

**Reaction of *o*-Methoxybenzophenone Anil with Benzylmagnesium Chloride.**—To a Grignard reagent prepared from 7.0 g. of magnesium and 37.2 g. of benzyl chloride in 140 ml. of ether was added a solution of 8.0 g. of *o*-methoxybenzophenone anil in 150 ml. of benzene. The mixture was heated under reflux for 20 hours and then poured into a dilute solution of ammonium chloride. The product, isolated by usual procedures, was recrystallized from carbon tetrachloride; m.p. 151–152°; yield 88%.

*Anal.* Calcd. for  $C_{27}H_{25}NO$ : C, 85.45; H, 6.64; N, 3.69. Found: C, 85.63; H, 6.52; N, 3.93.

Absorption bands assignable to a secondary nitrogen group ( $3420\text{ cm}^{-1}$ ), an ether linkage ( $1040, 1250\text{ cm}^{-1}$ ), mono-substituted benzene ( $690, 698\text{ cm}^{-1}$ ) and *ortho*-disubstituted benzene ( $750\text{ cm}^{-1}$ ) were present in its infrared spectrum. The absence of *para*-disubstituted benzene absorption indicates that the benzyl group did not enter the *para*-position.

**Reaction of Benzophenone Anil with *t*-Butylmagnesium Chloride.**—The *t*-butylmagnesium chloride was prepared from 3.98 g. of magnesium and 18.4 g. of *t*-butyl chloride in 50 ml. of ether. A solution of 8.0 g. of benzophenone anil in 60 ml. of benzene was added and the mixture was heated under reflux for 7 hours before it was decomposed with a solution of dilute ammonium chloride. The yellow solid, obtained from the reaction mixture by chromatographic separation, weighed 0.5 g., m.p. 142–146°. Two recrystallizations of the compound from ethanol raised the melting point to 152–152.5°.

*Anal.* Calcd. for  $C_{23}H_{25}N$ : C, 87.57; H, 7.99. Found: C, 87.65; H, 8.24.

The infrared spectrum has bands assignable to a conjugated imino group ( $1595\text{ cm}^{-1}$ ), to  $C-CH_3$  ( $1370, 1410\text{ cm}^{-1}$ ), to a conjugated olefin ( $1565\text{ cm}^{-1}$ ) and to mono-substituted benzene ( $693\text{ cm}^{-1}$ ).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

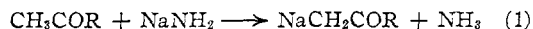
## Synthesis of Certain $\beta$ -Diketones from Acid Chlorides and Ketones by Sodium Amide. Mono versus Diacylation of Sodio Ketones with Acid Chlorides<sup>1</sup>

By BRUCE O. LINN<sup>2</sup> AND CHARLES R. HAUSER

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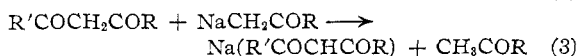
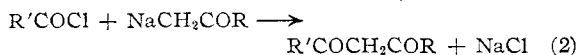
A number of acylations of sodio ketones that have not been satisfactory with ethyl or methyl esters were effected successfully with acid chlorides to form  $\beta$ -diketones. The sodio ketone was prepared by means of sodium amide, and three equivalents of it treated with one equivalent of the acid chloride. This ratio of reactants avoided the possible further acylation of the  $\beta$ -diketone. The present method is particularly useful for acylations of sodio ketones with  $\alpha,\beta$ -unsaturated acid chlorides or nitrobenzoyl chlorides, and for acylations of cyclopentanone. It is comparable to an earlier phenyl ester method for certain acylations.

The acylation of methyl or methylene ketones with esters by means of bases furnishes probably the best general method for the synthesis of many  $\beta$ -diketones.<sup>3</sup> However, a number of such acylations with the common ethyl or methyl esters have been unsuccessful even when the ester was added to the reactive, intermediate sodio ketone which was prepared by means of sodium amide (equation 1).

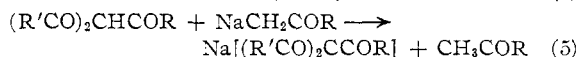
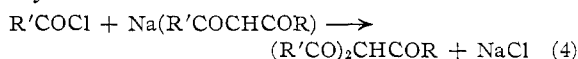


Recently<sup>4–6</sup> some of these acylations of sodio ketones were effected satisfactorily with phenyl esters which are more reactive than the corresponding ethyl or methyl esters.

In the present investigation certain of these and some other acylations of sodio ketones were carried out with the still more reactive acid chlorides. As with an ester,<sup>3</sup> the acylation of a sodio ketone with an acid chloride is accompanied by a relatively rapid acid-base reaction between the resulting  $\beta$ -diketone and the sodio ketone (equations 2 and 3).



However, in contrast to an ester,<sup>7</sup> an acid chloride may effect the further acylation of the sodio  $\beta$ -diketone<sup>8</sup> to form the sodio triketone<sup>9</sup> (equations 4 and 5) or the O-acyl derivative of the  $\beta$ -diketone. The over-all reaction may be regarded as the diacylation of the sodio ketone.



Such a diacylation to form the triketone (66%) has been observed, for example, in connection with a general study of 1,2- versus 1,4-addition<sup>5</sup> in which sodio acetophenone was treated with an equivalent of cinnamoyl chloride. Similarly diacylation to give the O-acyl derivative of the  $\beta$ -diketone has been reported with sodio cyclohexanone and benzoyl chloride.<sup>10</sup> Of course diacylation is to be expected with equivalents of the reactants since half of the sodio ketone is then neutralized according to

(7) Although ethyl esters do not effect appreciable acylation of sodio  $\beta$ -diketones or sodio  $\beta$ -ketoesters, such an acylation evidently occurs, accompanied by cleavage, on heating ethyl benzoate with sodio acetoacetic ester in which the relatively volatile ethyl acetate is removed by distillation to form sodio ethyl benzoylacetate; see S. M. McElvain and K. H. Weber, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 379.

(8) Analogous acylations of sodio  $\beta$ -keto esters with acid chlorides are well known. In fact the acylation of sodio acetoacetic ester with acid chlorides, followed by cleavage of the resulting triketone, furnishes a useful method of synthesis of certain  $\beta$ -keto esters; see C. R. Hauser and B. E. Hudson, Jr., "Organic Reactions," Vol. I, Chapter 9, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 298.

(9) Even the further acylation of the sodio triketone to form a tetraketone or the O-acyl derivative of the triketone is possible; see L. Claisen, *Ann.*, **277**, 196 (1893).

(10) E. Bauer, *Ann. chim. et phys.*, [9] **1**, 408 (1914).

(1) Supported in part by the Office of Naval Research.

(2) American Cyanamid Company Fellow, 1954–1955.

(3) See C. R. Hauser, F. R. Swamer and J. T. Adams, "Organic Reactions," Vol. VIII, Chapter 3, John Wiley and Sons, Inc., New York, N. Y., 1954.

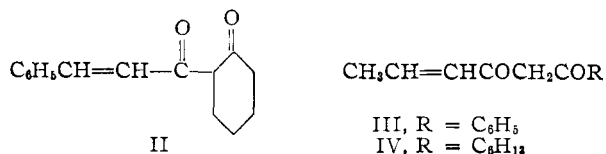
(4) C. R. Hauser, B. I. Ringler, F. W. Swamer and D. R. Thompson, *THIS JOURNAL*, **69**, 2649 (1947).

(5) C. R. Hauser, R. S. Yost and B. I. Ringler, *J. Org. Chem.*, **14**, 261 (1949).

(6) E. H. Man, F. W. Swamer and C. R. Hauser, *THIS JOURNAL*, **73**, 901 (1951).

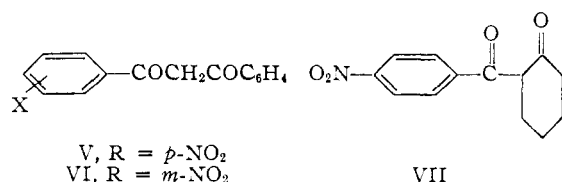
(15) We are indebted to the Tennessee Eastman Company, Kingsport, Tennessee, for a generous sample of crotonic acid from which this acid chloride was prepared.

used and the temperature kept at  $-30$  to  $-40^\circ$ . Preliminary experiments employing the usual three-to-one ratio of reactants at  $0^\circ$  produced mixtures of products. These apparently arose from further conjugate addition of  $\beta$ -diketones III and IV with the excess sodio ketones.

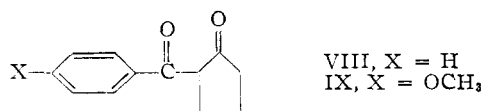


It should be mentioned that  $\beta$ -diketone IV has been reported<sup>16</sup> to be formed from ethyl crotonate and methyl *n*-hexyl ketone in the presence of sodium ethoxide, but the properties given are different from those of our product.<sup>17</sup>

The acylations of sodio ketones with nitrobenzoyl chlorides are useful since corresponding acylations with ethyl esters have been unsuccessful.<sup>18</sup> Thus, sodio acetophenone was acylated with *p*- and *m*-nitrobenzoyl chlorides to form  $\beta$ -diketones V and VI in yields of 63 and 66%, respectively. The similar acylation of sodio cyclohexanone to form VII was also realized but the yield was only 15%.



The acylations of cyclopentanone are of interest since an earlier attempt to prepare the  $\beta$ -diketone from this ketone and methyl benzoate resulted in the self condensation of the ketone, followed by acylation.<sup>4</sup> Thus, sodio cyclopentanone was acylated with benzoyl and anisoyl chlorides to form  $\beta$ -diketones VIII and IX in yields of 53<sup>19</sup> and 22%, respectively. Because of the tendency of cyclopentanone to undergo self-condensation these reactions required careful control (see Experimental).



The next four acylations listed in Table I gave  $\beta$ -diketones X–XIII in yields of 39–60% which are roughly equal to the yields obtained previously with phenyl esters. Benzoylcyclohexanone (X) has also been prepared satisfactorily employing methyl benzoate and sodium hydride.<sup>20</sup>

(16) C. D. Hurd and C. D. Kelso, *THIS JOURNAL*, **62**, 2184 (1940).

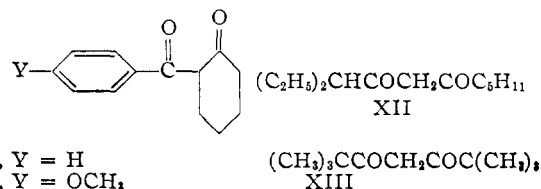
(17) Whereas the earlier product failed to give the ferric chloride enol test characteristic of  $\beta$ -diketones, our product gave not only this test but also that involving the formation of a copper chelate. The compound produced under the conditions employed by the earlier workers is being studied.

(18) W. Bradley and R. Robinson, *J. Chem. Soc.*, **129**, 2364 (1926).

(19) This  $\beta$ -diketone can also be prepared in good yield through the Friedel-Crafts acylation of benzene with 4-carbomethoxyvaleroyl chloride followed by cyclization by means of sodium amide; see S. Grateau, *Compt. rend.*, **191**, 947 (1930).

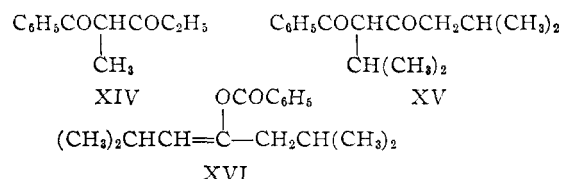
(20) F. W. Swamer and C. R. Hauser, *THIS JOURNAL*, **68**, 2647 (1946). The yield (40%) obtained by this method was somewhat lower than that (57%) realized by the present acid chloride method or that (69%) produced by the phenyl ester method (ref. 4).

The choice between the acid chloride and phenyl ester methods for such  $\beta$ -diketones will depend in the following considerations. In contrast to the acid chloride method, the phenyl ester method does not require the removal of the ammonia liberated



in the preparation of the sodio ketone (equation 1).<sup>21</sup> Moreover the two-to-one ratio of sodio ketone to phenyl ester produces satisfactory yields since further acylation of the sodio  $\beta$ -diketone does not appear to occur. On the other hand, acid chlorides are more readily available than the corresponding phenyl esters which have generally been prepared from acid chlorides. Also, acid chlorides do not result in a by-product such as the phenol liberated from the phenyl esters which is sometimes difficult to remove from the  $\beta$ -diketone.

The last two acylations listed in Table I formed  $\beta$ -diketones XIV and XV in yields of 66 and 11%, respectively. The latter acylation produced also a 22% yield of O-benzoyl derivative XVI and a 5% yield of dibenzamide which was formed presumably through benzamide.<sup>22</sup>



Although the benzoylation of diethyl ketone has apparently not been described previously,<sup>3</sup> the related acetylation has been effected satisfactorily with ethyl acetate.<sup>3</sup> However an attempt to acetylate sodio diisobutyl ketone with ethyl acetate has resulted in the self-condensation of the ester.<sup>23</sup> It is of interest that the present acylation of this sodio ketone produced more of the O-benzoyl derivative (XVI) than the  $\beta$ -diketone (XV).<sup>24</sup>

(21) Sodio ketones may be prepared by certain other reagents, the by-products from which would not react with the acid chloride. One of these reagents is sodium triphenylmethide; see, E. Baumgarten, R. Levine and C. R. Hauser, *THIS JOURNAL*, **66**, 862 (1944). Another such reagent appears to be sodium *t*-amylate (see ref. 11) or potassium *t*-amylate. Sodium amide was chosen in the present investigation because of the convenience with which it can be prepared and handled, and since the removal of the by-product ammonia is readily accomplished.

(22) This is the only acylation listed in Table I that was observed to be accompanied by amide formation. Apparently, in contrast to the other ketones, diisobutyl ketone was not converted completely to its anion by the equivalent of amide ion, and some of the latter ion reacted with the acid chloride. Similar treatment of the reaction mixture of diisopropyl ketone and sodium amide with propionyl chloride produced a 10% yield of dipropionamide along with other products that were not isolated.

(23) R. Levine, J. A. Conroy, J. T. Adams and C. R. Hauser, *THIS JOURNAL*, **67**, 1510 (1945).

(24) This type of O-acylation has been observed with hindered ketones under certain conditions; see R. C. Fuson, D. H. Chadwick and M. L. Ward, *ibid.*, **68**, 389 (1946).

TABLE II  
DATA FOR  $\beta$ -DIKETONES

$\beta$ -Di- ketones	°C.	B.p.	Mm.	$n_D^{20}$	Empirical formula	Analyses, %				Enol test <sup>a</sup>	Copper chelate <sup>b</sup> m.p., °C.
						Carbon		Hydrogen			
						Calcd.	Found	Calcd.	Found		
I	M.p. 111–112 <sup>c</sup>			....	.....	...	...	...	...	..	259–260 <sup>d</sup>
II	M.p. 92.5–93.5			....	C <sub>15</sub> H <sub>16</sub> O <sub>2</sub>	78.92	78.82	7.06	7.19	Brown	.....
III	125		0.8	1.6245	C <sub>12</sub> H <sub>12</sub> O <sub>2</sub>	76.57	76.75	6.43	6.61	Red	220 <sup>d</sup>
IV	100–101.5		0.8	1.4898	C <sub>12</sub> H <sub>20</sub> O <sub>2</sub>	73.43	73.46	10.27	10.40	Red	120–121 <sup>e</sup>
V	M.p. 162–163 <sup>f</sup>			....	C <sub>15</sub> H <sub>11</sub> O <sub>4</sub> N <sup>g</sup>	66.91	66.79	4.12	4.21	Red	305–306 <sup>h</sup>
VI	M.p. 135–136 <sup>i</sup>			....	C <sub>15</sub> H <sub>11</sub> O <sub>4</sub> N <sup>j</sup>	66.91	66.77	4.12	4.15	Red	.....
VII	M.p. 102–103			....	C <sub>13</sub> H <sub>13</sub> O <sub>4</sub> N <sup>k</sup>	63.15	63.37	5.30	5.20	..	.....
VIII	160–162		8.0 <sup>l</sup>	....	.....	...	...	...	...	..	226–228 <sup>d</sup>
IX	M.p. 74–75			....	C <sub>13</sub> H <sub>14</sub> O <sub>3</sub>	71.54	71.61	6.47	6.45	Purple	.....
X	M.p. 86.5–88.5 <sup>m</sup>			....	.....	...	...	...	...	..	.....
XI	M.p. 112–113.5 <sup>n</sup>			....	.....	...	...	...	...	..	.....
XII	127–130		10°	1.4565	.....	...	...	...	...	Red	.....
XIII	89–89.5		18 <sup>p</sup>	1.4572	C <sub>13</sub> H <sub>24</sub> O <sub>2</sub>	73.53	73.76	11.39	11.39	Red	197–198 <sup>q</sup>
XIV	134–135		5.0	1.5267	C <sub>12</sub> H <sub>14</sub> O <sub>2</sub>	75.76	75.86	7.42	7.42	Purple	187 <sup>r</sup>
XV	146–149		1.6	1.5367	C <sub>16</sub> H <sub>22</sub> O <sub>3</sub>	78.01	77.93	9.00	9.18	Red	102°
XVI <sup>a</sup>	114		1.6	1.4952	C <sub>16</sub> H <sub>22</sub> O <sub>2</sub>	78.01	78.26	9.00	9.00	Slight <sup>t</sup>	Negative

<sup>a</sup> Ferric chloride test. <sup>b</sup> Prepared by a method previously described; see ref. 26. <sup>c</sup> Reported m.p. 108.5–109.5°; ref. 5. <sup>d</sup> Green. <sup>e</sup> Gray. <sup>f</sup> Reported m.p. 160°; H. Wieland, *Ber.*, [1] 37, 1151 (1904). <sup>g</sup> *Anal.* Calcd. for C<sub>15</sub>H<sub>11</sub>O<sub>4</sub>N: N, 5.20. Found: N, 5.09. <sup>h</sup> Green. Reported m.p. 305°; ref. 18. <sup>i</sup> Reported m.p. 135°; S. Bodforss, *Ber.*, [2] 49, 2803 (1916). <sup>j</sup> *Anal.* Calcd. for C<sub>15</sub>H<sub>11</sub>O<sub>4</sub>N: N, 5.20. Found: N, 5.17. <sup>k</sup> *Anal.* Calcd. for C<sub>15</sub>H<sub>13</sub>O<sub>4</sub>N: N, 5.67. Found: 5.81. <sup>l</sup> Reported b.p. 172–173° at 12 mm.; ref. 10, p. 397. <sup>m</sup> Reported m.p. 88–89°; ref. 4. <sup>n</sup> Reported m.p. 114–116°; ref. 30. <sup>o</sup> Reported b.p. 127–130° at 10 mm.; ref. 6. <sup>p</sup> Reported b.p. 93–94 at 35 mm.; ref. 6. <sup>q</sup> Purple. Reported purple, m.p. 192–193°; ref. 6. <sup>r</sup> Gray-green. <sup>s</sup> An enol benzoate. <sup>t</sup> See note 33.

Experimental<sup>25</sup>

**Acylation of Sodio Ketones with Acid Chlorides to Form  $\beta$ -Diketones (Table I).**—A suspension of 0.30 mole of sodium amide in 300 ml. of liquid ammonia was prepared as described previously.<sup>26</sup> The liquid ammonia was evaporated on the steam-bath as 100 ml. of dry ether was being added, and the resulting ether suspension of sodium amide was stirred and refluxed 0.5 hour. After adding 200 ml. more of dry ether, 0.30 mole of the ketone in 75 ml. of dry ether was added with stirring during 10–15 minutes; then dry nitrogen gas was bubbled through the mixture for 20 minutes.<sup>27</sup> The resulting ether suspension of the sodio ketone (protected by a Drierite drying tube attached to the reflux condenser) was cooled in an ice-bath, and 0.10 mole of the acid chloride in 50 ml. of dry ether added with stirring as rapidly as possible (much heat generated). After stirring 5 minutes in the ice-bath and 15 minutes longer with the ice-bath removed, the reaction mixture was poured carefully onto a mixture of 27 ml. of concentrated hydrochloric acid and 100 g. of crushed ice. The mixture was shaken<sup>28</sup> and the two layers separated. The ether layer, which was combined with an ether extract of the aqueous layer, was washed with saturated sodium bicarbonate solution until acidification of a sample of the bicarbonate washing failed to produce a precipitate. The ether solution, which was combined with an ether extract of the bicarbonate washings, was dried over Drierite and the solvent removed. The unacylated ketone was recovered by distillation, and the residue either fractionally distilled *in vacuo* through an electrically heated 50 cm. wire-coil packed column or recrystallized from appropriate solvents to give the  $\beta$ -diketone. Certain of the solid  $\beta$ -diketones were isolated through the copper chelate procedure<sup>29</sup> as noted in Table I.

In the acylations with crotonyl chloride, the ethereal suspension of the sodio ketone (0.30 mole) was cooled to –40°, and 0.15 mole of the acid chloride in ether then added. After stirring for 20 minutes longer at –30 to

–40°, the reaction mixture was acidified by the cautious addition of the iced hydrochloric acid. The products were isolated as described above.

In the benzoylation of cyclopentanone, the ketone was added over 15 minutes to the cold suspension of sodium amide (nitrogen bubbling through), and the acid chloride immediately introduced (nitrogen cut off). After 20 minutes (nitrogen bubbling through) the reaction mixture was acidified to give a 53% yield<sup>29</sup> of 2-benzoylcyclopentanone (VIII), and a 31% yield of the self-condensation product of the ketone. The acylation of cyclopentanone with anisoyl chloride to form  $\beta$ -diketone IX was carried out in a similar manner.

The yields of  $\beta$ -diketones and the equivalents and percentages of recovered ketones are given in Table I.

**Identification of Products.**—The  $\beta$ -diketones listed in Table I were characterized by boiling or melting points, refractive indices, analyses and copper chelates as summarized in Table II. Further identifications are described below.

The copper chelates of  $\beta$ -diketones III and IV were analyzed.

*Anal.* Calcd. for CuC<sub>24</sub>H<sub>22</sub>O<sub>4</sub>: Cu, 14.51; C, 65.81; H, 5.06. Found: Cu, 14.37; C, 65.60; H, 4.95.

*Anal.* Calcd. for CuC<sub>24</sub>H<sub>28</sub>O<sub>4</sub>: Cu, 13.99; C, 63.48; H, 8.44. Found: Cu, 13.71; C, 63.42; H, 8.35.

Cinnamoylacetophenone (I), 2-benzoylcyclohexanone (X) and 2-anisoylcyclohexanone (XI) gave no depression in melting point when mixed with authentic samples prepared by known procedures.<sup>4,5,30</sup>

$\beta$ -Diketones VI, VII, IX, X and XI were cyclized with urea to form pyrimidols.<sup>31</sup>

2-Benzoylcyclopentanone (VIII) gave a semicarbazone, m.p. 224–225°; reported<sup>19</sup> m.p. 223°. The self-condensation product of the ketone, 2-cyclopentylidene cyclopentanone, boiled at 110–115° at 8 mm., reported<sup>32</sup> b.p. 117–119° at 12 mm.; m.p. of the oxime 124–125°, reported<sup>32</sup> m.p. 123–124°.

(29) Yields of 30 and 18% of VIII were obtained when the addition times of the ketone were 5 and 30 minutes, respectively. Apparently the former time was not sufficient for the complete formation of the sodio ketone while the latter time produced mainly the self-condensation product of the ketone.

(30) C. R. Hauser, F. W. Swamer and B. I. Ringler, *This Journal*, **70**, 4023 (1948).

(31) Unpublished results of C. R. Hauser and B. O. Linn.

(32) O. Wallach, *Ber.*, [3] **29**, 2963 (1896).

(25) Melting points and boiling points are uncorrected. Microanalyses were determined by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

(26) See ref. 3, p. 122.

(27) This was accomplished by replacing the separatory funnel by a bent glass tube fitted with a standard taper adapter and reaching almost to the bottom of the flask.

(28) During the preparation of V and VI, partial precipitation of the  $\beta$ -diketones occurred at this point. These products were collected by filtration and washed with water and ether. More product was obtained by working up the filtrates as described above.

The isomeric products,  $\beta$ -diketone XV and the ketone enol benzoate XVI, from the benzylation of diisobutyl ketone (see Table I) boiled 32 to 35° apart at 1.6 mm. and gave satisfactory analyses (see Table II). The higher boiling product gave an enol test and a copper chelate which are characteristic of  $\beta$ -diketones, whereas the lower boiling product failed to produce a distinct enol test<sup>33</sup> or to form a

copper chelate. Moreover, only the latter isomer XVI gave a positive test for unsaturation with bromine in carbon tetrachloride as should be expected for the ketone enol benzoate.

may be ascribed to the presence of a trace of the isomeric  $\beta$ -diketone XV.

(33) The slight enol test recorded in Table II for this product XVI

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

## Methyl and Ethyl Trichloromethyl Ethers<sup>1,2</sup>

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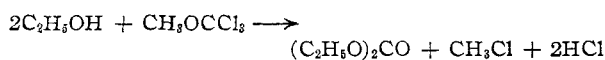
RECEIVED JULY 9, 1956

Methyl and ethyl trichloromethyl ethers,  $\text{ROCCl}_3$ , have been prepared by the action of anhydrous chlorine on the corresponding alkoxydichloromethanesulfonyl chloride or bis-[alkoxythiocarbonyl] disulfide. Methyl trichloromethyl ether reacts readily with water, benzoic acid, sodium phenate, ethanol, methanethiol and aniline to form methyl chloroformate, benzoyl chloride and methyl chloroformate, methyl phenyl carbonate, diethyl carbonate, dimethyl dithiocarbonate, and diphenylurea, respectively. Ethyl trichloromethyl ether appears to be somewhat less reactive.

Douglass and Marascia<sup>3</sup> have reported that methoxydichloromethanesulfonyl chloride,  $\text{CH}_3\text{OC}-\text{Cl}_2\text{SOCl}$ , reacts with anhydrous chlorine to form methyl trichloromethyl ether,  $\text{CH}_3\text{OCCl}_3$ , I. The present study has revealed that the latter compound can also be prepared by the direct chlorination at 0–25° of crude bis-(methoxythiocarbonyl) disulfide,  $(\text{CH}_3\text{OCS})_2\text{S}_2$ . Sulfur mono- and dichlorides are also formed in the reaction, but these can be separated from the reaction mixture by distillation and by reaction with cyclohexene to produce higher boiling compounds which remain behind when the ether is distilled. In a similar manner ethyl trichloromethyl ether (II) can be prepared from bis-(ethoxythiocarbonyl) disulfide.

Methyl trichloromethyl ether is a highly reactive compound. In some of its reactions it behaves in a manner analogous to benzotrichloride, undergoing hydrolysis to the acid chloride  $\text{CH}_3\text{OCOC}_2\text{H}_5$  and reacting with benzoic acid to form benzoyl chloride and methyl chloroformate. The reaction with sodium phenoxide shows a similar type of reaction in forming methyl phenyl carbonate.

With alcohols the reaction of I follows an unexpected course. Treatment with methyl alcohol leads to the formation of dimethyl carbonate. With ethyl alcohol the methyl group was eliminated from the ether as methyl chloride and a 61% yield of diethyl carbonate was obtained. A similar reaction was observed with methyl mercaptan in that dimethyl dithiocarbonate was the only product isolated.



With aniline Marascia<sup>4</sup> found that compound I reacted to give a nearly quantitative yield of di-

phenylurea, although no other products were isolated.

All attempts to prepare methyl orthocarbonate from I were unsuccessful. There was also no evidence of reaction between hydrogen sulfide and I.

Ethyl trichloromethyl ether (II) was not investigated extensively but it does not appear to be as reactive as I. It failed to react with benzoic acid, but with methylaniline it formed N,N'-dimethylcarbanilide.

## Experimental

**The Preparation of Bis-(methoxythiocarbonyl) Disulfide.**—To a stirred solution of 160 g. of sodium hydroxide, 600 ml. of water and 800 ml. of methanol, cooled by means of an ice-bath, was added dropwise over a 1-hour period 240 ml. of carbon disulfide.

After the addition was complete, 0.1 g. of potassium iodide was added and chlorine was bubbled through the mixture until the color of free iodine indicated that the end-point had been reached. The iodine color was discharged with 10% sodium bisulfite and the xanthate disulfide was separated, washed repeatedly with water, and dried over calcium chloride. The crude disulfide was used for later experiments because it cannot be distilled, even at reduced pressure, without decomposition.

**The Preparation of Methyl Trichloromethyl Ether (I).**—In a chlorination flask fitted with a mechanical stirrer was placed 212 g. of crude bis-(methoxythiocarbonyl) disulfide. While the flask and its contents were cooled in an ice-salt-bath a stream of anhydrous chlorine was passed in at such a rate that the temperature did not rise above 10° except at night when chlorination was discontinued. Chlorination was continued until the weight had increased 420 g., and required 58 hours including two overnight periods.

The reaction mixture was distilled using a 12-in. column packed with glass beads. The first fraction boiling 57–60° (760 mm.) consisted chiefly of sulfur dichloride. The second, a pale yellow liquid, boiled 48–51° (100 mm.) and contained the major part of the I. The residue consisted chiefly of sulfur monochloride and intermediate products from the reaction.

The second crude fraction was cooled in an ice-salt-bath while anhydrous cyclohexene was added dropwise with stirring until the yellow color had been discharged. The resulting mixture was then distilled through a 12-in. packed column and yielded 110 g. of nearly colorless I. Sometimes the last traces of yellow color were hard to eliminate but careful redistillation usually gave a colorless, pure product in 30% yield or better with the properties: b.p. 109.5–110° (760 mm.),  $d_{20}^{20}$  1.4349 and  $n_D^{20}$  1.4520.

*Anal.* Calcd. for  $\text{CH}_3\text{OCCl}_3$ : C, 16.08; H, 2.02; Cl,

(1) This work was supported by the Office of Naval Research under contract Nonr 647(00) with the University of Maine.

(2) Taken in part from the Master's Thesis of Glenn H. Warner.

(3) I. B. Douglass and Frank J. Marascia, *THIS JOURNAL*, **77**, 1899 (1955).

(4) Frank J. Marascia, Master's Thesis, University of Maine, 1954.