zene, and dried in a vacuum oven at 65°, weight 7.0 g. An analytical sample was recrystallized from dimethylformamide giving yellow-green plates, m.p. 305–307° (Kofler).

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.40, 84.30; H, 6.68, 6.67.

Reaction of p-xylylenebis(phosphonium salt) with 9-anthraldehyde. To a solution of 7.0 g. (0.01 mole) of the bis(phosphonium salt) in 100 cc. of alcohol was added 5.0 g. (0.024 mole) of 9-anthraldehyde and 100 ml. of 0.2M lithium ethoxide solution. The mixture turned immediately an orange-red color and a brick red precipitate formed. This was allowed to stand overnight and was filtered. It was noted that the product was light sensitive changing from brick red to yellow orange on exposure to light. The yield was 4.25 g. (88%) of a product melting at 300° on the hot bar. The product was recrystallized from dimethyl sulfoxide to give well developed yellow-orange crystals melting sharply at 320–322°.

Anal. Calcd. for $C_{38}H_{26}$: C, 94.34; H, 5.66. Found: C, 94.28, 94.32; H, 5.60, 5.70.

Acknowledgments. We wish to thank Dr. W. B. McCormack, Organic Chemical Department, for generously supplying the triphenylphosphine used. Also, to Dr. C. Sly of Pressure Research Laboratory who carried out all of the catalytic hydrogenations.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE ILLINOIS STATE GEOLOGICAL SURVEY]

Oxidation of 2,6-Di-*tert*-butyl-4-methylphenol. The Structure of $C_{14}H_{22}O_3$[1]

G. R. YOHE, J. E. DUNBAR,[2] MYRA W. LANSFORD,[2] R. L. PEDROTTI,[2] F. M. SCHEIDT,[2] FRED G. H. LEE,[2] AND EARLE C. SMITH[2]

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The acidic compound $C_{14}H_{22}O_3$, previously reported without assignment of structure as an oxidation product of 2,6-di-*tert*-butyl-4-methylphenol, is now believed to be DL-*trans*-5,6-di-*tert*-butyl-2-hydroxy-1,4-diketo-2-cyclohexene (I). Chemical properties are described and infrared spectra are presented in support of this structure.

This structure is of interest in relation to the problem of the existence of *o*-di-*tert*-alkylbenzene derivatives. The relatively easy racemization of optically active I suggests that its completely enolized form, 5,6-di-*tert*-butyl-1,2,4-trihydroxybenzene, is capable of transitory existence.

A previous publication[3] described the formation of a compound $C_{14}H_{22}O_3$ by the oxidation of 2,6-di-*tert*-butyl-4-methylphenol in aqueous sodium hydroxide with oxygen gas at about 100°. It was also pointed out that this same compound could be made by similar oxidation of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, 3,5-di-*tert*-butyl-4-hydroxybenzoic acid, and 2,6-di-*tert*-butyl-1,4-benzoquinone. Some of the properties of this compound were described briefly, but no attempt was made to assign a structure to it. The present paper gives the results of a detailed study of its properties, and proposes that it has the structure of *dl-trans*-5,6-di-*tert*-butyl-2-hydroxy-1,4-diketo-2-cyclohexene (I).

I is a nearly white, crystalline compound capable of being sublimed at diminished pressure; it melts at 134–135°. Its solutions in organic solvents are pale yellow. Its percentage composition confirms the molecular formula $C_{14}H_{22}O_3$, and the determined molecular weight (250) indicates that it is monomeric.

It reacts as a monobasic acid of sufficient strength to dissolve in aqueous sodium bicarbonate. Its neutral equivalent in aqueous solution (241) agrees with the calculated formula weight (238.32), and the fact that it titrates as a monobasic acid (neut. equiv. 232) with sodium aminoethoxide in ethylenediamine indicates the absence of additional (*e.g.*, hindered) acidic groups. Its saponification equivalent (244) indicates the absence of saponifiable groups or acidic hydrogens other than that involved in its patent acidic properties. It gives a positive (red) enol test with ferric chloride, but a negative phosphomolybdic acid test for the phenol structure.

It shows absorption in the infrared at 3400 cm.$^{-1}$ (position unchanged upon dilution), consistent with the presence of a hydroxyl situated as shown in the formula (I), and carbonyl absorption at 1670 and 1650 cm.$^{-1}$ Peaks at 1470, 1395, and 1370 cm.$^{-1}$ are consistent with the presence of *tert*-butyl groups. Absorption characteristic of the carboxyl group is absent.

It forms a chloride (II) upon reaction with thionyl chloride; this chloride in turn reacts with methanol to form the methoxyl compound (III) which may also be made by the reaction of I with diazomethane or with methanol and hydrochloric acid. Saponification of III reconverts it to I.

III shows no hydroxyl absorption in the infrared. The presence of three peaks in the carbonyl region (1685, 1650, and 1610 cm.$^{-1}$) is not readily explained; possibly one of them is to be ascribed to the carbon-carbon unsaturation.

Compound I forms a monoacetate (IV) with

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(1) Publication authorized by the Chief, Illinois State Geological Survey.

(2) Formerly research assistant.

(3) G. R. Yohe, J. E. Dunbar, R. L. Pedrotti, F. M. Scheidt, Fred G. H. Lee, and Earle C. Smith, *J. Org. Chem.*, **21**, 1289 (1956).

acetic anhydride or acetyl chloride; IV shows no hydroxyl absorption in the infrared, shows the ester peak at 1770 cm.$^{-1}$, and carbonyl peaks at 1685 and 1665 cm.$^{-1}$ An attempt to force the formation of a more highly acetylated derivative with excess acetyl chloride failed; only IV was isolated.

The benzoate (V) formed when I was treated with benzoyl chloride in pyridine. It shows no hydroxyl absorption, gives the ester peak at 1740 cm.$^{-1}$ and carbonyl peaks at 1685 and 1665 cm.$^{-1}$

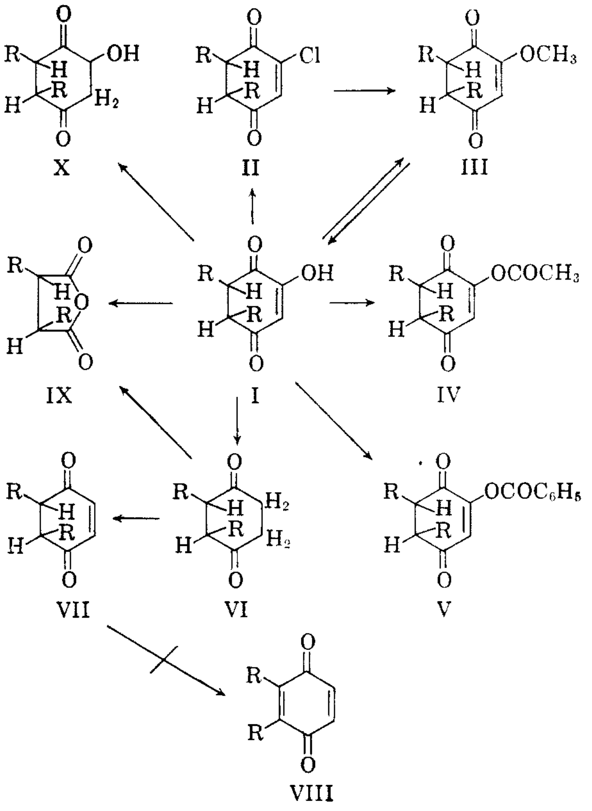
The reduction of I with hydriodic acid in a sealed tube gave $C_{14}H_{24}O_2$ (VI), which was dehydrogenated with bromine to $C_{14}H_{22}O_2$ (VII). An attempt to dehydrogenate VII further to the quinone (VIII) with chloranil failed. VI showed no hydroxyl absorption in the infrared, and gave a single strong carbonyl peak at 1690 cm.$^{-1}$ Compound VII likewise showed no hydroxyl absorption; carbonyl appeared at 1665 cm.$^{-1}$

It was reported previously[3] that the potassium permanganate oxidation of I at room temperature yielded the succinic anhydride (IX); the similar permanganate oxidation of VI also produced this same anhydride (identical infrared spectra, melting point of the mixture not depressed).

The reduction of I with lithium aluminum hydride gave an acidic compound $C_{14}H_{24}O_3$. It showed hydroxyl absorption at 3490 cm.$^{-1}$, carbonyl absorption at 1693 with a weak peak at 1720 cm.$^{-1}$ Structure X is suggested for this compound, although its ability to enolize is indicated by positive tests with ferric chloride and copper acetate. It was not investigated further. It is of interest to note that similar reduction of cyclohexane-1,2-dione is reported to give cyclohexanol-2-one as the only identifiable product.[4]

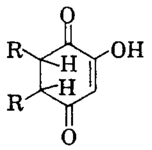
Although it was previously reported[3] that I did not form a hydrazone, it has since been found that it is converted reluctantly to a monohydrazone on long boiling with an ethanol solution of 2,4-dinitrophenylhydrazine. It is not known whether the hydrazine attacks one of the carbonyl groups pictured at positions 1 and 4, or one at position 2 which would result from the ketonization of structure I.

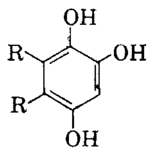
The compound (I) readily forms a crystallizable salt with brucine. Repeated recrystallization of this salt from 95% ethanol or from more dilute aqueous ethanol and subsequent hydrolysis gave partially resolved I with positive $[\alpha]_D$ values ranging from barely perceptible to a little more than 4°. I recovered from the original mother liquor of the first crystallization, however, showed $[\alpha]_D$ as high as $-41.4°$. Subsequent experiments showed that optically active I is easily racemized by solution in aqueous alkali and reprecipitation, by conversion to the benzoate, or by recrystallization from ethanol. Apparently repeated recrystallizations of the brucine salt likewise caused racemization, thus frustrating attempts to obtain the pure (+)-I in this manner.

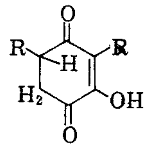


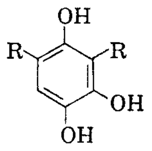
R = *tert*-Butyl

Other alternatives which should be considered for the structure of I are shown in the *cis* form (XI), the trihydroxybenzene form (XII), and 2,6-di-*tert*-butyl-3-hydroxy-1,4-diketo-2-cyclohexene (XIII) or its tautomer (XIIIa).


XI


XII


XIII


XIIIa

Structures XII and XIIIa are eliminated because of their inability to exist in enantiomorphic forms.

The construction of scale models shows that although the *trans* form (I) may be built easily, the *tert*-butyl groups are too bulky to occupy the *cis* positions as in XI. The same steric hindrance factor also rules against structure XII, and explains the existence of structure I in preference to its trienolic form (XII), although the transitory existence

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(4) L. W. Trevoy and W. G. Brown, *J. Am. Chem. Soc.*, 71, 1678 (1949).

of XII is indicated by the relative ease of racemization of optically active I.

This is in harmony with the observations of Brown and coworkers[5–7] who were unable to prepare homomorphs of *o*-di-*tert*-butylbenzene, and stated that such compounds "should be exceedingly difficult, if not impossible, to prepare." Kahle attempted an indirect synthesis of *o*-di-*tert*-butylbenzene without success.[8] However, the 1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalenes and their derivatives described by Bruson and coworkers[9,10] can be constructed in scale models, although they are compounds of the *o*-di-*tert*-alkylbenzene type.

Similar steric considerations also explain the failure of the attempted dehydrogenation of VII to VIII, and indicate that the succinic anhydride IX must also have the *trans* configuration.

The elimination of structure XIIIa as a possible alternative for I in effect eliminates XIII, as there is no reason for the stabilization of such a diketone in preference to the benzene ring form. Moreover, the observed chemical properties are not consistent with structure XIII.

The infrared absorption spectrum of IX has been reported[3]; those of I, III, IV, V, VI, VII, and X are shown in Fig. 1.

EXPERIMENTAL

Melting points (capillary tube method) are uncorrected.

Trans-5,6-di-tert-butyl-2-hydroxy-1,4-diketo-2-cyclohexene (I). A supply of this compound was prepared, part from 2,6-di-*tert*-butyl-4-methylphenol and part from 2,6-di-*tert*-butyl-1,4-benzoquinone by methods already described.[3]

Neutral equivalent by nonaqueous titration. This was done with sodium aminoethoxide in ethylenediamine solution.[11,12] The titration curve showed only one inflection; 0.1805 g. of I required 3.59 ml. of 0.217*N* titrant. Calcd. equivalent weight for $C_{14}H_{22}O_3$ (one acid hydrogen): 238.32; found: 231.7.

2,4-Dinitrophenylhydrazone. A mixture of 0.24 g. of I and 0.2 g. of 2,4-dinitrophenylhydrazine (0.001 mole each) in 25 ml. of 95% ethanol was heated to boiling and 0.2 ml. of concentrated hydrochloric acid added. After this had refluxed 48 hr., about half was withdrawn, but no derivative could be isolated. The remainder of the solution was refluxed an additional 72 hr., evaporated to dryness on the steam cone, dissolved in ether, extracted with aqueous sodium bicarbonate, the ether solution evaporated to dryness, and the residue recrystallized from benzene, then twice from benzene-low petroleum ether. The yellow solid melted at 202–204° (depressed upon admixture with 2,4-dinitrophenylhydrazine).

Anal. Calcd. for $C_{20}H_{26}N_4O_6$: C, 57.40; H, 6.27; N, 13.39. Found: C, 57.38; H, 6.53; N, 13.32.

The resolution of I. A solution of 1.1916 g. (0.005 mole) of I in 10 ml. of 95% ethanol was mixed with a solution of 1.9723 g. (0.005 mole) of anhydrous brucine alkaloid in 10 ml. of the same solvent, diluted to about 100 ml. with water, and allowed to stand at room temperature 6 hr. The crystals were filtered off and recrystallized twice from 95% ethanol, giving 0.73 g. of the brucine salt—white crystals which decomposed with partial melting at 225–235°.

Anal. Calcd. for $C_{37}H_{48}N_2O_7$: C, 70.23; H, 7.65; N, 4.43. Found: C, 70.08; H, 7.74; N, 4.39.

This salt was suspended in water, acidified with hydrochloric acid, extracted with ether, the ether solution extracted with dilute aqueous sodium hydroxide, and I precipitated from this solution with hydrochloric acid. The yield was 0.22 g., m.p. 133–134.5°.

Anal. Calcd. for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.43; H, 9.25. Five ml. of an ethanol solution containing 0.1882 g. of this compound gave an observed rotation of +0.16° in a 1-dm. tube; $[\alpha]_D^{25}$ 4.25°.

Other experiments in which the less soluble brucine salt was recrystallized repeatedly gave erratic results. The salt itself was not sufficiently soluble at room temperature to use in the polarimetry, and the I regenerated from various fractions showed low positive specific rotations ranging from barely perceptible to 4.23°. It was subsequently shown that partial racemization of active I occurred when it was dissolved in aqueous sodium hydroxide and reprecipitated with hydrochloric acid ($[\alpha]_D$ dropped from 2.4°–0.6°) or when it was recrystallized from aqueous ethanol ($[\alpha]_D$ dropped from 2.4°–0.5°). It appears likely that attempts to obtain pure (+)-I were frustrated by racemization during the recrystallization of the brucine salt itself.

Oddly, higher specific rotations were obtained in the levorotatory form isolated from the more soluble brucine salt, particularly where the latter was concentrated by evaporation and removal of the successive crops of crystals formed. In one such experiment, in which the precipitated crystals were subjected to further recrystallization before the mother liquors were investigated, the more soluble brucine salt yielded 0.65 g. of I, m.p. 133–134°; 5 ml. of an ethanol solution containing 0.2418 g. of this gave an observed rotation of −2.00° in a 1-dm. tube; $[\alpha]_D^{28}$ −41.36°. Benzoylation (see below) of this gave 0.62 g. (67%) of the benzoate, m.p. 137–138.5°, and saponification of the benzoate with alcoholic potassium hydroxide gave 0.32 g. (74%) of I, m.p. 133.5–134.5°, which was optically inactive. A separate experiment showed that racemization occurred during the benzoylation.

Trans-5,6-di-tert-butyl-2-chloro-1,4-diketo-2-cyclohexene (II). A mixture of 1 g. of I and 3 ml. of thionyl chloride was refluxed for one hr., dissolved in benzene, the benzene solution washed with water, 5% sodium hydroxide, and water, dried over anhydrous magnesium sulfate, and the benzene evaporated. The residue was recrystallized from low-boiling petroleum ether to give 0.3 g. of light yellow crystals, m.p. 129–130.5°.

Anal. Calcd. for $C_{14}H_{21}O_2Cl$: C, 65.48; H, 8.24; Cl, 13.81. Found: C, 65.49; H, 8.03; Cl, 14.45.

Trans-5,6-di-tert-butyl-2-methoxy-1,4-diketo-2-cyclohexene (III). (A) *From I with diazomethane.* A solution of 0.5 g. of I in 50 ml. of ether was treated at −5° with the ether solution of diazomethane obtained by reacting 4 ml. of 40% potassium hydroxide with 1 g. of nitrosomethylurea under 10 ml. of ether, was shaken well, and allowed to stand in an ice bath for 1 hr. Hydrochloric acid was added to destroy the excess diazomethane, the ether layer washed with two 5-ml. portions of 5% sodium hydroxide, dried over anhydrous magnesium sulfate, the ether evaporated, and the solid recrystallized from 95% ethanol with cooling to

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(5) H. C. Brown, Geraldine K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson, and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 1 (1953).

(6) H. C. Brown and R. B. Johannesen, *J. Am. Chem. Soc.*, **75**, 16 (1953).

(7) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 24 (1953).

(8) G. R. Kahle, *Dissertation Abstracts*, **17**, 2420 (1957).

(9) H. A. Bruson and J. W. Kroeger, *J. Am. Chem. Soc.*, **62**, 36 (1940).

(10) H. A. Bruson, F. W. Grant, and E. Bobko, *J. Am. Chem. Soc.*, **80**, 3633 (1958).

(11) M. L. Moss, J. H. Elliott, and R. T. Hall, *Anal. Chem.*, **20**, 784 (1948).

(12) We are indebted to Mr. T. P. Maher for this determination.

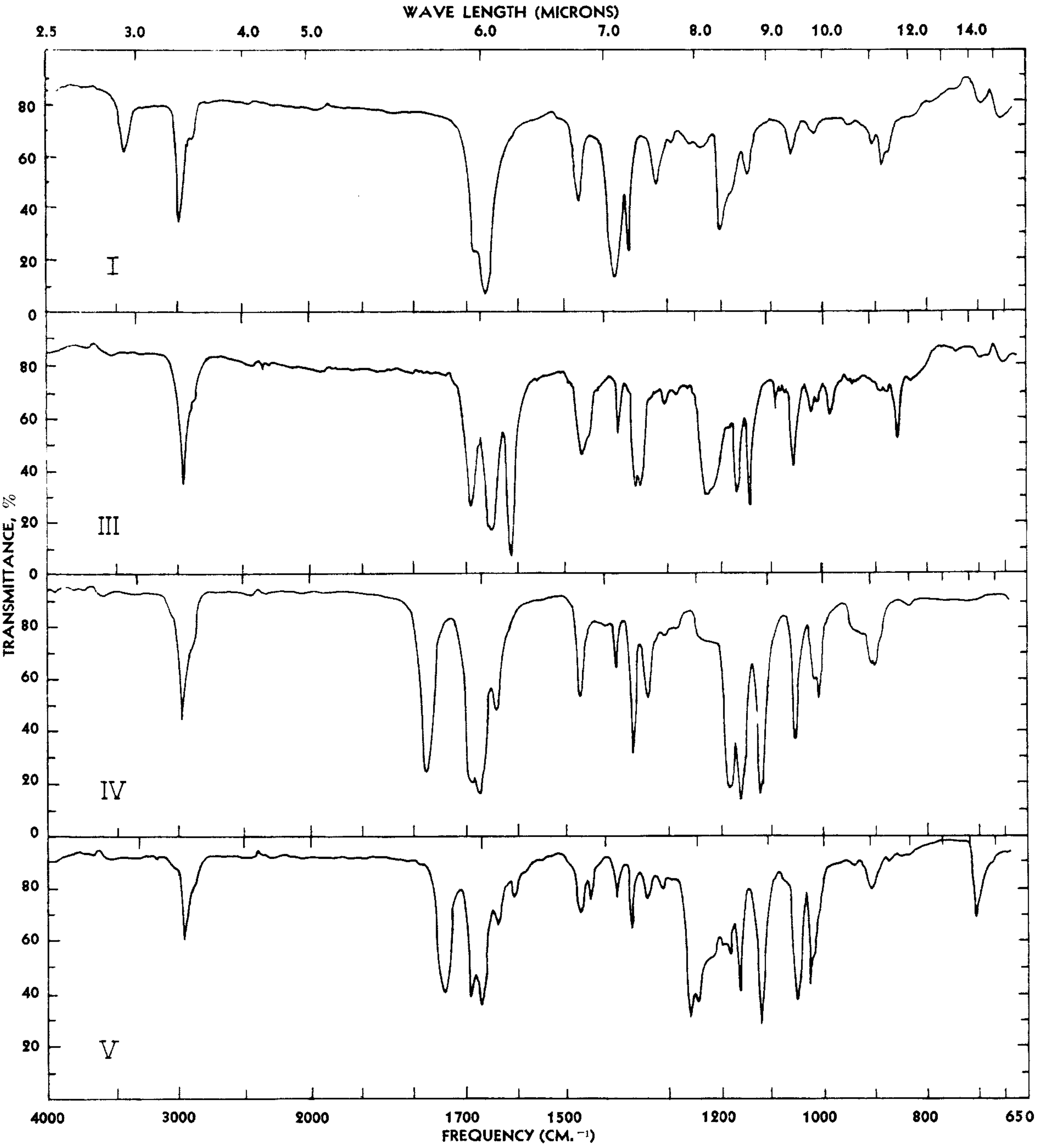

Fig. 1. Infrared spectra. Roman numerals designate compounds identified in the formula chart. All were run on approximately 5% solutions in chloroform except VII, which was in carbon tetrachloride, and X, which was <1% in chloroform

−30°. There was obtained 0.38 g. of white crystals, m.p. 151.5–152°.

Anal. Calcd. for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.15; H, 9.42.

(B) *From I with methanol and hydrochloric acid.* A solution of 0.1 g. of I in 20 ml. of methanol and two drops of concentrated hydrochloric acid was refluxed 1 hr., cooled, diluted with water, extracted with ether, and the ether extract washed with water. After removal of the ether there remained 0.08 g. of crude product, m.p. 145°. This was washed with aqueous sodium hydroxide and recrystallized from low-boiling petroleum ether. The m.p. (151–152°) was not depressed upon admixture with the methylated product obtained by other methods.

(C) *From II with methanol.* The crude chloride (II) prepared from 0.4 g. of I as described above, after removal of the excess thionyl chloride by evaporation at diminished pressure, was refluxed 1 hr. with methanol, the excess methanol evaporated, and the residue recrystallized from low-boiling petroleum ether, giving 0.1 g. of III, m.p. 149.5–151°.

Saponification of III. A mixture of 0.1 g. of III and 10 ml. of 20% aqueous sodium hydroxide was refluxed 45 min. As some of the material remained undissolved, more solid sodium hydroxide was added to bring the concentration to about 25% and the refluxing continued another 30 min. The mixture was cooled, filtered, and acidified with dilute sulfuric acid. The precipitate, after being washed and dried, melted at 131–132.5°; mixed with I, m.p. 131–133°.

Trans-5,6-di-tert-butyl-2-acetoxy-1,4-diketo-2-cyclohexene (IV). A solution of 0.2 g. of I in 25 ml. of acetic anhydride, 5 ml. of glacial acetic acid, and 5 drops of concentrated sul-

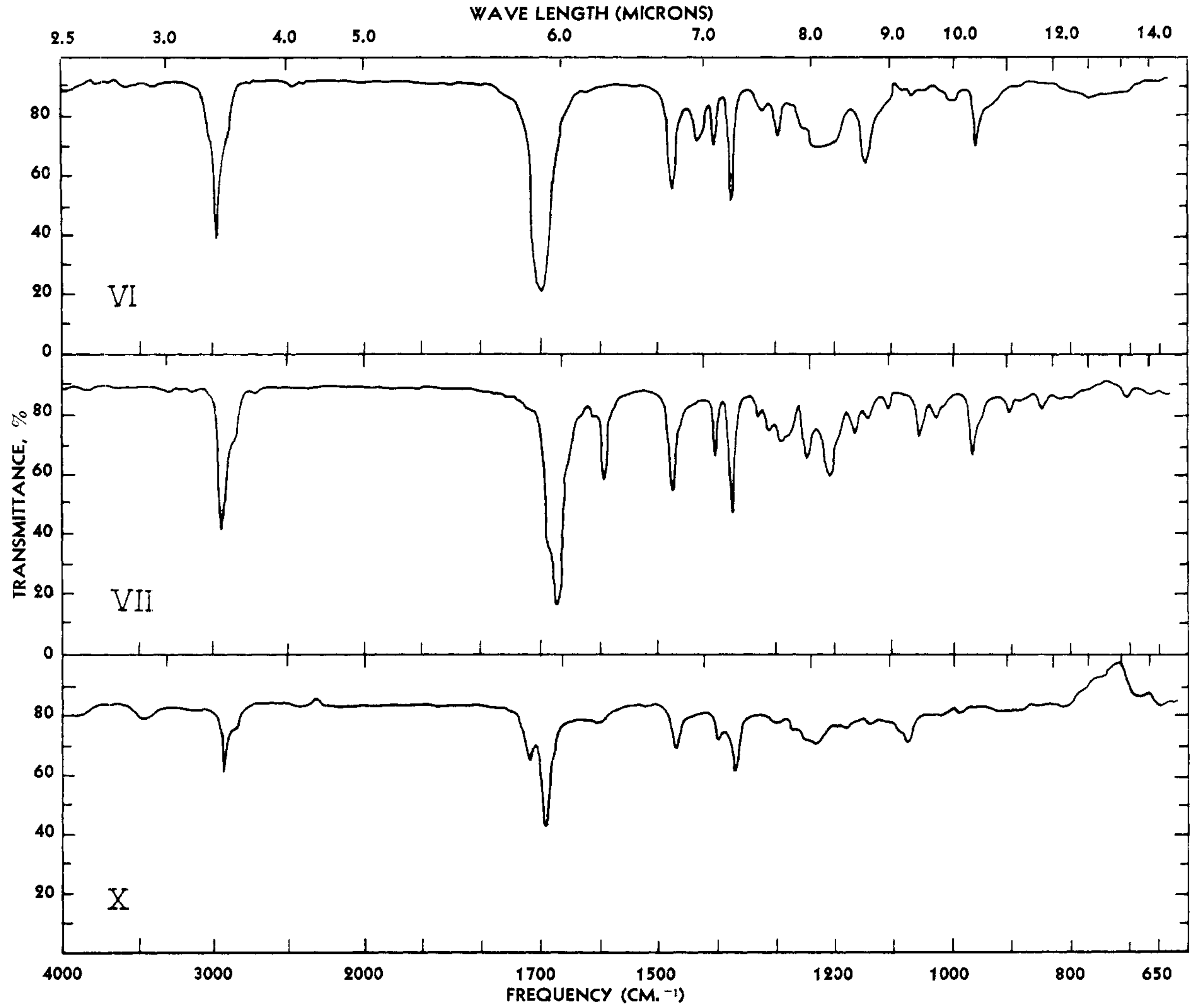

Fig. 1 (*Contd.*). Infrared spectra. Roman numerals designate compounds identified in the formula chart. All were run on approximately 5% solutions in chloroform except VII, which was in carbon tetrachloride, and X, which was <1% in chloroform

furic acid was refluxed 3 hr. On cooling and dilution with 200 ml. of water a solid precipitated; this was recrystallized from 50% ethanol to give 0.12 g. of IV, pale yellow needles, m.p. 115–115.3°. This gave a negative enol test with ferric chloride.

Anal. Calcd. for $C_{16}H_{24}O_4$: C, 68.54; H, 8.62. Found: C, 68.75; H, 8.42.

A mixture of 0.002 mole of I and 0.042 mole of acetyl chloride in 10 ml. of pyridine and 10 ml. of benzene was refluxed 4.5 hr. and allowed to stand 4 days. This yielded 58% of the monoacetate (IV), but there was no evidence of the formation of a more highly acetylated product.

Trans-5,6-di-tert-butyl-2-benzoyloxy-1,4-diketo-2-cyclohexene (V). One ml. of benzoyl chloride was added dropwise to a solution of 1 g. of I in 20 ml. of pyridine, and the mixture kept at room temperature 5 min. with intermittent shaking. Thirty ml. of ether was added and the solution washed successively with 10-ml. portions of water, 5% hydrochloric acid, water, 5% sodium hydroxide, and water. Evaporation of the ether and four recrystallizations from 95% ethanol gave 0.5 g. (35%) of faintly yellow crystals, m.p. 138–138.5°.

Anal. Calcd. for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65; mol. wt., 342.42; sapon. equiv., 171.21. Found: C, 73.63; H, 7.61; mol. wt. (Rast-camphor), 316; sapon. equiv., 185.

An attempt to prepare this benzoate by the usual Schotten-Baumann procedure with aqueous sodium hydroxide and benzoyl chloride was unsuccessful; I was recovered.

Trans-2,3-di-tert-butyl-1,4-cyclohexanedione (VI). Five sealed tubes, each charged with 0.3 g. of I and 3 ml. of 48% hydriodic acid and flushed with nitrogen prior to sealing were heated 5 hr. at 130–135° in a micro-Carius furnace. The brown liquid layer from the combined products was extracted with ether, the ether solution washed with 5% sodium thiosulfate and twice with water, and the product purified by chromatography on an alumina column, using ether as the eluant. The resulting 0.6 g. (42.5%) of white crystals melted at 142–143°, and were further purified by sublimation at 100° and 4 mm. pressure. M.p. 142–142.8°.

Anal. Calcd. for $C_{14}H_{24}O_2$: C, 74.95; H, 10.79; mol. wt., 224.33. Found: C, 75.06; H, 10.69; mol. wt. 208.

VI gave a negative enol test with both ferric chloride and copper acetate, and failed to form a 2,4-dinitrophenylhydrazone in 2 hr. reaction time. Its infrared spectrum (Fig. 1) showed the absence of hydroxyl and the presence of the carbonyl group.

Trans-5,6-di-tert-butyl-1,4-diketo-2-cyclohexene (VII). A solution of 0.2 g. of VI in carbon tetrachloride was treated with a 5% bromine solution in the same solvent until rapid decolorization ceased, then a slight excess of the bromine solution was added. Evaporation to dryness and sublimation at 3 mm. gave 0.1 g. (50%) of light yellow crystals, m.p. 138.8–139.8°.

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.98. Found: C, 75.57; H, 9.81. The infrared spectrum is shown in Figure 1.

Attempt to dehydrogenate VII. A solution of 0.0001 mole each of VII and tetrachloroquinone in 10 ml. of xylene was refluxed 24 hr., allowed to stand at room temperature 48 hr., and worked up by chromatography on an alumina-filled column. Elution with petroleum ether, petroleum ether-benzene, benzene, and benzene-alcohol gave no fraction corresponding to the structure (VIII); unchanged VII was recovered in the second fraction.

Trans-2,3-di-tert-butylsuccinic anhydride (IX) from VI. A suspension of 1.0 g. of VI in an excess of 3% potassium permanganate made basic with 5% potassium hydroxide was stirred overnight. Destruction of the excess permanganate with formic acid and acidification with sulfuric acid gave a precipitate which was filtered off, washed, and dried. The resulting 0.5 g. (53%) of the succinic anhydride IX melted at 112–114°, or 114–115° after sublimation. The melting point was not depressed upon admixture with the product obtained by the permanganate oxidation of I,[3] and the two samples gave identical infrared spectra.

This compound was subjected to titration with sodium aminoethoxide in ethylene diamine: 0.0376 g. of IX required 0.57 ml. of 0.315*N* base. Calcd. for $C_{12}H_{20}O_3$: mol. wt. 212.28. Found: Neut. equiv. 209.4.[13]

Lithium aluminum hydride reduction of I (formation of X). Four g. of I was treated with an excess of lithium aluminum hydride in anhydrous ether over a period of about 2 hr. The excess hydride was destroyed carefully with water, the solution acidified, separated, and the ether evaporated to give 1.8 g. (45%) of white crystals. This material was sublimed at 150° and 4-mm. pressure to give 1.7 g. of X, m.p. 178–179°. It gave a positive enol test with both ferric chloride and copper acetate, and was sufficiently acidic to dissolve in 5% aqueous sodium bicarbonate.

Anal. Calcd. for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07; neut. equiv. 240.33. Found: C, 70.13; H, 9.84; neut. equiv. 242.

Acknowledgment. The writers wish to thank Dr. D. Y. Curtin of the University of Illinois for assistance in interpreting infrared spectra and for his helpful criticism of the manuscript.

URBANA, ILL.

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[13] Succinic anhydride itself under the same conditions gave the following: 0.1022 g. of succinic anhydride required 3.33 ml. of 0.315*N* base. Calcd. for $C_4H_4O_3$: mol. wt. 100.07. Found: Neut. equiv. 97.4. We are indebted to Mr. J. M. Harris for these determinations.

[CONTRIBUTION FROM UNIVERSITY OF CALIFORNIA, LAWRENCE RADIATION LABORATORY]

Fluorine-Containing Nitrogen Compounds. I. Trifluoroethylamines

EUGENE R. BISSELL AND MILTON FINGER

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The complete series of methyltrifluoroethylamines having one trifluoroethyl group and 0, 1, 2, or 3 methyl groups has been synthesized. Physical data are reported, and a number of derivatives suitable for characterization have been prepared.

As a part of a study of the properties of fluorine containing nitrogen compounds, we have synthesized and characterized the complete series of methyltrifluoroethylamines containing one trifluoroethyl group and 0, 1, 2, or 3 methyl groups.

2, 2, 2-Trifluoroethylamine, the first member in the series, was first prepared in 1943 by Gilman and Jones[2] by the catalytic hydrogenation of trifluoroacetonitrile. It is also formed in low yield by the Hofmann degradation of β,β,β-trifluoropropionamide or by the Schmidt-Curtius rearrangement of β,β,β-trifluoropropionic acid azide.[3] A United States patent[4] has been issued covering trifluoroethylamine and its production by ammonolysis of trifluoroethyl halides. A more convenient synthesis involving lithium aluminum hydride reduction of trifluoroacetamide was later reported by Bourne, Henry, Tatlow, and Tatlow[5] and by McKay and Vavasour.[6] The process has been patented in Great Britain by the Minnesota Mining and Manufacturing Co.[7]

Some of the higher homologs of methyl-2,2,2-trifluoroethylamine have been prepared by the reduction of carbamates[8] or isocyanates,[9] but methyl-2,2,2-trifluoroethylamine itself, the second member in the series, has not been reported. No tertiary amines or quaternary ammonium salts containing trifluoroethyl groups appear to have been reported.

We have applied the lithium aluminum hydride reduction method to *N*-methyltrifluoroacetamide and to *N*,*N*-dimethyltrifluoroacetamide and obtained methyl-2,2,2-trifluoroethylamine and dimethyl-2,2,2-trifluoroethylamine. Both the amides and the amines were previously unknown. The reduction proceeds with greater vigor and the yields decrease as the degree of substitution of the nitrogen atom increases. With the tertiary amide the reaction is too violent to be controlled easily.

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

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