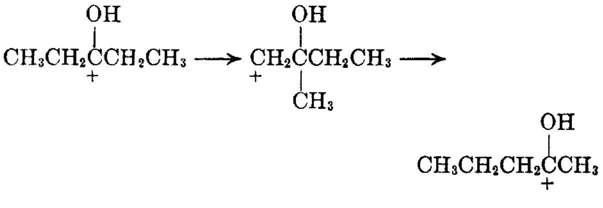
When diethyl ketone was heated on the steam bath for three hours with 70% perchloric acid, it rearranged to the extent of approximately 63% to methyl propyl ketone. Since the boiling points of diethyl ketone and methyl propyl ketone are almost identical, no attempt was made to fractionate the recovered ketone mixture.[9] Instead, the mixture was degraded by the haloform reaction, and iodoform and butyric acid were isolated and characterized.

The simplest interpretation of these rearrangements involves rearrangement of the conjugate acid of the ketone as illustrated here for diethyl ketone.[10]



$$CH_3CH_2\overset{OH}{\underset{+}{C}}CH_2CH_3 \longrightarrow \underset{+}{CH_2}\overset{OH}{\underset{CH_3}{C}}CH_2CH_3 \longrightarrow CH_3CH_2CH_2\overset{OH}{\underset{+}{C}}CH_3$$

The scope of ketone rearrangement reactions is being investigated further.

EXPERIMENTAL

Diethyl ketone. Ten grams of diethyl ketone dissolved in 50 ml. of 70% perchloric acid were heated on the steam bath for 3 hr. The solution, which had turned yellow, was poured onto ice, neutralized with sodium hydroxide, and extracted with ether. The combined ether extract was washed and dried, and the ether evaporated. The residue was distilled under vacuum and a wide cut was taken centering on the boiling point of a mixture of diethyl ketone and methyl propyl ketone. The gas chromatograph of this material was essentially identical with that of the starting material. Sodium hypoiodite was added to 1.6 g. of the mixed ketones and 2.1 g. of iodoform of characteristic odor and m.p. 115–119°, reported[11] m.p. 119° was obtained. The filtrate was acidified with sulfuric acid, treated with excess silver sulfate and distilled, extra water being added several times. The acid in the distillate was identified as butyric acid by titrating with standard sodium hydroxide (10.3 mmoles), evaporating the solution to dryness and weighing the sodium salt, and by preparation of the *p*-toluide, m.p. 73–75°, reported[12] m.p. 74–75°, mixed melting point with an authentic sample 73–74°. The yield of sodium butyrate corresponded to 1.015 g. of methyl propyl ketone, indicating that approximately 63% of the diethyl ketone had rearranged. A sample of the diethyl ketone used was subjected to the same degradation procedure and neither iodoform nor butyric acid was obtained. A known mixture of diethyl ketone and methyl propyl ketone gave exactly the expected results when subjected to the degradation procedure.

Diisopropyl ketone. Ten milliliters of diisopropyl ketone and 50 ml. of concd. sulfuric acid (or, in a separate experiment, 3 ml. of ketone and 50 ml. of 70% perchloric acid) were heated at 90° for 3 hr. The mixed ketone fraction was recovered as above and shown by gas chromatography to consist of 30% of diisopropyl ketone and 70% of another compound which was identified as 3,4-dimethyl-2-pentanone by comparison with an authentic sample prepared by the acetoacetic ester synthesis following the procedure of Willstatter and Hatt.[13] No other rearrangement product could be found from the gas chromatograph. The 3,4-dimethyl-2-pentanone from the rearrangement was also characterized as the semicarbazone, m.p. 112°, reported[14] m.p. 112°, mixed melting point with an authentic sample 112°. Under milder conditions comparable to those previously used[7] (5 g. of ketone and 50 g. of concd. sulfuric acid at room temperature for 8 days) a small amount (about 3–4%) of rearrangement was observed.

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[9] Even gas chromatography failed to separate the two ketones; however only a fifty-foot polyester column was tried, and separation might be possible with other columns.

[10] A mechanisn whereby the movement of the methyl and ethyl groups is concerted is not ruled out, although the geometrical requirements of such a mechanism are such that it is not attractive; however, see ref. 4.

[11] I. Heilbron and H. M. Bunbury, eds., *Dictionary of Organic Compounds*, Oxford University Press, New York, N. Y., 1953, Vol. III, p. 29.

[12] I. Heilbron and H. M. Bunbury, eds., *Dictionary of Organic Compounds*, Oxford University Press, New York, N. Y., 1953, Vol. I, p. 403.

[13] R. Willstatter and D. Hatt, *Ann.*, **418**, 148 (1919).

[14] J. Colonge and K. Mostafar, *Bull. soc. chim.*, **6**, 335 (1939).

Acetolysis and Trifluoroacetolysis of *tert*-Butyl Nitrate[1]

ROBERT BOSCHAN AND GERALD C. WHITNACK

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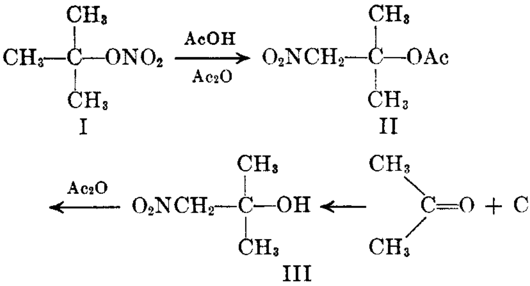
In the course of a polarographic study of the acetolysis of *tert*-butyl nitrate (I), it was observed (see Table I) that the diffusion current increased markedly during the course of a run when acetic anhydride was present in the acetolysis medium. In the absence of acetic anhydride, however, the diffusion current changed very little. I, therefore, appeared to be converted into a much more readily reducible species, possibly a nitro compound. A large scale acetolysis of I yielded, in very low yield, a high boiling ester, suspected to be nitro-*tert*-butyl acetate (II). Independent synthesis of II showed that the acetolysis product was indeed II, as shown by comparison of infrared spectra.



$$\underset{\text{I}}{CH_3-\overset{CH_3}{\underset{CH_3}{C}}-ONO_2} \xrightarrow[Ac_2O]{AcOH} \underset{\text{II}}{O_2NCH_2-\overset{CH_3}{\underset{CH_3}{C}}-OAc}$$

$$\xleftarrow{Ac_2O} \underset{\text{III}}{O_2NCH_2-\overset{CH_3}{\underset{CH_3}{C}}-OH} \longleftarrow (CH_3)_2C{=}O + CH_3NO_2$$

In the hope that solvolysis in trifluoroacetic acid would give a better yield of a product similar to II,

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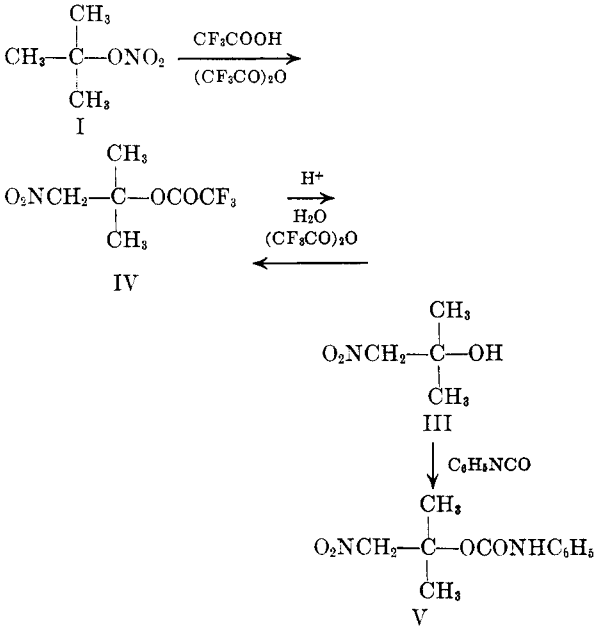
[1] Reported in part at the Pacific Southwest Regional Meeting of the American Chemical Society, Redlands, California, October 25, 1958, p. A-7 of abstracts.

the trifluoroacetolysis of I in the presence of trifluoroacetic anhydride was attempted. This solvolysis was quite rapid and exothermic, the reaction apparently being over in a few minutes. A 36% yield of the expected product, nitro-*tert*-butyl trifluoroacetate (IV), was isolated upon work-up of the reaction mixture.



The structure of IV was verified by its independent synthesis from III, and by its hydrolysis to III and conversion to the phenyl urethane(V).

One can only speculate as to the mechanism of the conversion of I to II (or IV). A likely possibility is the elimination of nitric acid from I to isobutylene, followed by the addition of acetyl nitrate (or trifluoroacetyl nitrate) to give the observed products. The formation of isobutylene seems to be a reasonable explanation for the low product yields and poor product balances, as this gas could be easily lost during either the reaction period or the work-up.

A number of attempts were made to see whether the increase in polarographic wave height (see Table I) would conform to some simple rate law. Simple first and second order rate laws, and consecutive first and second order rate laws were tried, but without success.

EXPERIMENTAL

Polarographic study. tert-Butyl nitrate produces a polarographic wave with an $E_{1/2}$ *vs.* Hg. pool of −1.00 volts in a 50% ethanol solution of tetramethylammonium chloride. However, a solution of *tert*-butyl nitrate in acetic anhydride that has stood for several hours produces a polarographic wave with an $E_{1/2}$ *vs.* Hg. pool of −0.90 volts when placed in a 50% ethanol solution of tetramethylammonium chloride.

The acetolysis solution was prepared as follows: 1.0 Ml. of *tert*-butyl nitrate and 1 ml. of acetic anhydride were placed in a 25-ml. volumetric flask and diluted to volume with glacial acetic acid. This solution was heated in a constant temperature bath at 52.17°. For the polarograms, a 1-ml. aliquot of the *tert*-butyl nitrate-acetic anhydride solution was placed in a 25-ml. volumetric flask. Fifteen milliliters of a 50% ethanol solution of 0.1*M* tetramethylammonium chloride was added to the flask. Five drops of a 0.1% solution of methyl red were added and a 10*M* sodium hydroxide solution was slowly added with stirring until the solution just turned yellow. The solution was then diluted to volume with the 50% ethanol solution of tetramethylammonium chloride. Approximately 15 ml. of this solution was introduced into a polarographic cell, held at a constant temperature (25° ± 0.1°), and flushed with nitrogen for 5 min. The polarogram was then recorded from −0.30 to −1.50 volts.

The change in the wave height with time at $E_{1/2} = -0.90$ volts for a typical experiment is summarized in Table I. In this table the polarographic wave height at 0 hr. is for the original *tert*-butyl nitrate–acetic anhydride solution ($E_{1/2}$ vs. Hg. pool = −1.00 volts).

TABLE I

POLAROGRAPHIC STUDY OF THE ACETOLYSIS OF *tert*-BUTYL NITRATE AT 52.17°

Time (min.)	Polarographic Wave Height (μa)
0	0.60
64	9.03
93	14.88
110	17.32
191	20.40
249	30.70
304	33.20
451	34.20
1347	47.00

Nitro-tert-butyl alcohol and nitro-tert-butyl acetate. Nitro-*tert*-butyl alcohol, b.p. 56–60° (2 mm.), n_D^{25} 1.4256, and nitro-*tert*-butyl acetate, b.p. 45° (1.5 mm.) n_D^{24} 1.4352, were prepared according to the directions of Lambert and Lowe.[2]

Nitro-tert-butyl phenyl urethane. To 2.00 g. (0.0168 mole) of nitro-*tert*-butyl alcohol was added 2.00 g. (0.0168 mole) of phenyl isocyanate and the mixture was heated 20 hr. on the steam bath. After this heating period, the mixture was very viscous, and crystals appeared when the side of the tube was scratched gently with a stirring rod. The mixture was taken up in benzene and petroleum ether (b.p. 60–80°) was added. An oil appeared which readily crystallized to yield 2.26 g. of crystals, m.p. 81°; m.p. 82° after six recrystallizations.

Anal. Calcd. for $C_{11}H_{14}N_2O_4$: C, 55.45; H, 5.92. Found: C, 55.23; H, 5.96.

Nitro-tert-butyl trifluoroacetate. To 12.0 g. (0.10 mole) of nitro-*tert*-butyl alcohol (cooled in ice) was added gradually 30 ml. of trifluoroacetic anhydride. The mixture was allowed to warm gradually to room temperature and then was refluxed for 2 hr. Removal of excess trifluoroacetic acid and anhydride and distillation of the residue yielded 14.79 g. (65%) of nitro-*tert*-butyl trifluoroacetate, b.p. 42° (1 mm). The infrared spectrum of this material was nearly identical with that of the product from the trifluoroacetolysis of *tert*-butyl nitrate.

Trifluoroacetolysis of tert-butyl nitrate. To a mixture of 20 ml. of trifluoroacetic anhydride and 50 ml. of trifluoroacetic acid (cooled in Dry Ice until crystals of trifluoroacetic acid appeared) was added 10 ml. (*ca.* 10 g., 0.0926 mole) of *tert*-butyl nitrate. The mixture was allowed to warm very gradually to nearly room temperature until a slight discoloring was observed. As long as an exothermic reaction seemed to take place, the mixture was kept cool. After the reaction appeared to be over, the mixture stood at room

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[2] A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947).

temperature for 2 hr. The solvent mixture of acid and anhydride was removed by distillation at aspirator pressure and the residue was collected at 60° (2 mm.) to yield 6.43 g. (36%) of nitro-*tert*-butyl trifluoroacetate. The infrared spectrum of this material was virtually identical with that of authentic nitro-*tert*-butyl trifluoroacetate.

Hydrolysis of nitro-tert-butyl trifluoroacetate. To 2.0 g. (0.0168 mole) of nitro-*tert*-butyl trifluoroacetate were added 10 ml. of water and 3 drops of concd. sulfuric acid. The mixture was refluxed for *ca.* 5 min., and then solid sodium bicarbonate was added in sufficient quantity to neutralize the sulfuric and trifluoroacetic acids. The product was extracted with ether and the dried ether extract evaporated; 1.5 ml. of phenyl isocyanate was added to the residue and the mixture was heated overnight on the steam bath. The mixture was worked up as in the preparation of the phenyl urethane of nitro-*tert*-butyl alcohol to yield 2.39 g. of crude product, m.p. 80–85° after one recrystallization.

Characterization of the tert-butyl nitrate trifluoroacetolysis product. Two grams of the trifluoroacetolysis product was worked up as in the hydrolysis of nitro-*tert*-butyl trifluoroacetate to yield 2.17 g. of urethane, m.p. 80–81°, after one recrystallization. The mixture melting point with nitro-*tert*-butyl phenyl urethane was 81–82°. The infrared spectra of the two samples were identical.

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Studies of the Cyclization of *o*-Benzoylbenzoic-Carboxyl-C^{14} Acid

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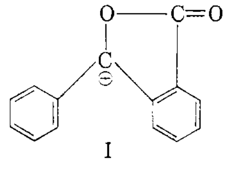
Received October 1, 1959

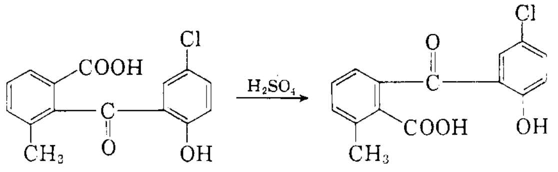
Newman and co-workers[1,2] have presented strong arguments that when *o*-benzoylbenzoic acid is dissolved in concentrated sulfuric acid, the organic acid is almost entirely converted to a cyclic positive ion, I. According to their views the cyclization of the dissolved *o*-benzoylbenzoic acid upon heating this sulfuric acid solution involves a rate-determining conversion of the cyclic positive ion to anthraquinone with the ejection of a proton.

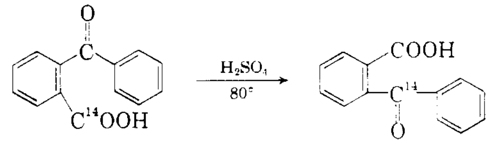


I

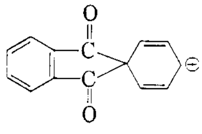
Studies of the cyclization of *o*-benzoylbenzoic-carboxyl-C^{14} acid have provided additional information bearing on the mechanism of the cyclization in concentrated sulfuric acid.

Hayashi rearrangement[3,4] accompanies cyclization of certain substituted *o*-benzoylbenzoic acids. This rearrangement is exemplified by the reaction[3]: It is apparent that any Hayashi rearrangement accompanying the cyclization of *o*-benzoylbenzoic acid could be detected only by the use of isotopic labeling. A sample of *o*-benzoylbenzoic-*carboxyl*-C^{14} acid was cyclized to the extent of 16% at 80° in concentrated sulfuric acid. The 84% unchanged acid was recovered, purified, and degraded by decarboxylation at 275° to benzophenone. As the pure 2,4-dinitrophenylhydrazone prepared from this benzophenone contained little more than background activity, no measurable degree of Hayashi rearrangement could be detected. Hayashi rearrangement of *o*-benzoylbenzoic-*carboxyl*-C^{14} acid would lead to carbon-14 in the keto group:





This result also eliminates any intermediate in the cyclization reaction in which the two nonaromatic carbon atoms are equilibrated with each other and with the unchanged acid at a rate which is rapid in comparison with the overall reaction rate. The symmetrical ion, for example, is not a significant part of the reaction path. The present result is in accord with the Newman[1] mechanism, inasmuch as the latter does not provide a path for Hayashi rearrangement during cyclization of *o*-benzoylbenzoic acid to anthraquinone.



It now appears that the 3.5% carbon-14 isotope effect[5] in the cyclization of *o*-benzoylbenzoic-carboxyl-C^{14} acid is *not* an effect of carbon-14 substitution on the pre-rate equilibrium between *o*-benzoylbenzoic acid and the oxocarbonium ion, $C_6H_5COC_6H_4CO^+$ (II), as was suggested earlier.[5] Rather, this carbon-14 isotope effect, being of *intermediate magnitude*, appears to be either (a) an isotope effect on a pre-rate equilibrium between I and II or (b) a kinetic isotope effect on a concerted process which converts I directly to anthraquinone with ejection of a proton.

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[1] M. S. Newman, *J. Am. Chem. Soc.*, **64,** 2324 (1942).

[2] M. S. Newman, H. G. Kuivala, and A. B. Garrett, *J. Am. Chem. Soc.*, **67,** 704 (1945).

[3] M. Hayashi, *J. Chem. Soc.*, 2516 (1927).

[4] R. B. Sandin, R. M. Melby, R. Crawford, and D. McGreer, *J. Am. Chem. Soc.*, **78,** 3817 (1956).

[5] Gus A. Ropp, *J. Chem. Phys.*, **23,** 2196 (1956).