·9%). McBee, Pierce, and Marzluff[18] gave b. p. 63·5° for the ketone, and m. p. 76·5° for the derivative.

Hydrolysis of the ketone and treatment of the solution by the standard procedure gave *S*-benzylthiuronium acetate, m. p. and mixed m. p. 134—135° (Found : C, 53·3; H, 6·1. Calc. for $C_{10}H_{14}O_2N_2S$: C, 53·1; H, 6·2%). Berger[10] gave m. p. 136°.

*Reaction of Trifluoroacetic Acid with Methylmagnesium Iodide in the Presence of Magnesium Bromide–Di-*n*-butyl Ether Complex.*—Magnesium (2·43 g.) was stirred in di-*n*-butyl ether (50 c.c.) while bromine (16·0 g.) was added dropwise. When the colour of the bromine had disappeared, trifluoroacetic acid (11·4 g.) in di-*n*-butyl ether (25 c.c.) was added dropwise with continuous stirring. After 1 hr., methylmagnesium iodide (*ca.* 0·2 mole), prepared from methyl iodide (31·3 g.) in di-*n*-butyl ether (65 c.c.), was added slowly, with continuous stirring, whilst the flask was cooled in a water-bath (*ca.* 10°). After 16 hr. at 10—15° the complex was decomposed with water (20 c.c.) and 7N-hydrochloric acid (75 c.c.). Isolation as usual afforded 1 : 1 : 1-trifluoroacetone (4·6 g., 42%), b. p. 19·8—23°.

Reaction of Trifluoroacetic Acid with iso*Propylmagnesium Bromide in the Presence of Magnesium Bromide–Di-*n*-butyl Ether Complex.*—Magnesium (0·1 g.-atom) was treated with bromine (0·1 mole) and trifluoroacetic acid (0·1 mole) was added, followed by *iso*propylmagnesium bromide (*ca.* 0·24 mole), prepared from *iso*propyl bromide (0·3 mole). After 90 min. the complex was decomposed to give *iso*propyl trifluoromethyl ketone (40%), b. p. 49—58°. The 2 : 4-dinitrophenylhydrazone had m. p. and mixed m. p. 80°.

Oxidation of 1 : 1 : 1-*Trifluorobutan*-2-*ol.*—This secondary alcohol (5·5 g.), prepared by the method of Pierce, Siegle, and McBee,[14] was heated on a water-bath with 50% sodium dichromate solution (25 c.c.) and concentrated sulphuric acid (10 c.c.). Ethyl trifluoromethyl ketone (3·8 g., 70%) was collected in a solid carbon dioxide–ethyl alcohol trap. Gas-chromatographic analysis showed a peak identical with that given by the other sample. In the usual way the ketone gave the 2 : 4-dinitrophenylhydrazone (87%), m. p. and mixed m. p. 90—91·5°.

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[18] McBee, Pierce, and Marzluff, *J. Amer. Chem. Soc.*, 1953, **75**, 1609.