iodide was isolated and the dimethylammonium salt (IIf) of IIc was obtained in good yield.

In another experiment designed to replace the chlorine in 1-chloro-2-methoxyhexafluorocyclopentene-1 with fluorine in dimethylformamide, the dihydrate of potassium fluoride was inadvertently used. Once again the product was the corresponding dimethylammonium salt IIf.

In both cases a possible explanation for the formation of the salt involves the decomposition of dimethylformamide to give dimethylamine, which acts as a nucleophile and forms the 1-amino derivative.[16] Vigorous hydrolysis of the latter gave the observed product.

Spectroscopic Studies

The spectroscopic results for the potassium salts are reported in Table I. The fluorine n.m.r. spectra are consistent with the proposed structures in both the correct multiplet observed and the expected ratios.

In each case the infrared absorption spectrum contains three bands characteristic of the $O=C=C=C=O$ system. Actually, four bands should be present due to the two $C=O$ and two $C=C$ bonds[17]; however, one of these centered around 8 μ is not observed owing to C–F absorption. The doublet found at the highest frequency is due to crystal splitting.

An analogy can be made between these fluorinated salts and certain metal chelates of acetylacetonates.[17] Of course, the exact position of the various bands is affected by the substituents on the ring and by the size of the ring as indicated in Table I.

The ultraviolet absorption spectra show a bathochromic shift with increasing ring size and a definite increase in absorptivity when a chlorine atom is replaced by a fluorine atom,[18] but the λ_{max} remains unchanged.

Experimental[19]

General Procedure for Hydrolysis.—Potassium hydroxide (4 moles) was added to diglyme (350 ml.) and the olefin (1 mole) was slowly added thereto while vigorously stirring. The reaction was fairly exothermic. In the sealed-tube reactions the exotherm appeared to be sufficient to effect mixing of the solution.

The solution was then cooled and filtered to remove inorganic salts, and the filtrate was concentrated to dryness under vacuum. The residue was dissolved in hot isopropyl alcohol, treated with activated charcoal, and filtered. Upon evaporating the solvent the salt was obtained as a solid precipitate. Alternatively, the salt could also be obtained by adding ethyl ether to a concentrated solution in isopropyl alcohol.

General Procedure for Preparing the Acid Form.—The potassium salts were eluted with a known quantity of distilled water through Dowex 50W-M8, an ion-exchange resin in hydrogen ion form.

In the case of IIc the aqueous solution was concentrated to near dryness and sublimed at 90–100° (1–2 mm.). This gave a very hygroscopic acidic material[20] which was soluble in both water and polar organic solvents.

The analyses and melting points of the acid forms were variable, probably owing to the amount of water present. The infrared curves of the acid forms are similar to those of the potassium salts, with the exception of two bands at *ca.* 2.78 and 3.00 μ which are characteristic of the hydroxyl group.

Acknowledgment.—The authors wish to acknowledge the assistance of Dr. J. E. Lancaster for the fluorine n.m.r. spectra, Dr. W. M. Banick for the nonaqueous titrations, Mr. A. Ferri for the ultraviolet spectra, Mr. N. B. Colthup for the infrared interpretation, and Mr. J. J. Kobliska for the analyses. The authors are also grateful to Professor W. Bailey, University of Maryland, for helpful discussions during this work.

---

[16] C. O. Parker, *J. Am. Chem. Soc.*, **81**, 2183 (1959).

[17] N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press Inc., New York, N. Y., 1964, pp. 244–246.

[18] W. W. Robertson and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5252 (1950).

[19] See Table II for experimental details, yields, and analytical results.

[20] In a recent publication [E. D. Weil and J. Linder, *J. Org. Chem.*, **28**, 2218 (1963)] the chlorine analog of this compound was reported. These authors have observed broad bands between 6.1 and 6.4 μ and acidities similar to those of the compound we have prepared.

A New High-Temperature Free-Radical Source

GEORGE A. MORTIMER

Plastics Division, Monsanto Company, Texas City, Texas

Received January 18, 1965

A new free-radical initiator, azobisisobutanol diacetate, has been prepared from azobisisobutyronitrile in good yield in three steps: (1) methanolysis to convert the nitrile groups to ester functions; (2) reduction of the diester to a diol; and (3) acetylation. Thus, it is more easily synthesized than other azo compounds having similar free-radical-generating properties and may be easily tagged with C^{14} if desired. Steady production of free radicals at 167° was demonstrated.

Azobisisobutyronitrile has been widely used in the laboratory as a thermal initiator for polymerization because its decomposition rate is independent of the medium and therefore accurately known. Labeled with C^{14}, it has been used to trace initiator residues in polymers because the radicals formed upon elimination of nitrogen do not undergo any further fragmentation. Despite these advantages, its usefulness is limited by the fact that above about 80° its rate of decomposition is too fast for kinetic experiments. This report describes the preparation and initiating characteristics of a new initiator which has the same advantages but decomposes thermally about 100° higher than azobisisobutyronitrile.

The major objective of this work was to provide an easily prepared, free-radical initiator useful for kinetic work at approximately 150–200°. Azoisobutane yields free radicals at a useful rate in this temperature range,[1] but its synthesis is not facile. The procedure of Kooy-

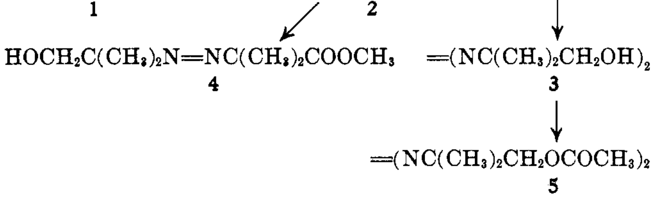
---

[1] J. B. Levy and B. K. W. Copeland, *J. Am. Chem. Soc.*, **82**, 5314 (1960).

man[2] is laborious, inconsistent, and gives poor yields at best. The Stevens method[3] is better, but involves handling hazardous fluorinating agents in a special nickel apparatus and gives a product that cannot be easily purified. This report describes the preparation of a new initiator, azobisisobutanol diacetate, which is readily prepared and purified using standard laboratory techniques. Furthermore, if desired, it can be conveniently tagged with C^{14} in the last step of the synthesis.

In the present work, for the preparation of azobisisobutanol diacetate (**5**) azobisisobutyronitrile (**1**) was first converted to dimethyl azobisisobutyrate (**2**); the latter was reduced with lithium aluminum hydride to azobisisobutanol (**3**) which was acetylated to give **5**. For obtaining C^{14}-tagged initiator, C^{14}-acetyl chloride could be used in the final step.

The products of the first and last steps were essentially pure as obtained. However, the product of the reduction step deserves further comment. Repeated recrystallization from benzene–cyclohexane led to a consistently less pure, yellowish product. Since the azobisisobutanol was found to initiate polymerization satisfactorily at 199°, it was not felt that the yellowing was due to thermal decomposition during recrystallization. Treatment with dilute acid, however, did give an immediate color change. In order to test the effect of acid, a little dry HCl was bubbled into an ether solution of **3**. The ether was quickly evaporated and the solid residue was examined by infrared. Total absence of some bands present in pure **3** indicated its complete destruction. No effort was made to identify the decomposition products. In the presence of an acid scavenger, however, azobisisobutanol was stable.



In one reduction, an insufficient amount of reducing agent was used. By chromatographic separation of the mixture of products, a substance tentatively identified as **4** was isolated. Attempted recrystallization in the absence of an acid scavenger resulted in its decomposition.

The data on thermal decomposition of azobisisobutanol diacetate are given in Table I. These data are fit by the equation $k_d = 6 \times 10^{16} e^{-42,800/RT}$

TABLE I

DECOMPOSITION OF AZOBISISOBUTANOL DIACETATE

Temp., °C.	No. of points	$k_d \times 10^4$/sec.
170.0	8	0.486 ± 0.005
180.0	8	1.27 ± 0.04
189.0	6	3.47 ± 0.24
199.9	8	10.1 ± 0.3

In order to check its effectiveness as a controllable source of free radicals, polymerizations of ethylene at 20,000 p.s.i. and 167° were carried out for 20, 40, and 60 min. using a constant concentration of 5.2×10^{-5} moles/l. of the azo diacetate. The over-all rates of polymerization, determined as previously described,[4] were 7.1, 6.5, and 6.8%/hr., respectively. These rates are well within experimental error of the average. It is concluded that kinetically steady-state polymerization was achieved and that the initiator furnished free radicals at an essentially constant rate under these conditions.

Experimental

Dimethyl Azobisisobutyrate.[5]—In a 1-l. four-necked flask fitted with a stirrer, immersion thermometer, and two gas-inlet tubes were placed 90.0 g. (0.548 mole) of azobisisobutyronitrile and 600 ml. of methanol. The slurry was stirred, and a cooling bath was used to lower the temperature to −5°. Dry HCl was passed into the mixture at a high rate, and the cooling bath was held near −20° in order to hold the reaction temperature between 5 and 10°. After 2 hr., no more HCl was absorbed, and the slurry became a clear solution. The solution was allowed to stand overnight at 0°.[8] The mixture was cooled to −70° to complete precipitation of the diimino ester dihydrochloride and rapidly suction filtered. The precipitate was stirred into a mixture of ice and water until all the solid disappeared. The liquid mixture was filtered to remove particulate matter. The organic layer was separated, water washed, dried over Na_2SO_4, and filtered to yield 85.0 g. (74%) of liquid diester, which after cooling and solidification had m.p. 28–30° (lit. m.p. 30°,[7] 33°[6]).

Azobisisobutanol.—In a 1-l. flask fitted with stirrer, dropping funnel, and reflux condenser were placed (under N_2 purge) 300 ml. of ether and 17.1 g. (0.450 mole) of $LiAlH_4$. A solution of 85.0 g. (0.354 mole) of dimethyl azobisisobutyrate in 150 ml. of ether was added in 45 min. at a rate to keep a good reflux. The reaction was refluxed for an additional hour. Excess hydride was decomposed by slow addition of a solution of 40 ml. of water and 20 ml. of tetrahydrofuran. Potassium hydroxide solution (45%) was added until the salts coagulated and left a clear aqueous layer. The mixture was diluted with 10% KOH and extracted with ether; the ether layers were filtered and dried over Na_2SO_4. Evaporation of ether left 41.3 g. (67%) of solid azobisisobutanol.[9] Recrystallization from 1:10 pyridine–cyclohexane gave pure, white crystals, m.p. 108° (hot stage, cor.). The infrared spectrum was in agreement with the assigned structure.

Azobisisobutanol Diacetate.—A mixture of 125 ml. of methylene chloride, 16.6 g. (0.095 mole) of azobisisobutanol, 25 ml. (0.31 mole) of pyridine, and 25 ml. (0.26 mole) of acetic anhydride was placed in a stoppered flask, swirled, and allowed to stand overnight. The solution was thoroughly extracted with Na_2CO_3 and HCl solutions and dried over Na_2SO_4, and the solvent was evaporated to give 21.3 g. (86% yield) of crude diacetate. Vacuum distillation gave 19.2 g. (77%) of yellow liquid, b.p. 90–92.5° (1.5 mm.), m.p. 16.5–17.0°, $n^{25}\text{D}$ 1.4317, $\lambda_{\max}^{\text{cyclohexane}}$ 370 mμ (ε 16). The infrared and n.m.r. spectra were consistent with the assigned structure.

Anal. Calcd. for $C_{12}H_{22}N_2O_4$: C, 55.79; H, 8.58; N, 10.85. Found: C, 55.54; H, 8.57, 11.05.

Thermal Decomposition of Azobisisobutanol Diacetate.—In a constant-temperature bath held at ±0.1° were placed sealed tubes containing 3.5-ml. aliquots of a solution of 3.2 g. of azobisisobutanol diacetate in 100 ml. of Spectrograde cyclohexane.

---

(2) E. Farenhorst and E. C. Kooyman, *Rec. trav. chim.*, **72**, 993 (1953).

(3) T. E. Stevens, *J. Org. Chem.*, **26**, 2531 (1961).

(4) L. Boghetich, G. A. Mortimer, and G. W. Daues, *J. Polymer Sci.*, **61**, 3 (1962).

(5) This procedure, adapted from one developed by W. M. Padgett of this laboratory, is given here inasmuch as the procedure of Thiele and Heuser[6] for the solvolysis of the hydrazonitrile, both in our hands and in the hands of others,[7] when used for the azonitrile gives an impure product that must be recrystallized before use.

(6) J. Thiele and K. Heuser, *Ann.*, **290**, 1 (1896).

(7) J. S. Mackie and S. Bywater, *Can. J. Chem.*, **35**, 570 (1957).

(8) In one experiment in which the mixture stood overnight at −70°, much of the product was the half-ester half-nitrile resulting from partial solvolysis.

(9) Extraction data indicated that a continuous extraction would have given a higher recovery of the product.

When the tubes had come to constant temperature, they were removed individually from the bath at fixed times and quenched by cooling. The concentration of undecomposed initiator was determined from the intensity of the 370-mμ band. Experiments generally were run to 90% decomposition. The results, given in Table I, were obtained by least squares. Where decomposition had been extensive, N_2 evolution was obvious when the tube was opened, and the odor of isobutyl acetate was prominent.

Lithium Aluminum Methide as an Alkylating Agent[1]

D. J. PASTO AND R. SNYDER, O.S.F.

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana

Received November 30, 1964

The aluminum tetramethide anion has been characterized by proton magnetic resonance and its use as an alkylating agent has been studied. Reaction with benzaldehyde leads to the utilization of two of the available methyl groups, whereas with aliphatic aldehydes only one methyl group is utilized. Ketones undergo a very slow alkylation giving low yields of tertiary alcohols. Acid chlorides react to give methyl ketones with the utilization of only 1 equiv. of the reagent. Esters, nitro compounds, nitriles, and sulfonate esters do not undergo reaction with lithium aluminomethide (lithium aluminum methide).

The first complex aluminum alkide, lithium aluminomethide (LAM), was apparently first prepared by Hurd[2] in 1948. LAM was described as a stable solid at 80° but was very reactive to moisture. Baker and Sisler prepared sodium and lithium aluminoethide in 1953 and studied the reactions of the reagents with several inorganic compounds.[3] Sodium aluminoethide was also prepared in 1959 as an intermediate in the synthesis of triethylaluminum[4] and Ziegler and co-workers studied the addition of this compound to olefins.[5] Walter prepared lithium aluminoethide by reaction of diazomethane with lithium aluminum hydride and observed the formation of diethyl ketone and propionic acid on treatment with carbon dioxide.[6]

Similar boroalkide complexes have also been described in the literature. Schlesinger and Brown have described lithium trimethylethylboron as a fairly stable solid.[7] Blitzen and Pearson prepared lithium boroethide which proved to be a very stable compound which could be sublimed at 160–170° without decomposition.[8] These authors reported that sodium boroethide was a good alkylating agent for producing tertiary alcohols from ketones; however, no experimental details were given. Ashby has observed that complex boroalkides are capable of reducing acids and ketones and the alkylation of carbonyl compounds.[9]

Although Hurd[2] indicated the possible utility of complex alumino- and boroalkides in organic synthesis in 1948 the only results appearing in the literature concern the complex boroalkides. It seemed of interest to study the potential utility of a complex aluminoalkide, namely LAM, as an alkylating agent. This article reports the results of this investigation.

Lithium aluminomethide is readily prepared by the addition of an ethereal solution of trimethylaluminum to a cooled ethereal solution of methyllithium. The complex was characterized by its proton magnetic resonance (p.m.r.) spectrum which displayed a singlet at +63 c.p.s. relative to internal tetramethylsilane. Mixtures of trimethylaluminum and methyllithium in which the former is in excess display a single p.m.r. peak intermediate between pure ethereal trimethylaluminum (+55 c.p.s., 2.0 *M* in diethyl ether) and LAM indicating a rapid exchange of methyl groups in the system. Similar chemical shifts changes are observed for the α-protons of the ether solvent owing to changes in the extent of complexing of the ether. Addition of an excess of methyllithium (+116 c.p.s., 1.69 *M* in diethyl ether) to LAM solutions results in two peaks in the p.m.r. spectrum which remain constant in position with changes in the relative amounts of the two reactants present. Both peaks correspond to the peak positions for pure LAM and methyllithium. This latter data would indicate that the dissociation of LAM to methyllithium and trimethylaluminum, followed by possible exchange, is a relatively slow process if it occurs at all. This is pertinent in considering the alkylation reactions involving LAM.

Ethereal solutions of LAM hydrolyze rather slowly in the presence of water or aqueous base, the rate of the hydrolysis decreasing markedly with the extent of hydrolysis. Hydrolysis with 10% sulfuric acid is initially quite vigorous and requires approximately 10 min. for completion at 0°. The extent of reaction in the alkylation reactions was determined by gas evolution measurements during hydrolysis. These results agreed closely with the gas–liquid chromatographic analytical results. Ethereal solutions of LAM undergo air oxidation unless protected from oxygen. The p.m.r. spectra of ethereal solutions left open to the air develop additional peaks which correspond to peaks formed if one adds methanol to pure ethereal LAM. Reactions of oxidized LAM solutions with benzoyl chloride produced substantial amounts of methyl benzoate.

The alkylation of benzaldehyde appears to result in the utilization of only two of the available four methides. The reactions appear to be quite rapid at 25° in ether. When the alkylation is carried out in refluxing tetrahydrofuran (66°), 2 equiv. of methide are utilized, but the yield of 1-phenylethanol decreases. This is primarily due to the incursion of a hydride transfer

---

[1] This work was supported by the Petroleum Research Fund of the American Chemical Society, Grant No. PRF 1225-A1,3.

[2] G. T. Hurd, *J. Org. Chem.*, **13**, 711 (1948).

[3] E. B. Baker and H. H. Sisler, *J. Am. Chem. Soc.*, **75**, 5193 (1953).

[4] Bergwerksgesellshaft Hibernia Akt. Ges., British Patent 822,971 (Nov. 4, 1959); *Chem. Abstr.*, **54**, 14125*i* (1960).

[5] K. Ziegler, H-G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Soll, and W-R. Kroll, *Ann.*, **629**, 121 (1960).

[6] H. A. Walter (to the Monsanto Chemical Co.), U. S. Patent 2,864,842 (Dec. 16, 1958); *Chem. Abstr.*, **53**, 7014*e* (1959).

[7] H. J. Schlesinger and H. C. Brown, *J. Am. Chem. Soc.*, **62**, 3429 (1940).

[8] S. M. Blitzen and T. H. Pearson (to the Ethyl Corp.), U. S. Patent 2,944,084 (July 5, 1960); *Chem. Abstr.*, **54**, 24398*f* (1960).

[9] E. C. Ashby (to the Ethyl Corp.), U. S. Patent 3,007,970 (April 28, 1958); *Chem. Abstr.*, **56**, 6000*b* (1962).