[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Reactions of Nitrous Oxide with Organolithium Compounds[1]

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While nitrous oxide did not react with Grignard reagents, it did react with many organolithium compounds and with triphenylmethylsodium. With primary alkyllithium compounds nitrous oxide gave alkylalkylidenehydrazines, while 9-fluorenyllithium gave fluorenone azine. An azo compound, ditertiarybutyldiimide, was obtained in small yield from *t*-butyllithium. Aryllithium compounds gave mixtures of products including diazotates, phenols, azo compounds and triarylhydrazines. It is proposed that the initial product is a lithium diazotate in each of these reactions (possibly excepting the formation of phenols). Also it was shown that in some cases a diazo compound may be a subsequent intermediate. The lithium derivatives of the more acidic hydrocarbons cyclopentadiene and phenylacetylene were inert as were the sterically hindered mesityllithium and 2,6-dimethoxyphenyllithium.

Introduction

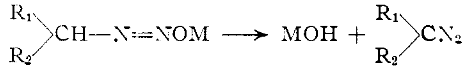
The similarity of the electronic structures of nitrous oxide,[2] hydrazoic acid and the azides,[3] diazo compounds[4] and nitrile oxides[5] leads to a similarity of reactions.[6] For example, all react with olefins to form five-membered rings. Further, Grignard reagents have been reported to react with azides,[7a] diazo compounds[7b] and nitrile oxides,[7c] but not with nitrous oxide.[7b] However, nitrous oxide was found to react with triphenylmethylsodium to give a colored salt converted by treatment with ethanol into triphenylcarbinol.[8] By analogy with the reactions of Grignard reagents with azides, diazo compounds and nitrile oxides, the product from the reaction of triphenylmethylsodium with nitrous oxide was probably sodium triphenylmethanediazotate.[9]

$$(C_6H_5)_3CNa + N_2O \longrightarrow (C_6H_5)_3CN{=}NONa$$

Based on the foregoing facts and analogies, reasonable expectations might be: (1) that suitable organometallic compounds, RM, should react with nitrous oxide to give diazotates

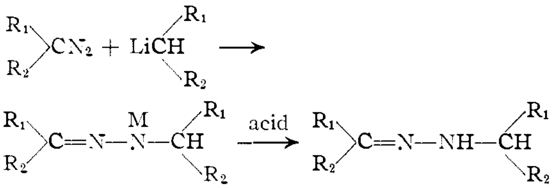
$$\text{A: } RM + N_2O \longrightarrow RN{=}NOM$$

(2) that primary or secondary alkanediazotates should lose the elements of a metal hydroxide, MOH, to give diazoalkanes

B:


$$\text{B: } \substack{R_1\\ R_2}{>}CH{-}N{=}NOM \longrightarrow MOH + \substack{R_1\\ R_2}{>}CN_2$$

(3) that the diazo compounds might react with more organometallic compounds to give hydrazones

C:


$$\text{C: } \substack{R_1\\ R_2}{>}CN_2 + LiCH{<}\substack{R_1\\ R_2} \longrightarrow \substack{R_1\\ R_2}{>}C{=}N{-}\overset{M}{N}{-}CH{<}\substack{R_1\\ R_2} \xrightarrow{\text{acid}} \substack{R_1\\ R_2}{>}C{=}N{-}NH{-}CH{<}\substack{R_1\\ R_2}$$

Results and Discussion

After confirmation of the unreactivity of Grignard reagents toward nitrous oxide,[7b] it was found that nitrous oxide reacted with primary, second and tertiary alkyllithium compounds and with most aryllithium compounds. It is with an exploratory study of the above reactions that this paper is concerned.

The reactions of aryllithium compounds with nitrous oxide were first studied in the hope that these would be straightforward, as reaction B to form a diazo compound would not be possible. It was found, however, that from the reaction of phenyllithium with nitrous oxide there was obtained (besides benzene, biphenyl and recovered bromobenzene) lithium benzenediazotate, azobenzene, triphenylhydrazine and phenol. The presence of the lithium diazotate in small amount was demonstrated by the formation of benzeneazoresorcinol from the acidified reaction mixture and resorcinol. Apparently under the reaction conditions the lithium benzenediazotate as formed reacts with more phenyllithium to give azobenzene and triphenylhydrazine. The triphenylhydrazine probably does not arise from the azobenzene, however, as we confirmed the report of Gilman and Bailie[10] that azobenzene[11] with phenyllithium does not give triphenylhydrazine.

Two paths for the formation of phenol might be considered. The first is hydrolysis of the diazotate in the work-up of the reaction mixture. The other, which seems more attractive to the present authors, is direct oxidation of the alkyllithium to the lithium alkoxide by nitrous oxide. This reaction would be similar to the oxidations of organo-

$$RLi + N_2O \longrightarrow ROLi + N_2$$

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[1] This paper is taken from the dissertations of James A. Farr, Jr., and Seymour Sands submitted in partial fulfillment of the requirements of the degree of Doctor of Philosophy in June, 1953.

[2] E. F. Barker, *Phys. Rev.*, **41**, 369 (1932); L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1940, p. 126.

[3] S. B. Hendricks and L. Pauling, THIS JOURNAL, **47**, 2904 (1925); L. O. Brockway and L. Pauling, *Proc. Nat. Acad. Sci.*, **19**, 860 (1933); A. Langseth and J. R. Nielsen, *Phys. Rev.*, **44**, 326 (1933).

[4] H. Boersch, *Sitz. Akad. Wiss. Wien*, *IIb*, **144**, 21 (1935), and *Monatsh.*, **65**, 331 (1935).

[5] L. Pauling and S. B. Hendricks, THIS JOURNAL, **48**, 641 (1926).

[6] Interest in these compounds was stimulated by the report that although diazo compounds are best known for their reactions with electrophilic reagents, ethyl diazoacetate reacted with sodiomalonic ester and with sodiocyanoacetic ester to give 4-hydroxy- and 4-amino-3,5-dicarbethoxypyrazole: A. Bertho and H. Nüssell, *Ann.*, **457**, 278 (1927).

[7] (a) O. Dimroth, *Ber.*, **36**, 909 (1903); **38**, 670 (1905); **39**, 3905 (1906); **40**, 2390 and 2395 (1907); (b) E. Zerner, *Monatsh.*, **34**, 1609 and 1631 (1913); (c) H. Wieland, *Ber.*, **40**, 1667 (1907).

[8] W. Schlenk and E. Bergmann, *Ann.*, **464**, 1 (1928).

[9] While aromatic diazotates are generally stable, alkanediazotates are apparently highly reactive. Thus sodium methanediazotate is reported to explode in moist air and to be converted to diazomethane by treatment in ether suspension with carbon dioxide: J. Thiele, *Ann.*, **376**, 255 (1910). It might be noted that alkanediazotates are probable intermediates in the preparation of diazo compounds from nitrosoalkylureas and nitrosoalkylurethans and by the mesityl oxide method.

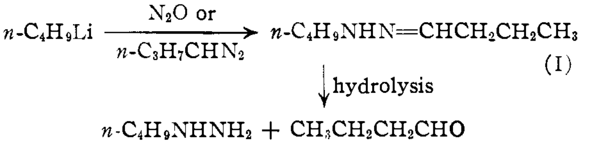
[10] H. Gilman and J. C. Bailie, *J. Org. Chem.*, **2**, 84 (1937).

[11] The formation of triphenylhydrazine from the higher energy *cis*-azobenzene is not excluded.

metallic compounds by oxygen and by amine oxides.[12] Further work is required to establish the mode of formation of the oxidized product.

Organolithium compounds from *o*- and *p*-bromotoluene and from α-bromonaphthalene with nitrous oxide gave azo compounds and phenols. In some cases high-melting, difficultly soluble products were also formed but were not further investigated.

In the aliphatic series the compound whose reactions with nitrous oxide were most carefully studied was *n*-butyllithium, which gave two nitrogen-containing products. The larger fraction was *n*-butyl-*n*-butylidenehydrazine (the *n*-butylhydrazone of butyraldehyde, I), possibly formed by the sequence A → B → C. The structure of I was proved by its hydrolysis to *n*-butylhydrazine[13] and butyraldehyde. That 1-diazobutane was a possible intermediate in the formation of I was demonstrated by the conversion of 1-diazobutane to I by *n*-butyllithium. The hydrazone I was accompanied by an imperfectly characterized material of empirical formula $C_{12}H_{26-28}N_2$, apparently derived from three moles of *n*-butyllithium and one of nitrous oxide. The only other primary alkyllithium compound studied was ethyllithium, which gave ethylethylidenehydrazine (the ethylhydrazone of acetaldehyde).



$$n\text{-}C_4H_9Li \xrightarrow[n\text{-}C_3H_7CHN_2]{N_2O \text{ or}} n\text{-}C_4H_9NHN{=}CHCH_2CH_2CH_3 \quad \text{(I)}$$

$$\downarrow \text{hydrolysis}$$

$$n\text{-}C_4H_9NHNH_2 + CH_3CH_2CH_2CHO$$

Neither of the two secondary alkyllithium compounds investigated gave the expected alkylalkylidenehydrazine. The product from the reaction of isopropyllithium with nitrous oxide in ethyl ether had an empirical formula $C_8H_{18-20}N_2$, and on acid hydrolysis gave acetone and isoamylamine hydrochloride.[14] As the material was analytically impure, no structure is assigned. In an attempt to simplify the reaction by using petroleum ether as the solvent a new product, $C_9H_{22}N_2$, apparently arising from the reaction of three moles of isopropyllithium with one of nitrous oxide, was obtained.

9-Fluorenyllithium gave with nitrous oxide fluorenone azine and fluorenol. That 9-diazofluorene was a possible intermediate in the formation of the azine was shown by the conversion of 9-diazofluorene by 9-fluorenyllithium to fluorenone azine. The greater unsaturation of this product is probably related to the resonance stabilization achieved by formation of the more extended conjugated system.

The only tertiary alkyllithium compound studied, *t*-butyllithium, gave in small yield an aliphatic azo compound, di-tertiary-butyldiimide (2,2′-azoisobutane). The structural assignment is based on the mode of synthesis, the analysis and the similarity of the infrared spectrum to that of 2,2′-azoisobutyronitrile[15] and is in accord with the observed inertness of the compound toward reducing agents.

No nitrogen-containing products were obtained by the introduction of nitrous oxide into ethereal solutions of cyclopentadienyllithium, lithium phenylacetylide, mesityllithium and 2,6-dimethoxyphenyllithium. Reactions occurred with indenyllithium and 2-pyridylmethyllithium but were not further investigated.

Acknowledgment.—The generous support of this work by a Frederick Gardner Cottrell Grant of the Research Corporation is gratefully acknowledged.

Experimental[16]

Description of the Apparatus.—All runs were made in a 500-ml. three-necked flask equipped with a stirrer, dropping funnel, reflux condenser and nitrogen inlet. Turning a stopcock in this inlet allowed nitrogen pressure to force the solution through glass wool into a second flask, previously flushed with nitrogen. This second flask was a 500- or 1000-ml. three-necked flask equipped with a stirrer and reflux condenser. After transfer of the solution, a gas inlet tube for the introduction of nitrous oxide[17] was inserted into the neck through which the solution had entered.

Reactions and Isolation of Products.—Nitrous oxide was passed in large excess through the solutions of the organolithium compounds at temperatures ranging from −40° to that of the refluxing ether. The reaction mixtures were hydrolyzed with water, and any insoluble materials were collected by filtration. Phenols were recovered from the aqueous layers, while the dried ether layers were worked up by distillation or chromatography (on alumina) to give neutral and basic materials.

Ethyllithium with Nitrous Oxide.—From the reaction of ethyllithium (from one mole of ethyl bromide and two g.-atoms of lithium wire in ether) with excess nitrous oxide at −10 to −15° there was obtained 5.2 g. (60 mmoles, 30% yield, based on 40% yield of ethyllithium) of ethylethylidenehydrazine, b.p. 45–48° at 44 mm., n^{25}D 1.4314. Repeated fractionations failed to give analytically pure material.

Anal. Calcd. for $C_4H_{10}N_2$: C, 55.78; H, 11.70; N, 32.52. Found: C, 57.7; H, 11.5; N, 31.0. (This corresponds to $C_4H_{9.6}N_{1.85}$.)

Acid hydrolysis of this product and treatment with Brady's reagent gave the 2,4-dinitrophenylhydrazone of acetaldehyde, m.p. 147°; lit.[18] 148°.

Isopropyllithium with Nitrous Oxide. (a) In Ethyl Ether.—Excess nitrous oxide was passed into 0.254 mole of isopropyllithium in ethyl ether over two hours at room temperature. There was obtained 4.0 g. of a yellow oil, b.p. 136–137°, n^{25}D 1.4240.

Anal. Calcd. for $C_8H_{18}N_2$: C, 67.6; H, 12.6; N, 19.7. Calcd. for $C_8H_{20}N_2$: C, 66.6; H, 13.9; N, 19.4. Found: C, 66.4; H, 12.5; N, 18.0.

After hydrolysis of this oil with hot aqueous oxalic acid there was obtained with Brady's reagent the 2,4-dinitrophenylhydrazone of acetone, m.p. 122°; no depression on admixture with an authentic sample.

An ethereal solution of this oil was treated with gaseous hydrogen chloride. The white precipitate formed on crystallization from ethanol–ether gave white platelets, m.p. 208–210°.

Anal. Calcd. for $C_5H_{14}NCl$: C, 48.5; H, 11.4; N, 11.3; Cl, 28.7. Found: C, 49.1; H, 11.3; N, 11.0; Cl, 29.1.

There was no depression on admixture of this salt with a sample of isoamylamine hydrochloride, m.p. 207°.

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[12] For example, phenol was formed from phenylmagnesium bromide by reaction with the N-oxide of N,N-dimethylaniline: V. N. Belov and K. K. Savich, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 262 (1947); *C. A.*, **42**, 530 (1948). Nitrous oxide and the amine oxide may be formulated similarly: $\overset{+}{N}_2{-}O^-$ and $R_3\overset{+}{N}{-}O^-$.

[13] G. Gever and K. Hayes, *J. Org. Chem.*, **14**, 813 (1949).

[14] A private communication from Dr. P. D. Bartlett in 1951 disclosed a similar experience, in which carbonation of isopropyllithium in ethyl ether gave as one product diisoamyl ketone.

[15] Kindly supplied by Dr. Overberger. See C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, THIS JOURNAL, **71**, 1681 (1949).

[16] Melting points, taken in a modified Hershberg apparatus, and boiling points were not corrected. Microanalyses were performed by F. Schwarzkopf, K. Ritter and Weiler and Strauss.

[17] The nitrous oxide, of stated 98.0% purity, was used as received from the Matheson Co., Inc., East Rutherford, N. J.

[18] W. M. D. Bryant, THIS JOURNAL, **60**, 2815 (1938).

(b) **In Petroleum Ether.**—Excess nitrous oxide was passed into 0.174 mole of isopropyllithium in petroleum ether over two hours at room temperature. There was obtained 2.7 g. of a yellow oil, b.p. 132–134°, $n^{25}\mathrm{D}$ 1.4268.

Anal. Calcd. for $C_9H_{22}N_2$: C, 68.3; H, 13.9; N, 17.7. Found: C, 68.1; H, 14.0; N, 17.8.

***n*-Butyllithium with Nitrous Oxide.**—Excess nitrous oxide was passed into a refluxing ether solution of 0.48 mole of *n*-butyllithium.[19] The main product was *n*-butyl-*n*-butylidenehydrazine (I), b.p. 98–102° at 29 mm., $n^{25}\mathrm{D}$ 1.4490. In a series of runs the average yield of I, based on *n*-butyllithium, was 24%.

Anal. Calcd. for $C_8H_{18}N_2$: C, 67.55; H, 12.75; N, 19.81. Found: C, 67.58; H, 12.75; N, 19.81.

After hydrolyzing I with 1:10 sulfuric acid, treatment of the distillate with Brady's reagent gave the 2,4-dinitrophenylhydrazone of butyraldehyde, m.p. 121–121.5°; lit.[20] 122°; no depression on admixture with an authentic sample.

Hydrolysis of I with aqueous oxalic acid gave the oxalate of *n*-butylhydrazine, m.p. 163.5–165°, lit.[13] 165°; no depression on admixture with an authentic sample.

After distillation of I there was obtained 2.3 g. of a light yellow liquid, b.p. 130–135° at 28 mm., $n^{25}\mathrm{D}$ 1.4527.

Anal. Found: C, 71.9; H, 12.4; N, 15.3. (This corresponds to $C_{12}H_{24\cdot8}N_{2\cdot18}$.)

The analytical figures for this fraction are intermediate between I and $C_{12}H_{26-28}N_2$ and suggest incomplete removal of the former. Further purification by distillation was not successful because of decomposition.

***n*-Butyllithium with 1-Diazobutane.**—Ethereal 1-diazobutane,[21] prepared from 43.5 g. (0.3 mole) of N-*n*-butylnitrosourea, was added to 0.250 mole of *n*-butyllithium in ether dropwise and with stirring. There was obtained 11.03 g. (78 mmoles, 32%) of *n*-butyl-*n*-butylidenehydrazine (I), b.p. 101–104° at 30 mm., $n^{25}\mathrm{D}$ 1.4495.

Anal. Calcd. for $C_8H_{18}N_2$: C, 67.55; H, 12.75. Found: C, 67.5; H, 12.8.

***t*-Butyllithium with Nitrous Oxide.**—Excess nitrous oxide was passed into *t*-butyllithium[22] (from 0.5 mole of *t*-butyl chloride and 1.5 g.-atom of lithium sand in ether) at −40°. There was obtained 2.7 g. (19 mmoles, 3.8%) of ditertiarybutyldiimide (2,2′-azoisobutane), a yellow oil, b.p. 107–108°, $n^{25}\mathrm{D}$ 1.3940.

Anal. Calcd. for $C_8H_{18}N_2$: C, 67.55; H, 12.75; N, 19.70. Found: C, 68.57; H, 13.26; H, 18.73.

The high carbon and hydrogen values and the low nitrogen value suggest contamination with the Wurtz product, 2,2,3,3-tetramethylbutane.

The infrared spectra of this material (peaks at 3.4, 6.75, 6.88, 7.24, 8.08, 8.28, 8.48 and 11.52 microns) and of 2,2′-azoisobutyronitrile[15] (peaks at 3.32, 3.38, 6.78, 6.86, 7.20, 7.28, 8.10, 8.50 and 11.50 microns) are in accord with a similarity of structure.

All attempts to reduce this material to *sym*-ditertiarybutylhydrazine or to *t*-butylamine with chemical reducing agents or with catalytic hydrogenation were unsuccessful.

Phenyllithium with Nitrous Oxide.—Excess nitrous oxide was passed into phenyllithium (from 0.5 mole of bromobenzene and 1.5 g.-atoms of lithium in ether) for one hour at −20° and then at room temperature for two hours. From the aqueous layer of the hydrolyzed mixture 2.3 g. (24 mmoles, 4.8%) of phenol (characterized as phenyl benzoate, m.p. 68–69°) was obtained. From the neutral layer there was obtained by distillation 3.8 g. of benzene and 3.2 g. of bromobenzene. By chromatography there was isolated 1.3 g. of biphenyl, 3.24 g. (18 mmoles, 7.2%) of azobenzene as orange crystals, m.p. 66° (no depression on admixture with an authentic sample) and 9.0 g. (35 mmoles, 21%) of triphenylhydrazine, m.p. 141–142° (lit.[23] 142°).

Anal. Calcd. for $C_{18}H_{16}N_2$: C, 83.04; H, 6.20; N, 10.76. Found: C, 83.13; H, 5.96; N, 10.78.

In one preparation the entire reaction mixture was added to 200 ml. of water containing 55 g. of resorcinol. Acidification gave 0.5 g. of 4-benzeneazoresorcinol, m.p. 169–170° (lit. 170°,[24] no depression on admixture with an authentic sample).

***o*- and *p*-Tolyllithium with Nitrous Oxide.**—Excess nitrous oxide was passed into *o*- and *p*-tolyllithium (from 0.5 mole of *o*- and *p*-bromotoluene in ether). The reaction mixture was at −40° in the first case and at reflux in the second.

The only product isolated from the reaction of *o*-tolyllithium was 8.1 g. (39 mmoles, 15.6%) of 2,2′-azotoluene, red crystals, m.p. 53–55°, lit.[25] 55°.

Anal. Calcd. for $C_{14}H_{14}N_2$: C, 79.96; H, 6.71; N, 13.32. Found: C, 79.6; H, 6.53; N, 13.1.

From the aqueous layer of the *p*-tolyllithium reaction there was obtained 2.15 g. (20 mmoles, 4%) of *p*-cresol (α-naphthylurethan, m.p. 144°, lit.[26] 146°).

From the ether layer there was obtained by chromatography, besides bis-*p*-tolyl, 2.6 g. (12 mmoles, 4.8%) of 4,4′-azotoluene, orange crystals, m.p. 141–141.5°, lit.[27] 144°.

Anal. Calcd. for $C_{14}H_{14}N_2$: C, 79.96; H, 6.71; N, 13.32. Found: C, 80.2; H, 6.8; N, 12.9.

There were also obtained dark purple crystals, m.p. 120–124°, not further identified.

Anal. Found: C, 88.5; H, 6.55; N, 4.59.

1-Naphthyllithium with Nitrous Oxide.—To 52 g. (0.25 mole) of 1-bromonaphthalene there was added a filtered solution of *n*-butyllithium from 0.25 mole of *n*-butyl bromide and 0.64 g.-atom of lithium wire in 150 ml. of anhydrous ether. After ten minutes of stirring under an atmosphere of nitrogen, nitrous oxide was introduced in large excess.

Water was added *cautiously* to the reaction mixture, from which 5.5 g. of a precipitated yellow solid was removed by filtration. This material was insoluble in most solvents, but was soluble in concentrated sulfuric acid (blue solution), and in hot dioxane, from which it was recovered unchanged. It decomposed with melting at about 280°.

From the aqueous layer there was obtained 1.1 g. (7.6 mmoles, 3%) of 1-naphthol, m.p. 91° (no depression on admixture with an authentic sample); 1-naphthylurethan, m.p. 150° (no depression on admixture with an authentic sample).

The residue from evaporation of the dried ether layer was chromatographed to give 2.8 g. of naphthalene, m.p. 80°, and 3.8 g. (13 mmoles, 10%) of 1,1′-azonaphthalene, orange crystals, m.p. 190.5°, lit.[28] 189°.

Anal. Calcd. for $C_{20}H_{14}N_2$: C, 85.1; H, 5.0; N, 9.9. Found: C, 84.8; H, 4.8; N, 9.9.

1,1′-Azonaphthalene was reduced with zinc and sodium hydroxide to 1,1′-hydrazonaphthalene, m.p. 280°, lit.[29] 276°.

9-Fluorenyllithium with Nitrous Oxide.—A solution of *n*-butyllithium prepared from 8.4 g. (1.2 g.-atoms) of lithium and 68.5 g. (0.5 mole) of *n*-butyl bromide was added slowly with stirring to 70 g. (0.427 mole) of fluorene in 100 ml. of ether, and the mixture was refluxed for 30 minutes. Excess nitrous oxide was passed through the cooled reaction mixture for three hours.

Addition of 200 ml. of water precipitated 11.5 g. of solid. It was not found possible to recrystallize this highly insoluble material satisfactorily or to get interpretable analytical figures. There was, however, obtained from toluene a small quantity of material of m.p. 233.5–235°. An attempt to dissolve the main portion of this solid in dimethylformamide at 100° gave 8.5 g. (24 mmoles) of fluorenone azine, m.p. 270°; no depression on admixture with an authentic sample.

The ether layer gave 16.5 g. (0.091 mole, 21.2%) of 9-fluorenol, m.p. 154–155° after recrystallization from toluene; lit.[30] 153°.

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(19) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, This Journal, **71**, 1499 (1949).

(20) O. L. Brady and G. V. Elsmie, *Analyst*, **51**, 77 (1926).

(21) F. Arndt. "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

(22) P. B. Bartlett, C. G. Swain and R. B. Woodward, This Journal, **63**, 3229 (1941).

(23) M. Busch and R. Hobein, *Ber.*, **40**, 2099 (1907).

(24) A. Hantzsch, *ibid.*, **46**, 1557 (1913).

(25) S. Hoogewerf and W. A. van Dorp, *Ber.*, **11**, 1203 (1878).

(26) H. E. French and A. F. Wirtel, This Journal, **48**, 1736 (1926).

(27) J. Barzilowski, *Ann.*, **207**, 103 (1881).

(28) L. Wacker, *ibid.*, **317**, 375 (1901).

(29) H. Hepworth, *J. Chem. Soc.*, **118**, 1012 (1920).

(30) H. Staudinger and A. Gaule, *Ber.*, **49**, 1956 (1916).

Anal. Calcd. for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.70; H, 5.38.

The fluorenol was oxidized to fluorenone, m.p. 83–84°; no depression on admixture with an authentic sample.

Concentration of the fluorenol mother liquor gave an additional 13 g. of fluorenone azine, m.p. 270°, giving a total of 21.5 g. (0.06 mole, 28.2%) of this compound by both routes.

9-Fluorenyllithium with 9-Diazofluorene.—Fluorenone hydrazone[31] was oxidized with yellow mercuric oxide to 9-diazofluorene in 48% yield according to the method of Nenitzescu and Solomonica.[32]

A solution of 13 g. of 9-diazofluorene in 50 ml. of ether was added to a solution of 9-fluorenyllithium prepared from 10.5 g. of fluorene and *n*-butyllithium in 200 ml. of ether.

There was isolated in the usual way 7.8 g. of fluorenone azine as a red-brown powder, m.p. 269–270° after crystallization from xylene. A mixed m.p. with an authentic sample showed no depression, and infrared spectra of the two samples were superimposable.

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[31] H. Staudinger and O. Kupfer, *Ber.*, **44**, 2207 (1911).

[32] C. D. Nenitzescu and E. Solomonica, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 496.

BROOKLYN 2, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. XXX. Alkylation of Dimethylketene Dimethylacetal

BY S. M. MCELVAIN AND CLYDE L. ALDRIDGE[1]

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Dimethylketene dimethylacetal (I) is readily converted to a trisubstituted acetic ester when heated with such halides as benzoyl chloride, benzyl bromide, benzhydryl bromide and phenacyl bromide. With triphenylmethyl bromide the thermal reaction with I produces triphenylmethane, methyl methacrylate and its dimer VIII. These products are shown to arise from a concerted intramolecular thermal decomposition of the initially formed methyl β,β,β-triphenylpivalate (VI), which may be prepared from I and triphenylmethyl bromide in the presence of small amounts of mercuric chloride at temperatures below its decomposition point. I is alkylated by butyl bromide in 74% yield in presence of zinc chloride. Stannic chloride causes a rapid methylation of I with methyl chloride, but dehydrohalogenates higher primary alkyl halides and the halogen acid produced reacts with I. Zinc chloride produces a similar dehydrohalogenation reaction with secondary and tertiary halides.

The dealcoholation of methyl orthoisobutyrate to dimethylketene dimethylacetal (I) with aluminum *t*-butoxide[2] and a new procedure, which is now reported, for the preparation of this orthoester in good (70%) yields have made this disubstituted ketene acetal available for a further study of its properties. Compared to the unsubstituted and monosubstituted ketene acetals, I is quite resistant to polymerization, *e.g.*, it may be distilled unchanged from aluminum chloride.[3] The reactions of I are further simplified by the absence of hydrogen on the methylene carbon.[4]

This paper reports the reactions of I with a variety of organic halides. Benzoyl chloride, benzyl bromide, benzhydryl bromide reacted smoothly and in the expected manner with I to give high yields (81–95%) of the trisubstituted acetic esters II, III and IV and the corresponding methyl halide. Phenacyl bromide, however, gave only a 25% yield of methyl benzoylpivalate (V) together with methyl isobutyrate (57%) and a viscous red oil which was not characterized; 35% of the phenacyl bromide was recovered. Evidently under the conditions of the reaction hydrogen bromide is generated and converts a major portion of I to methyl isobutyrate.

$$RX + \underset{\text{I}}{(CH_3)_2C{=}C(OCH_3)_2} \longrightarrow$$

$$[RC(CH_3)_2{-}CX(OCH_3)_2 \text{ or}$$

$$RC(CH_3)_2{-}\overset{\oplus}{C}(OCH_3)_2 + X^{\ominus}] \longrightarrow$$

$$CH_3X + RC(CH_3)_2COOCH_3$$

II, R is C_6H_5CO
III, R is $C_6H_5CH_2$
IV, R is $(C_6H_5)_2CH$
V, R is $C_6H_5COCH_2$

In contrast to the relatively simple reactions in which II–IV were produced, triphenylmethyl bromide reacted with I to give a group of unexpected reaction products; triphenylmethane (80%), methyl methacrylate (64%), dimethyl α,α-dimethyl-α'-methyleneglutarate (VIII) (24%), methyl bromide (78%) and a viscous, yellow oil, which boiled over a wide range, amounted to 14.5% of the weight of the reactants and was not further identified. Apparently the initially formed methyl β,β,β-triphenylpivalate (VI) was pyrolyzed into these products at the temperature (100–120°) required for the reaction of I with triphenylmethyl bromide. That VI was initially produced was shown when it was discovered that this ester could be formed in 89% yield at or below the boiling point of ether from the reaction of I with triphenylmethyl bromide in the presence of 1 mole per cent. of mercuric chloride. When VI was heated to the temperature required for its formation in the absence of the catalyst, it yielded triphenylmethane (61%), methyl methacrylate (40%), VIII (19%) and 34% of the yellow oil. This oil appears to be formed from the interaction of VI with oxygen of the air as a sample of this ester exposed to the air on a watch glass is transformed after several hours to a similar oil.

$$(C_6H_5)_3CBr + \text{I} \xrightarrow{HgCl_2} \underset{\text{VI}}{(C_6H_5)_3C{-}C(CH_3)_2COOCH_3} + CH_3Br$$

This unique pyrolysis of VI is doubtless related to its hexasubstituted ethane structure as the methyl diphenylpivalate (IV) is quite stable and

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[1] U. S. Rubber Company Fellow 1951–1952; du Pont Summer Research Assistant 1951 and 1952.

[2] S. M. McElvain and W. R. Davie, THIS JOURNAL, **73**, 1400 (1951).

[3] *Cf.* the polymerization of ketene diethylacetal with such metal salts as cadmium chloride (P. R. Johnson, H. M. Barnes and S. M. McElvain, *ibid.*, **62**, 964 (1940)).

[4] *Cf.* Reactions of other ketene acetals with alkyl and acyl halides (S. M. McElvain, *et al.*, *ibid.*, **64**, 254 (1942); **74**, 1811, 2662 (1953)).