2,4-dinitrochlorobenzene gave a sulfide with the same infrared spectrum in 10% chloroform solution as the derivative of known structure. Three recrystallizations of this derivative from absolute ethanol yielded crystals melting first at 145–146° and, on resolidification, at 150.3–151°. A mixture melting point with the analytical sample of the sulfide did not show a depression.

Acknowledgment. The authors wish to express their gratitude for financial support of this work by the National Cancer Institute, National Institutes of Health, Grant CY-4536.

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

Examination of Synthetic Routes to Monosubstituted Diimides. II. Synthesis of *t*-Butyl Aryl- and Acylazoformates. Acid-Induced Cleavage of the Thionocarbo-*t*-butoxy Group[1,2]

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Received April 13, 1960

t-Butyl 2-substituted carbazates have been prepared by acylation of substituted phenylhydrazines by means of *t*-butyl azidoformate in pyridine or by alkylation or acylation of *t*-butyl carbazate. Oxidation of the appropriate hydrazo derivatives by means of *N*-bromosuccinimide and pyridine gave *t*-butyl phenyl-, *p*-bromophenyl-, *p*-nitrophenyl-, *o*-methoxyphenyl- and benzoylazoformates. *t*-Butyl hydrazodiformate gave *t*-butyl azodiformate. A description of the rapid acid-induced cleavage of the thionocarbo-*t*-butoxy and other alkyloxythiocarbonyl groups is presented.

Diimide (I) has recently been identified by mass spectrometry[3] as a product of the electric discharge decompositions of hydrazoic acid and hydrazine although no definitive evidence for the isolation of I or its monosubstituted derivatives has been presented.

Recently studies of acid-induced cleavages of substituted azoformates have been initiated[4] as routes to monosubstituted diimidium salts. Because of the moderate oxidizing properties of the azo linkage it was necessary to have available a protective group of the carbalkoxy type which could be cleaved by nonreducing acids such as hydrogen fluoride or trifluoroacetic acid. Such a blocking function is the carbo-*t*-butoxy group,[5] and consequently a number of azo compounds (III) protected by this group have been prepared for study. The substituted *t*-butyl azoformates were prepared by *N*-bromosuccinimide oxidation

$$\mathrm{RNHNH_2} \xrightarrow[C_5H_5N]{N_3COOC(CH_3)_3} \underset{\mathrm{II}}{\mathrm{RNHNHCOOC(CH_3)_3}} \xrightarrow[C_5H_5N]{NBS} \underset{\mathrm{III}}{\mathrm{RN{=}NCOOC(CH_3)_3}}$$

of the corresponding hydrazo derivatives (II) which were obtained by treatment of the appropriate hydrazine derivative with *t*-butyl azidoformate[6] or by alkylation or acylation of *t*-butyl carbazate. The hydrazo compounds not described in the experimental section are recorded in Table I.

No difficulty was encountered in the *N*-bromosuccinimide-pyridine oxidation of the 2-arylcarbazates (see Table II) although of the 2-acyl derivatives (III, R = $(CH_3)_3COCO$—, C_6H_5CO—, *p*-$NO_2C_6H_4CO$—, and CH_3CO—) only the first two gave azo compounds which were stable enough to be isolated under the conditions used. *t*-Butyl benzoylazoformate (III, R = C_6H_5CO—) was unstable at room temperature but could be stored for extended periods in a freezer (−18°). No precautions were necessary in the preparation and storage of *t*-butyl azodiformate (IV), a unique azo compound of considerable synthetic promise.[7]

$$\underset{\mathrm{IV}}{(CH_3)_3COCON{=}NCOOC(CH_3)_3} \xrightarrow{(CH_3)_3CMgCl} \xrightarrow{H_2O} \underset{\mathrm{V}}{\begin{matrix}(CH_3)_3CNNHCOOC(CH_3)_3\\ \vert\\ COOC(CH_3)_3\end{matrix}}$$

The azodiformate (IV) exhibits reactions typical of such esters, modified however by the bulk of the *t*-butyl groups. *t*-Butylmagnesium chloride adds slowly to the azo linkage of IV yielding V, cleavage of which gives *t*-butylhydrazine hydrochloride. In contrast to the exothermic reaction of ethyl azodiformate with reactive dienes, IV reacts sluggishly under Diels-Alder conditions. No reaction was observed under the usual conditions

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(1) Supported by a grant (NSF G 2368) from the National Science Foundation.

(2) Taken in part from the M.S. theses of P.H.T. and P.J.C.

(3) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, 28, 719 (1958).

(4) L. A. Carpino, *J. Am. Chem. Soc.*, 79, 96 (1957).

(5) L. A. Carpino, *J. Am. Chem. Soc.*, 79, 98 (1957).

(6) L. A. Carpino, C. A. Giza, aud B. A. Carpino, *J. Am. Chem. Soc.*, 81, 955 (1959).

(7) Compare the additive reactivity of methyl and ethyl azodiformate, K. Alder and T. Noble, *Ber.*, 76, 54 (1943).

TABLE I[a]

SUBSTITUTED *t*-BUTYL CARBAZATES

RNHNHCOOC(CH$_3$)$_3$

R	M.P.	Yield, %	Recryst. Solvent	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
p-$NO_2C_6H_4$—	130–131	33	A	$C_{11}H_{15}N_3O_4$	52.17	52.30	5.97	5.78
p-$CH_3C_6H_4$—	85.5–86.5	20	B	$C_{12}H_{18}N_2O_2$	64.84	64.96	8.16	8.30
o-$CH_3OC_6H_4$—	130–131.5	67	C	$C_{12}H_{18}N_2O_3$	60.48	60.60	7.61	7.41
CH_3CO—[b]	117–117.5	100	A	$C_7H_{14}N_2O_3$	48.26	48.13	8.10	8.23
p-$NO_2C_6H_4CO$—	175.5–178.5	68	D	$C_{12}H_{15}N_3O_5$	51.24	51.55	5.38	5.44

[a] Recrystallization solvents: (A) benzene–petroleum ether, (B) ligroin (b.p. 60–90°), (C) benzene-ligroin (b.p. 90–120°), and (D) benzene. [b] Acetic anhydride was used as the acetylating agent.

TABLE II[a]

SUBSTITUTED *t*-BUTYL AZOFORMATES

RN=NCOOC(CH$_3$)$_3$

R	M.P.	Recryst. Solvent	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
C_6H_5—[b]	25–26	A	94	$C_{11}H_{14}N_2O_2$	64.06	64.29	6.84	6.95
p-$NO_2C_6H_4$—	134–136 dec.	B	91	$C_{11}H_{13}N_3O_4$	52.58	52.76	5.22	5.27
o-$CH_3OC_6H_4$—	67.5–69.5	C	100	$C_{12}H_{16}N_2O_3$	61.00	60.79	6.82	7.03

[a] Recrystallization solvents: (A) ether–petroleum ether, (B) ethanol, and (C) ethanol-water. [b] After removal of the methylene dichloride solvent the crude azo compound solidified upon cooling in a Dry Ice–acetone bath. Recrystallization was effected by dissolving the compound in ether, adding one volume of petroleum ether and cooling in a Dry Ice–acetone bath.

with anthracene or 1,4-diphenyl-1,3-butadiene although cyclopentadiene readily afforded an adduct.

Lefevre and co-workers[8] examined the infrared spectra of ethyl and propyl azodiformate and found that the carbonyl stretching frequency appeared near 5.62 μ. In agreement with this work we find that *t*-butyl azodiformate and *t*-butyl phenylazoformates show strong carbonyl absorptions at 5.65–5.72 μ.[9]

The results obtained on cleavage of *t*-butyl phenylazoformates by means of trifluoroacetic acid, hydrogen fluoride and perchloric acid will be described in a separate communication. Unexpectedly cleavage occurred more slowly than in the case of model carbamic acid esters. Attempts were therefore made to devise a series of protective groups which could be cleaved more rapidly than the carbo-*t*-butoxy group. The results obtained on treatment of the three possible sulfur substitution products (VI, VII, and IX) of *t*-butyl carbanilate (VIII) with hydrogen chloride or hydrogen bromide in nitromethane are shown in Table III.

That the thionocarbo-*t*-butoxy group is cleaved considerably faster than is the carbo-*t*-butoxy group is shown by the fact that VI is cleaved by 48% aqueous hydrogen fluoride instantaneously at room temperature whereas cleavage of VIII by this reagent is sluggish under the same conditions. Neither of the *S*-alkyl derivatives (VII or IX) is affected by hydrogen chloride or hydrogen bromide in nitromethane. This is probably because the S—C bond is less likely to undergo rupture than the O—C bond because of the electronegativity difference between sulfur and oxygen.[10]

These observations suggest the thionocarbo-*t*-butoxy group as a promising and highly sensitive blocking function. Unfortunately no method has yet been found by which this group can be introduced other than through reaction of an isothiocyanate with *t*-butyl alcohol. Reaction of dialkyl xanthates with amino compounds has been used previously to introduce primary and secondary alkyloxythiocarbonyl groups.[11,12] References to the preparation of the xanthates of tertiary alcohols are rare.[13] Although the usual methods of prepara-

(8) R. J. W. Le Fevre, W. T. Oh, I. H. Reece, R. Roper, and R. L. Werner, *Australian J. Chem.*, 11, 92 (1958).

(9) The corresponding hydrazo compounds exhibit carbonyl absorptions at 5.85–5.91 μ.

(10) This effect shows up in numerous other instances such as the resistance of thio ethers to cleavage by acids as reported by D. S. Tarbell and D. P. Harnish, *J. Am. Chem. Soc.*, 70, 4123 (1948). P. N. Rylander and D. S. Tarbell [*J. Am. Chem. Soc.*, 72, 3021 (1950)] showed that the acid-catalyzed hydrolysis of *t*-butyl thiolacetate proceeded by cleavage between the sulfur atom and the carbonyl group rather than by separation of a *t*-butyl cation as is apparently the case for *t*-butyl acetate. The difference in ease of cleavage of VI and VIII may be related to the bond energy effects noted in comparison of the xanthate (Chugaev) and carboxylic ester pyrolyses discussed by G. L. O'Connor and H. R. Nace [*J. Am. Chem. Soc.*, 75, 2118 (1953)].

(11) P. Aubert, E. B. Knott, and L. A. Williams, *J. Chem. Soc.*, 2185 (1951).

(12) G. W. Kenner and H. G. Khorana, *J. Chem. Soc.*, 2076 (1952).

(13) For examples see (a) R. A. Benkeser and J. J. Hazdra, *J. Am. Chem. Soc.*, 81, 228 (1959); (b) G. J. Sutton, *J. Roy. Australian Chem. Inst.*, 17, 249 (1950); (c) D. A. Semenow, E. F. Cox, and J. D. Roberts, *J. Am. Chem. Soc.*, 78, 3221 (1956).

TABLE III

APPROXIMATE TIMES REQUIRED FOR CLEAVAGE OF CARBAMATES BY HYDROGEN HALIDES IN NITROMETHANE[a,b]

Carbamate, R = C_6H_5	HCl	HBr
VI $RNH(C{=}S)OC(CH_3)_3$[c]	Inst.	Inst.
VII $RNH(C{=}O)SC(CH_3)_3$[d]	N.C.	N.C.
VIII $RNHCOOC(CH_3)_3$[e]	1	Inst.
IX $RNHCS_2C(CH_3)_3$	N.C.	N.C.
X $RNHCOOCH_2C(CH_3)_3$[f]	N.C.	N.C.
XI $RNH(C{=}S)OCH_2C(CH_3)_3$	N.C.	41
XII $RNH(C{=}S)OCH(CH_3)_2$[g]	75	1
XIII $RNHCOOCH(CH_3)_2$[h]	N.C.	N.C.
XIV $RNH(C{=}S)OCH_3$[i]	N.C.	2
XV $RNH(C{=}S)OC_2H_5$[i]	N.C.	1
XVI $RNH(C{=}S)OCH_2C_6H_5$[i]	90	1

[a] Times were recorded in minutes when a definite precipitate of aniline hydrohalide appeared at room temperature; inst. = instantaneous; N.C. = not cleaved in 24 hr. at the concentrations used. [b] The approximate concentrations of the hydrogen halides were 0.2*M* hydrogen chloride and 0.5*M* hydrogen bromide. [c] R. W. Bost and E. R. Andrews, *J. Am. Chem. Soc.*, **65**, 900 (1943). [d] E. Dyer and J. F. Glenn, *J. Am. Chem. Soc.*, **79**, 366 (1957). [e] E. Knoevenagel, *Ann.*, **297**, 148 (1897). [f] A. Richard, *Ann. chim.* [8], **21**, 339 (1910). [g] W. R. Orndorff and F. A. Richmond, *Am. Chem. J.*, **22**, 458 (1899). [h] C. Weizmann and S. F. Garrard, *J. Chem. Soc.*, **117**, 328 (1920). [i] M. Roshdestvenski, *J. Russ. Phys. Chem. Soc.*, **41**, 1443 (1910); *Chem. Zentral.*, I, 910 (1910).

tion of xanthates were not applicable to the *t*-butyl derivative, potassium *t*-butoxide could be made to react with carbon disulfide under suitable conditions. The resulting xanthate could not be obtained sufficiently pure for elemental analysis although an infrared spectrum of the substance (Nujol mull) proved to be similar to the spectra of potassium ethyl and isopropyl xanthates. Reaction of the xanthate with methyl iodide in ether gave an unstable liquid the infrared spectrum of which was consistent with its assignment of structure as *S*-methyl *t*-butyl xanthate (XVII). The *S*-methyl derivative could not be distilled at 1–2 mm. and, in fact, upon heating to 70–80° (a remarkably low temperature for the Chugaev reaction) under-

$$\underset{\text{XVII}}{(CH_3)_3COCS_2CH_3} \xrightarrow{NH_2NH_2} \underset{\text{XVIII}}{NH_2NHCSOC(CH_3)_3}$$

went decomposition to isobutylene and other gaseous products. Treatment of XVII with hydrazine hydrate yielded a small amount of thiocarbohydrazide and an unstable oil which appeared to be impure *t*-butyl thionocarbazate (XVIII). The carbazate could not be distilled and underwent decomposition on standing. However, a benzal derivative was obtained which gave the correct elemental analysis and a consistent infrared spectrum. Because of the instability of XVII reactions with phenylhydrazine and other substituted hydrazino compounds have so far proved to be unsuccessful. Other routes to the thionocarbazates are under examination.

The driving force toward cleavage of the thionocarbalkoxy group is sufficiently great that cleavage occurs even in those cases in which the *t*-butyl group is replaced by primary and secondary alkyl groups (Table III, compounds XI, XII, XIV, XV, and XVI).[14]

It has been demonstrated that the acylation procedure of Sayre[15] may be used to introduce the isopropyloxythiocarbonyl group. For example potassium isopropyl xanthate reacts with ethyl chloroformate yielding the thionothiodiformate XIX which with aniline yields XII. The same method was used successfully with potassium benzyl xanthate but not with the *t*-butyl derivative.

$$(CH_3)_2CHOCS_2K \xrightarrow{ClCOOC_2H_5} \underset{\text{XIX}}{(CH_3)_2CHOCS_2COOC_2H_5}$$

EXPERIMENTAL[16–18]

t-Butyl 2-(p-bromophenyl)carbazate. A solution of 61.86 g. of *p*-bromophenylhydrazine and 47.4 g. of *t*-butyl azidoformate in 360 ml. of pyridine was placed in a round bottom flask, the cork wired in, and the solution allowed to stand at room temperature for 2 weeks. The addition of water caused separation of an oil which crystallized upon the introduction of seed crystals.[19] The orange solid, m.p. 120–124°, obtained in theoretical yield, was recrystallized by dissolution in benzene-ligroin (b.p. 90–120°) and addition of petroleum ether (b.p. 30–60°) to the cloud point. There was obtained 66.5 g. (70.4%) of white powder, m.p. 125–126°. The analytical sample, m.p. 126.5–127.5° (from ligroin, b.p. 90–120°, containing a small amount of benzene) was obtained in the form of long snow white needles.

Anal. Calcd. for $C_{11}H_{15}N_2O_2Br$: C, 46.00; H, 5.26. Found: C, 46.17; H, 5.17.

The *p*-nitro, *p*-methyl, and *o*-methoxyphenyl carbazates were prepared similarly. See Table I.

t-Butyl 2-benzoylcarbazate. To a mechanically stirred solution of 6.1 g. of *t*-butyl carbazate and 4.0 g. of pyridine dissolved in 50 ml. of methylene dichloride there was added during 15–20 min. with ice bath cooling a solution of 7.3 g. of benzoyl chloride in 15 ml. of methylene dichloride. The mixture was allowed to stand at room temperature overnight, an additional 75 ml. of methylene dichloride was added and the mixture washed with three 50-ml. portions of water. Removal of the solvent from a water bath with the aid of a water aspirator gave 11.3 g. (103%) of white solid, m.p. 148–157°. Recrystallization by dissolution in boiling alcohol and addition of water to the cloud point gave 8.5 g. (78%) of white crystals, m.p. 155–157°. The analytical sample (ethanol–water) had a m.p. of 156–157°.

(14) Release of carbon dioxide from ethyl carbamate by the action of 5% oleum requires a temperature of nearly 90° according to T. I. Bieber [*J. Am. Chem. Soc.*, **75**, 1409 (1953)]. See also R. A. Boissonnas and G. Preitner [*Helv. Chim. Acta*, **36**, 875 (1953)].

(15) R. Sayre, *J. Am. Chem. Soc.*, **74**, 3647 (1952).

(16) Melting points and boiling points are uncorrected.

(17) Analyses are by Drs. Weiler and Strauss, Oxford, England.

(18) Infrared spectra were recorded linearly in wave length on a Perkin-Elmer Model 21 spectrophotometer, sodium chloride optics.

(19) If seed crystals were not available and the oil did not solidify it was extracted with several portions of methylene dichloride and the extracts washed with 1% hydrochloric acid to remove pyridine. Removal of the solvent gave an oil which crystallized on cooling.

Anal. Calcd. for $C_{12}H_{16}N_2O_3$: C, 61.0; H, 6.82. Found: C, 61.3; H, 6.60.

t-Butyl 2-(p-nitrobenzoyl)carbazate and t-butyl 2-acetylcarbazate were prepared similarly. See Table I.

t-Butyl 2-triphenylmethylcarbazate. To a solution of 69.7 g. of trityl chloride in 300 ml. of dimethylformamide was added a solution of 33.04 g. of *t*-butyl carbazate and 25.3 g. of triethylamine in 30 ml. of dimethylformamide. Considerable heat was evolved and triethylamine hydrochloride separated at once. The reaction mixture was allowed to stand overnight at room temperature, filtered, and water added cautiously to the filtrate with vigorous shaking which gave a quantitative yield of the carbazate as a white solid, m.p. 80–96°. Several recrystallizations from aqueous ethanol gave white crystals, m.p. 122–123°.

Anal. Calcd. for $C_{24}H_{26}N_2O_2$: C, 76.97; H, 7.00. Found: C, 76.96; H, 6.98.

t-Butyl p-bromophenylazoformate. To a solution of 17.95 g. of *t*-butyl 2-(*p*-bromophenyl)carbazate and 4.94 g. of pyridine in 300 ml. of methylene dichloride there was added in small portions over a period of 15–20 min. 11.13 g. of *N*-bromosuccinimide. The red colored solution was allowed to stand at room temperature for 2–3 hr. and then washed twice with 100-ml. portions of water, once with 125 ml. of 10% sodium hydroxide solution, and twice again with 100-ml. portions of water. After drying over potassium carbonate the methylene dichloride was removed by distillation from a water bath (50°) with the aid of a water aspirator. The red liquid crystallized to a yellow-orange solid on standing and was purified by dissolution in cold methanol, decolorization with charcoal and precipitation with water which gave 15.34 g. (86%) of yellow-orange crystals, m.p. 66–67°. The analytical sample had a m.p. of 63–64° (ethanol).

Anal. Calcd. for $C_{11}H_{13}N_2O_2Br$: C, 46.33; H, 4.59. Found: C, 46.49; H, 4.61.

Other substituted *t*-butyl phenylazoformates were prepared similarly. See Table II.

t-Butyl benzoylazoformate. To a suspension of 11.8 g. of *t*-butyl 2-benzoylcarbazate in 50 ml. of methylene dichloride and 3.95 g. of pyridine cooled in an ice bath there was added in 3–5 min. 8.9 g. of *N*-bromosuccinimide. Toward the end of the addition the mixture was removed from the ice bath and allowed to stand at room temperature for 5–10 min. The carbazate dissolved and a new solid began to separate. The mixture was washed once with 50 ml. of water and twice with 50-ml. portions of 10% potassium carbonate solution, dried (magnesium sulfate), and the solvent removed from a water bath at 20–25° with the aid of a water aspirator (15–20 mm.). The clear red oil remaining amounted to 8.7 g. (74.4%). The azo compound appeared to be stable on storage in a deep freeze. A sample which was allowed to stand overnight at room temperature underwent decomposition. The azoformate was characterized by reduction with hydrazine hydrate to the original hydrazo compound, m.p. and mixture m.p. 156–157°.

t-Butyl azodiformate (IV). A solution of 23.2 g. of *t*-butyl hydrazodiformate (m.p. 124–126°) in 175 ml. of methylene dichloride and 7.9 g. of pyridine was cooled by a stream of cold tap water while 18.2 g. of *N*-bromosuccinimide was added during 6–7 min. with swirling. The solution was allowed to stand for 5–10 min. and then washed with two 100-ml. portions of water and one 100-ml. portion of 10% sodium hydroxide solution. The dried (magnesium sulfate) solution was allowed to evaporate in a flat dish. The yellow-orange crystalline residue [20.7–21.8 g. (90–94.5%), m.p. 90–91.5°] was recrystallized by covering the dry solid with 35–40 ml. of petroleum ether (b.p. 30–60°) and adding ligroin (b.p. 60–90°) to the boiling mixture until solution occurred. On cooling there was obtained 20.2–20.7 g. (88–90%) of well formed yellow crystals, m.p. 90–92°.

Anal. Calcd. for $C_{10}H_{18}O_4N_2$: C, 52.16; H, 7.88. Found: C, 51.92; H, 7.55.

Neopentyl N-phenylthionocarbamate. (XI). To a mixture of the sodium salt of neopentyl alcohol prepared from 7 g. of the alcohol and 1.8 g. of sodium in 10 ml. of anhydrou toluene there was added with cooling 10.8 g. of pheny isothiocyanate. After allowing the mixture to stand at room temperature for 2 hr. the solvent was removed with the aid of a steam bath and a water aspirator and 200 ml. of water added to the residue. The resulting yellow solid was recrystallized from ligroin (b.p. 65–75°) which gave 11.8 g. (67%) of the carbamate, m.p. 114–114.5°.

Anal. Calcd. for $C_{12}H_{17}ONS$: C, 64.53; H, 7.67. Found: C, 64.36; H, 7.58.

t-Butyl N-phenyldithiocarbamate (IX). To a solution of 13.5 g. of phenyl isocyanate in 100 ml. of benzene was added 11.2 g. of sodium *t*-butyl mercaptide while cooling by means of tap water. The mixture was heated briefly to the boiling point and allowed to stand at room temperature for 6 hr. The volatile material was removed with the aid of a steam bath and a water aspirator. The resulting solid was washed with dilute hydrochloric acid (1%). Recrystallization from ligroin (b.p. 60–110°) and benzene (3:1) gave 3.5 g. (15.5%) of the carbamate, m.p. 103–104.5°.

Anal. Calcd. for $C_{11}H_{15}NS_2$: C, 58.62; H, 6.71. Found: C, 58.61; H, 6.96.

Isopropyl N-phenylthionocarbamate. (XII). A suspension of 20 g. of potassium isopropyl xanthate in 200 ml. of acetone was stirred for 5 hr. after the addition of 12.4 g. of ethyl chloroformate. The mixture was diluted with 500 ml. of water and extracted with two 50-ml. portions of methylene dichloride. Removal of the solvent from the dried (magnesium sulfate) solution by distillation from a water bath with the aid of a water aspirator gave 17.5 g. (73%) of crude yellow-red thionothiodiformate XIX. A mixture of 2 g. of crude XIX and 2.8 g. of aniline was allowed to stand at room temperature for 30 min., acidified with dilute hydrochloric acid after the addition of 25 ml. of water, cooled, and filtered. There was obtained 1.4 g. (74.5%) of cream-colored needles after recrystallization from ligroin (b.p. 60–90°), m.p. 78–82°. A second recrystallization raised the m.p. to 84–85°, lit.[20] m.p. 85.5°. A mixture melting point with an authentic sample showed no depression.

Benzyl hydrazodithionodiformate. To a solution of 5.2 g. of crude *O*-benzyl *S*-carbethoxyxanthate[21] in 30 ml. of ethanol was added dropwise with stirring 0.5 g. of hydrazine hydrate. After stirring the solution at room temperature for 5 hr. it was just acidified with 10% hydrochloric acid after dilution with 10 ml. of water. Recrystallization of the precipitated solid from low- (b.p. 30–60°) and high-boiling (b.p. 90–120°) ligroin (3:1) gave 2 g. (61%) of the hydrazo compound, m.p. 116–118.5°, lit.[22] m.p. 118–119.5°.

S-Methyl-t-butyl xanthate (XVIII). To a well stirred solution of 60 g. of potassium dissolved in 1500 ml. of *t*-butyl alcohol there was added over a period of 10–15 min. 180 g. of carbon disulfide. The mixture was stirred for 10 min. longer and then filtered while still warm. The orange solid was washed twice with ether and after air-drying overnight amounted to 258 g. (89%). The infrared spectrum indicated contamination by *t*-butyl alcohol. Attempted drying of the crude solid at 70° caused decomposition. No method was found by which the xanthate could be purified for elemental analysis.

A suspension of 258 g. of crude potassium *t*-butyl xanthate in 600 ml. of ether and 220 g. of methyl iodide was stirred at room temperature for 15 hr. under a reflux condenser (at first gentle spontaneous refluxing occurred). After the addition of 500 ml. of water to dissolve the inorganic salts the ether layer was separated, dried (magnesium sulfate), and evaporated at 15–20 mm. in a water bath at 20–25°. The yellow oil remaining amounted to 148 g. (58.7%).

The infrared spectrum of the crude xanthate showed a strong, broad band at 7.94 μ, presumably due to the C=S

(20) Ref. *g* of Table III.

(21) Prepared as given for the isopropyl derivative.

(22) J. Waugel, *Arkiv. Kemi*, 1, 431 (1950); *Chem. Abstr.*, 44, 6818h (1950).

linkage[23] and a weak-to-medium contaminating carbonyl band at 5.86 μ. The least contamination by carbonyl-containing materials was noted when the xanthate was prepared by successive treatment of *t*-butyl alcohol with sodium hydride, carbon disulfide and methyl iodide in anhydrous ether according to the method of Roberts.[13c] In this case the band at 5.86 μ was barely perceptible.

Decomposition of the xanthate in a water bath at 70–80° gave isobutylene, identified by passage through a solution of acetonitrile and sulfuric acid in acetic acid which yielded *N*-*t*-butylacetamide, m.p. 99–100.5° (lit.[24] m.p. 97–98°).

Hydrazinolysis of S-methyl t-butyl xanthate. A mixture of 78 g. of freshly prepared *S*-methyl *t*-butyl xanthate and 60 g. of hydrazine hydrate (100%) was stirred at room temperature for 12 hr. (spontaneous warming occurred at first). There was added 75 ml. of methylene dichloride and the mixture filtered to remove 3 g. of thiocarbohydrazide,[25] m.p. 166–170° dec., lit.[26] m.p. 168° dec. The aqueous phase was extracted with two additional 25-ml. portions of methylene dichloride, the combined extracts dried (magnesium sulfate), and the solvent removed from a water bath (15–20°) with the aid of a water aspirator (15–20 mm.). The residual cloudy oil amounted to 26.5 g. (37.6%). An immediate test of this material with an equivalent amount of benzaldehyde in ethanol gave a 72% yield of the *benzal derivative*, m.p. 106–107° dec., from methanol.

Anal. Calcd. for $C_{12}H_{16}N_2OS$: C, 60.98; H, 6.83; N, 11.86. Found: C, 61.14; H, 6.72; N, 11.78.

Addition of a test portion of crude *t*-butyl thionocarbazate to 48% aqueous hydrofluoric acid caused immediate vigorous gas evolution.

Cleavage of carbanilates by hydrogen chloride and bromide in nitromethane. The solutions of hydrogen halide were prepared by passing the anhydrous gas into nitromethane at room temperature for 30 min., the concentrations being determined by addition of an excess of aniline to an aliquot and weighing the precipitated aniline hydrohalide. Cleavages were carried out by dissolving 0.005 mole of the carbanilate in 20 ml. of the standard hydrogen halide–nitromethane solution and allowing the solutions to stand at room temperature for a maximum of 24 hr. The aniline hydrohalide was filtered, dried and weighed. The yield of aniline hydrohalide was generally in the range 60–95%. From the preparative point of view it is preferable to pass the anhydrous hydrogen halide directly into a solution of the carbamate in nitromethane for several minutes. For example methyl *N*-phenylthionocarbamate was partially cleaved by hydrogen chloride under these conditions.

t-Butyl 1-t-butylhydrazo-1,2-dicarboxylate (V). A solution of *t*-butylmagnesium chloride prepared from 6.44 g. of *t*-butyl chloride, 1.67 g. of magnesium, and 75 ml. of anhydrous ether was added dropwise over a period of 15 min. to a solution of 8 g. of *t*-butyl azodiformate in 75 ml. of anhydrous ether while cooling in an ice bath. The mixture was stirred for 10 hr. and then decomposed by the addition of 50 ml. of saturated ammonium chloride solution followed by 100 ml. of water. After filtration of the two layers the ether layer was allowed to evaporate spontaneously. The residual tacky solid (5 g., 50%) was recrystallized from nitromethane which gave 2.9 g. (29%) of white slightly tacky crystals, m.p. 119–130°. Recrystallization from low- (b.p. 60–90°) and high-boiling (b.p. 90–120°) ligroin (1:1) followed by nitromethane gave 2.6 g. (26%) of the pure ester, m.p. 136–137°.

Anal. Calcd. for $C_{14}H_{28}N_2O_4$: C, 58.30; H, 9.79. Found: C, 58.68; H, 9.82.

t-Butylhydrazine hydrochloride. A solution of 1 g. of *t*-butyl 1-*t*-butylhydrazo-1,2-dicarboxylate (V) in 12 ml. of nitromethane was treated with a stream of anhydrous hydrogen chloride for 3–5 min. After cooling the mixture in an ice bath there was obtained 0.4 g. (92%) of the hydrochloride, m.p. 184–187° dec. Recrystallization from ethanol-ether raised the m.p. to 191–194° dec. There was no depression in melting point on admixture with an authentic sample.[27]

2,3-Dicarbo-t-butoxy-2,3-diazabicyclo[2.2.1]hept-5-ene. A solution of 0.66 g. of cyclopentadiene (b.p. 40–42°) and 2.3 g. of *t*-butyl azodiformate in 3 ml. of benzene was allowed to stand at room temperature for 9 hr. Evaporation by means of a slight air draft left 2.7 g. (91.3%) of the adduct, m.p. 101–103.5°. Recrystallization from ligroin (b.p. 60–90°) gave tiny white crystals, m.p. 104–105.5°.

Anal. Calcd. for $C_{15}H_{24}N_2O_4$: C, 60.80; H, 8.16; N, 9.46. Found: C, 60.67; H, 8.29; N, 9.20.

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(27) We wish to thank Prof. P. A. S. Smith for kindly providing a sample of *t*-butylhydrazine hydrochloride.[28]

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN CO., DIVISION OF EASTMAN KODAK CO.]

The Chemistry of Dimethylketene Dimer. III.[1] Reactions with Ammonia and Amines

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Received March 20, 1961

Attempts to convert tetramethyl-1,3-cyclobutanedione (dimethylketene dimer, I) to a reported monoimine invariably led to the cleavage product, 2,2,4-trimethyl-3-oxovaleramide. This cleavage reaction also occurred with primary and secondary aliphatic and alicyclic amines. Aromatic amines did not react with I to any practical degree unless a mineral acid catalyst was present, in which case Schiff bases of I were formed.

Wedekind and Miller treated tetramethyl-1,3-cyclobutanedione (dimethylketene dimer, I) with aqueous ammonia at 80–130° and obtained a crystalline product, m.p. 108.5°, to which they assigned the monoimine structure II.[2] The evidence for this

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