Castor-Based Derivatives: Synthesis of Some Acrylate Esters[1]

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Abstract

Acrylate esters of various hydroxy acid derivatives obtainable from castor oil have been synthesized and characterized. Synthetic methods evaluated include acid- and base-catalyzed alcoholysis of methyl acrylate, esterification with acrylic acid, acrylyl chloride, or acrylic anhydride, and esterification with β-chloropropionyl chloride or anhydride followed by dehydrohalogenation. The two-step esterification-dehydrohalogenation procedure gives most satisfactory yields and purity. Preparation, purification, and characterization of the compounds are described and the various synthetic methods are evaluated.

Introduction

ACRYLATE ESTERS have been commercially important for many years, and a wealth of literature exists covering the synthesis and use of these monomers (1). In connection with a research program aimed at development of new uses for castor oil, we explored synthetic routes leading to pure acrylate monomers from castor hydroxy fatty acids. Several patents describe acrylate synthesis from castor oil itself or from selected components (2). We sought, however, to start with pure derivatives of the free hydroxy acids in order to best utilize their unique polyfunctionality. Also, pure monomers would lead to soluble rather than highly cross-linked polymers.

Previously, we had prepared a series of mono- and disubstituted amides from ricinoleic (12-hydroxy-*cis*-9-octadecenoic) acid and the related ricinelaidic, 12-hydroxystearic, dihydroxy- and trihydroxystearic acids by means of a modified mixed carboxylic-carbonic anhydride synthesis (3,4). These amides appeared to be of particular interest as starting materials for synthesis of acrylates, because monomers containing polar pendant amide groups should impart distinct and unique properties to resulting polymers or copolymers. The properties of the castor amides themselves vary widely. Thus, their use as starting materials seemed to offer an opportunity to prepare a series of monomers quite distinct from one another and possibly tailored to specific uses. Some representative members of such a series were prepared and characterized. Acrylate esters have also been prepared from the hydroxy acid methyl esters and from ricinoleyl and 12-hydroxystearyl alcohols.

Experimental

Analytical Techniques

Infrared (IR) spectra were determined as smears or Nujol mulls on a Perkin-Elmer Model 137 Infracord equipped with NaCl optics, and an air path in the reference beam.

Thin-layer chromatography (TLC) on chromatostrips (5) was used both in assessing purity of samples and in following the course of column chromatography on silicic acid. Solvent systems used for development of silica gel G strips included 80:20 Skellysolve F: diethyl ether for derivatives of the alcohols and methyl esters and 95:5 diethyl ether: Skellysolve F for most of the amide derivatives. Spots were detected by spraying with 20% H_2SO_4 and charring at ~300C.

An F & M model 720 dual-column programmable instrument was used for gas-liquid chromatography (GLC). Columns used were 2-ft, 20% Apiezon L on 60–80 mesh Gas-Chrom P (Applied Science Laboratories), and 3-ft, 10% ECNSS-S on 100–120 mesh Gas-Chrom P.

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian model A60, in CCl_4 or $CDCl_3$ with tetramethylsilane as reference.

Methyl Acrylate. A readily available material [3] was used as received.

Acrylic Acid. A generous gift sample of stabilized glacial acrylic acid [4] was used as received.

Acrylyl Chloride. We tried to use several commercial lots.[5] Because this unstable material varied widely in quality from lot to lot, however, we found it more convenient to prepare our own acrylyl chloride as needed by the method of Stempel et al. (6).

Acrylic Anhydride. Our own attempts to prepare this material (7) were unsuccessful. A commercial material [5] was used as received.

β-Chloropropionyl Chloride. Readily available, stable material was used as received.[3]

Ricinoleyl Alcohol. Commercial material [6] was redistilled, and the fractions boiling at 175–176C at ~40μ Hg were used.

12-Hydroxystearyl Alcohol. From commercial material [6] distilled at ~40μ Hg, fractions boiling from 180–183C were used.

Methyl Ricinoleate. Methyl esters were prepared by sodium methoxide-catalyzed methanolysis of castor oil followed by fractional distillation at <100μ Hg (8). The material used boiled over the range 163–168C.

Methyl 12-Hydroxystearate. Distilled methyl ricinoleate was hydrogenated in a Paar apparatus with PtO_2 in methanol solution. The saturated ester was recrystallized from acetone and melted at 57.2–57.5C [lit. (9) 57.5–58C].

Castor Amides. The castor amides used as starting materials for acrylate synthesis were prepared via a mixed carboxylic-carbonic anhydride method as previously described (3,4) and were of high purity as judged by IR, TLC, and physical constants.

Castor Acrylates. Some representative examples of methods for monomer preparation follow. Only the two-step process, method (e), however, is suitable for large-scale work where high purity of product without extensive purification is required. The products are described in Table I.

a) Alcoholysis of Methyl Acrylate. One-tenth mole (28.6 g) of 12-hydroxystearyl alcohol, 400 mg of hydroquinone, 200 mg of *p*-toluenesulfonic acid, and 36 ml (0.4 mole) of methyl acrylate were placed in a 250-ml round-bottom flask equipped with a variable takeoff distilling head. The system was heated at total reflux until the head temperature dropped to 66C.

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[2] W. Utiliz. Res. Dev. Div., ARS, USDA.
[3] Eastman Organic Chemicals.
[4] B. F. Goodrich Company.
[5] Monomer-Polymer Laboratories, Borden Chemical Company.
[6] Baker Castor Oil Company.

TABLE I

Castor Acrylates Prepared[a]

Compound	Empirical formula	n_D^{25}	mp (bp/μHg) C	Analysis[b] Calculated % C	H	N	Found % C	H	N
From amides:									
12-acryloxyoleamide	$C_{21}H_{37}NO_3$	1.4804	.....	71.7	10.6	3.98	71.5	10.4	3.88
12-acryloxystearamide	$C_{21}H_{39}NO_3$	.....	52–54	.....	.....	.....	.....	.....	.....
9,10-diacryloxystearamide	$C_{24}H_{41}NO_5$	.....	87–89	.....	.....	.....	.....	.....	.....
9,10,12-triacryloxystearamide	$C_{27}H_{43}NO_7$	1.4825	.....	.....	.....	.....	.....	.....	.....
From substituted amides:									
N,N-dimethyl-12-acryloxyoleamide	$C_{23}H_{41}NO_3$	1.4787	(170/32)	72.7	10.9	3.69	72.4	10.8	3.65
N,N-dimethyl-12-acryloxystearamide	$C_{23}H_{43}NO_3$	1.4652	(155/4)	72.3	11.3	3.67	71.9	11.1	3.60
N-hexadecyl-12-acryloxyoleamide	$C_{37}H_{69}NO_3$	.....	60–61	.....	.....	.....	.....	.....	.....
N-methyl-12-acryloxystearamide	$C_{22}H_{41}NO_3$	.....	34–36	71.8	11.2	3.81	71.5	11.0	3.78
From methyl esters:									
Methyl 12-acryloxyoleate	$C_{22}H_{38}O_4$	.....	(155/1.5)	72.1	10.5	.....	72.2	10.3	.....
Methyl 12-acryloxystearate	$C_{22}H_{40}O_4$	1.4518	(140/1)	71.7	10.9	.....	71.6	10.7	.....
From alcohols:									
1-acryloxy-12-hydroxy-*cis*-9-octadecene[c]	$C_{21}H_{38}O_3$	1.4668	(150/1)	74.5	11.3	.....	74.2	11.2	.....
1,12-diacryloxy-*cis*-9-octadecene	$C_{24}H_{40}O_4$	1.4679	(140/35)	73.4	10.3	.....	73.6	10.3	.....
1-acryloxy-12-hydroxyoctadecane[c]	$C_{21}H_{40}O_3$	.....	42–44	.....	.....	.....	.....	.....	.....
1,12-diacryloxyoctadecane	$C_{24}H_{42}O_4$	.....	(165/1)	.....	.....	.....	.....	.....	.....

[a] All products purified by silicic acid column chromatography using benzene-methanol eluant mixtures. Unless noted otherwise, all products in the table were prepared by acrylyl chloride esterification.
[b] Where no analysis is reported, insufficient sample was available and characterization was based on IR and/or NMR spectroscopy.
[c] Prepared by alcoholysis of methyl acrylate.

Distillation to remove the methyl acrylate-methanol azeotrope was continued until the vapor temperature rose again to about 72C. Excess methyl acrylate was removed in vacuo on a rotary evaporator (80C). The product, 31 g, was 1-acryloxy-12-hydroxyoctadecane contaminated with starting dihydroxy compound. Essentially no diacrylate had formed. Longer reaction times did not lead to appreciably different results. Separation of the 1-monoacrylate from starting material by differential solubility was unsuccessful. A 1-g portion of the material purified by silicic acid column chromatography with benzene-methanol eluant mixtures (10) yielded 450 mg of product. Similar results were obtained with ricinoleyl alcohol, with yields of pure 1-acryloxy-12-hydroxy-*cis*-9-octadecene ranging from 45–60%. Although described for secondary butyl alcohol (11), this alcoholysis reaction also failed with the secondary alcohol function in methyl ricinoleate and N,N-dimethylricinoleamide. Conditions tried included catalysis with *p*-toluenesulfonic acid and hydroquinone inhibitor, and base catalysis with aluminum isopropoxide and phenyl β-naphthylamine inhibitor.

b) Esterification with Acrylyl Chloride or Acrylic Anhydride. A sample of N-hexadecylricinoleamide (3) (3.30 g, 0.0063 mole) was dissolved in 50 ml of tetrahydrofuran (THF) containing 20 mg of phenyl β-naphthylamine inhibitor and a 10% excess of acrylyl chloride (0.55 ml). The system was vigorously stirred and maintained near room temperature during the slow addition of 1.06 ml (a 10% excess) triethylamine in 10 ml THF. Stirring was continued for 30 min, the flask was transferred to the rotary evaporator over a hot water bath, and excess volatile materials were removed. The residue was taken up in diethyl ether and washed with 1N HCl, 1M Na_2CO_3, and water till neutral. The solution was dried over anhydrous magnesium sulfate and the ether evaporated, leaving 3.38 g of a waxy substance. Analysis by TLC suggested this was a mixture of approximately equal amounts of product and starting material with several side reaction products in minor amounts. These components were separated on a half-gram scale on a silicic acid column, and 200 mg of pure product recovered. Larger excesses of acrylyl chloride and triethylamine, longer reaction times, or higher temperatures did not greatly improve yields.

Use of solid anhydrous sodium carbonate in a well-stirred heterogeneous system, dimethylformamide, a catalyst effective with acid chlorides such as diethylphosphochloridate (12), or 2,6-lutidine, a hindered base, provided no improvement in yield or product purity.

Conditions tried with acrylic anhydride included perchloric acid catalysis in chloroform solution (13), refluxing pyridine with and without perchloric acid catalyst, methanesulfonic acid in diethyl ether, and sulfuric acid catalyst in refluxing benzene (2a). Yields at best were only fair (40–70%), and the impurities tenacious. We were not able to purify these preparations satisfactorily by liquid-liquid partition, low-temperature crystallization, or falling-film molecular distillation.

c) Esterification with Acrylic Acid. Ricinoleyl alcohol was converted to a mixture of mono- and diacrylates by warming it with glacial acrylic acid on the steam bath, and methyl ricinoleate under the same conditions was converted partially to 12-acryloxy derivative. Use of strong acid catalysts resulted in extensive decomposition. Heating under refluxing conditions (142C) caused extensive polymerization of the acid.

d) Solvolysis of Tosylates. 12-Tosyloxy derivatives were prepared from methyl ricinoleate and methyl 12-hydroxystearate, essentially by the method of Tipson (14). Attempted solvolysis in acrylic acid was unsuccessful either at room temperature or on the steam bath. We have not tried the conditions recently described by Tachibana and Kambara (15) for nucleophilic displacement of tosylate anion.

e) Two-Step Process. Methyl 12-Acryloxystearate. One-tenth mole (31.4 g) of pure methyl 12-hydroxystearate was dissolved in 150 ml of THF in a flask equipped with a powerful magnetic stirrer. A large excess of solid anhydrous sodium carbonate was added and vigorous stirring maintained during the addition of a four- to sixfold mole excess of β-chloropropionyl chloride. This heterogeneous system was continually stirred and heated to reflux for at least four hours. Moisture was rigorously excluded. When reaction was complete, an infrared spectrum (smear) from evaporated supernate showed no evidence of hydroxyl absorption. The entire solution was filtered, and the THF and excess acid chloride were removed in vacuo

on a rotary evaporator (80C). The residual oily methyl 12-β-chloropropionylstearate was taken up in ether and washed with dilute acid, base, and water, thoroughly dried, filtered, and evaporated in the usual fashion. It was then dissolved in 150 ml *dry* (over BaO) pyridine and refluxed overnight. The pyridine was removed in vacuo, and the residual mixture of fatty acrylate and pyridine hydrochloride taken up in ether and water. The organic solution was washed and dried as described above and the ether removed, leaving behind a 90% overall yield of methyl 12-acryloxystearate. This material was shown to be identical to the analytical sample (Table I) by NMR, IR, TLC, GLC on Apiezon L, and had a negative Beilstein (copper wire) flame test for chlorine. No further purification was necessary.

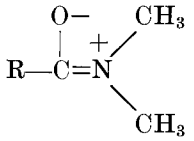
N,N-dimethyl-12-acryloxystearamide. With β-chloropropionyl chloride and N,N-dimethyl-12-hydroxystearamide, we obtained lower yields (70–80%) of less pure product than with methyl 12-hydroxystearate, and further purification was necessary. This was effected by passing the crude product (in several volumes of diethyl ether) through neutral alumina in a sintered glass funnel.

Results and Discussion

Product Characterization

Infrared spectroscopy is a valuable tool in following these reactions and in estimating product purity. Figure 1 shows the IR spectrum of the acrylate prepared from N,N-dimethylricinoleamide. Of interest are: the absence of hydroxyl absorption, ester carbonyl at 5.8μ, disubstituted amide carbonyl at 6.2μ, and strong C–O–C stretch showing up characteristically at about 8.4μ.

Another valuable analytical aid is NMR spectroscopy. Figure 2 shows the NMR Spectrum of N,N-dimethyl-12-acryloxyoleamide. Typical, characteristic acrylate and dimethylamide proton resonances clearly indicate the structure of the monomer. The integration curve is also shown, indicating presence of 2 terminal methylene protons (>6 ppm), one proton on double-bonded carbon shielded by proximity to the electron cloud on the acrylate carbonyl oxygen (5.5–5.9 ppm), 2 ordinary protons on double-bonded carbon 5.1–5.5 ppm), and one methine proton (4.7–5.1 ppm). Also readily apparent are the dimethylamide double resonance (2.85–3.0 ppm), methylene adjacent to a double bond (1.9–2.6 ppm), chain methylene (1.2–1.8 ppm), and terminal methyl (0.9 ppm). Double resonance of N-methyl protons is quite characteristic in the NMR spectra of dimethylamides and is explained by restricted rotation around the C–N bond. There appears to be a sizeable contribution from the resonance form



which leads to restricted rotation and the double peak. If rotation were completely free, all the dimethylamide protons would be equivalent and only one resonance would result.

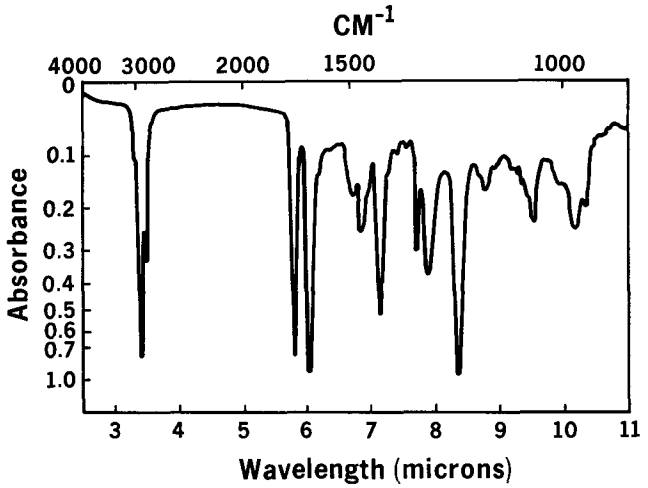


FIG. 1. Infrared spectrum of N,N-dimethyl-12-acryloxyoleamide, as thin film on NaCl plates.

Synthetic Approaches

We have previously explored and discussed in some detail (3,7) the relative inertness of the secondary alcohol functions in castor fatty acids, and have exploited this sluggish reactivity in preparing carboxyl group derivatives. The same degree of inertness was encountered in our attempted preparation of hydroxyl group derivatives from these materials. Thus, we were able to prepare (in 45–60% yield by alcoholysis) fatty monoacrylates containing free secondary hydroxyl functions.

Acrylate formation from the secondary alcohol groups was achieved on a small (0.01 mole) scale by the use of acrylyl chloride with triethylamine catalyst as described in the Expermiental section. This procedure, however, had a number of disadvantages which made it unattractive for larger-scale work. Yields varied widely, and the products were difficult to purify. TLC consistently revealed 5 or 6 components in these preparations.

A major factor in lowered yields appears to be complex formation between acid chloride and tertiary amine. Examples of this reaction are well known (16).

The consistent appearance of numerous impurities at low levels in products from acrylyl chloride esterification can perhaps be quite reasonably explained by formation of the acylium ion $CH_2{=}CHC{\overset{\overset{O}{\parallel}}{}}^{+}$ as part of the transition state. Since this ion has the mesomeric form $+CH_2CH{=}C{=}O$ it can react at its β-carbon to give a ketene derivative as well as at its carbonyl carbon to give the desired acrylate ester. Any ketene formed under these conditions could then undergo a variety of known reactions such as condensation, acetal formation, lactone and ester formation, etc. Small amounts of several different impurities would appear in the final product, as we have invariably observed (17). The same consideration applies to acrylic anhydride, since the same mesomeric acylium ion could be involved in the transition state. We have observed essentially the same impurities in product mixtures from systems containing acrylic anhydride.

Dehydrohalogenation of β-chloropropionate esters is a known route to acrylates (18), and we investigated the applicability of this procedure to our materials when it became apparent that other methods did not look promising for scaled-up preparations. As described in the Experimental section, this method led to high yields of clean products which did not require time-consuming or complicated purification.

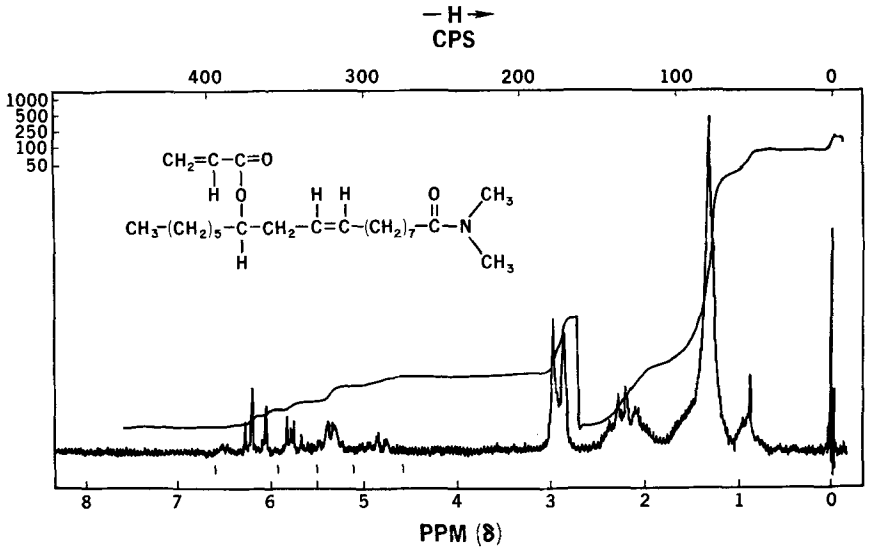
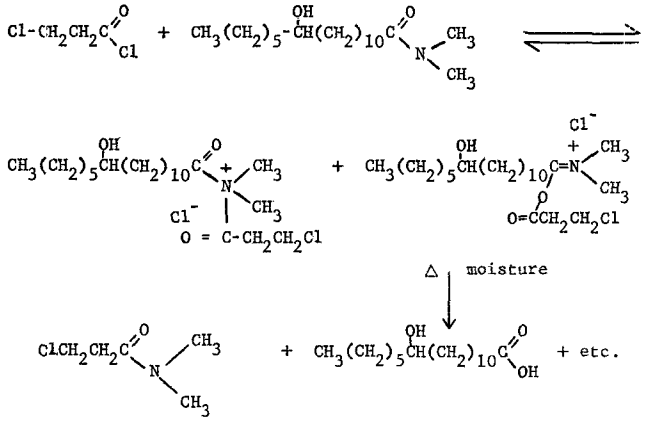


FIG. 2. NMR spectrum of N,N-dimethyl-12-acryloxyoleamide, relative to tetramethylsilane (TMS).

Tertiary amine bases must be avoided in the esterification step because they immediately complex with the β-chloropropionyl chloride, and no reaction with the fatty acid derivative occurs. In the second step, however, best results are obtained with a tertiary amine base as dehydrohalogenating agent. Strong inorganic bases such as KOH lead to some ester hydrolysis, and weak bases such as sodium carbonate fail to dehydrohalogenate the fatty acid derivatives in the temperature range where nitrogen bases are useful.

None of the methods utilizing active acid derivatives proceeds completely cleanly when the 12-hydroxy compound is a disubstituted amide. Reactions of acyl chlorides with disubstituted amide functions have been discussed (19,20) and apparently occur here as competitive side reactions. Thus, in addition to the desired preparative reaction, reactions such as the following may occur to some extent:



These complications can be reduced by proper choice of conditions, i.e., avoidance of heat and moisture, and the contaminated products are easier to purify than those prepared with acrylyl chloride or acrylic anhydride. One way to avoid these side reactions entirely is to substitute β-chloropropionic anhydride for acid chloride in the first step. This anhydride is readily preparable by our procedure (7). It is not as reactive as the acid chloride, but can be used to give fair yields of β-chloropropionate ester from N,N-dimethyl-12-hydroxystearamide. However, such preparations remain contaminated with starting hydroxy compound, which, as noted earlier, is difficult to remove.

In general, the two-step esterification-dehydrohalogenation process described here is a practical method for preparation of most castor-based acrylate monomers in evaluation-scale quantities. It uses readily available, relatively inexpensive, stable materials. It results in very high over-all yields of products requiring little or no further purification. Time-consuming or sophisticated manipulations or specialized equipment are not required. Selected castor acrylate derivatives prepared in sufficient quantity by this method are being subjected to homo- and copolymerization studies. The results will be reported elsewhere. Some of these acrylates may find uses in polymers for coatings, plastics, films, fibers, molded products, or other applications where incorporation of such monomers would be advantageous.

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REFERENCES

1. For a comprehensive review, see Clarke, J. T. in "Monomers," edited by E. R. Blout, W. P. Hohenstein and H. Mark, Interscience Publishers, New York, 1951.
2. (a) Lynn, J. W. (Union Carbide Corp.) U.S. 3,010,925 (1961); (b) CIBA, Ltd., Swiss 261,121 (1949); (c) CIBA, Ltd., Swiss 265,396–265,401 (1950); Medalia, A. I. U.S. 2,868,755 (1959).
3. Applewhite, T. H., J. S. Nelson and L. A. Goldblatt, JAOCS *40*, 101–104 (1963).
4. Applewhite, T. H., and J. S. Nelson, manuscript in preparation.
5. Applewhite, T. H., M. J. Diamond and L. A. Goldblatt, JAOCS *38*, 609–614 (1961).
6. Stempel, G. H., Jr., R. P. Cross and R. P. Mariella, J. Am. Chem. Soc. *72*, 2299–2300 (1950).
7. Nelson, J. S., L. A. Goldblatt and T. H. Applewhite, J. Org. Chem. *28*, 1905–1907 (1963).
8. Swern, D., and E. F. Jordan, Jr., Biochem. Preparations *2*, 104–105 (1952).
9. Straus, F., H. Heinze and L. Salzmann. Chem. Ber. *66*, 631–639 (1933).
10. Binder, R. G., T. H. Applewhite, G. O. Kohler and L. A. Goldblatt, JAOCS *39*, 513–517 (1962).
11. Rehberg, C. E., Org. Syn. *26*, 18–21 (1946).
12. Diamond, M. J., T. H. Applewhite, R. E. Knowles and L. A. Goldblatt, JAOCS *41*, 9–13 (1964).
13. Mattson, F. H., R. A. Volpenhein and J. B. Martin, J. Lipid Res. *5*, 374–377 (1964).
14. Tipson, R. S., J. Org. Chem. *9*, 235–241 (1944).
15. Tachibana, T., and H. Kambara, J. Am. Chem. Soc. *87*, 3015–3016 (1965).
16. Leduc, P., and P. Chabrier, Bull. Soc. Chim. France *1963*, 2271–2276 (1963).
17. See also Hickmott, P. W., J. Chem. Soc. *1964*, 883–887 (1964).
18. Marvel, C. S., and R. L. Frank, J. Am. Chem. Soc. *64*, 1675–1678 (1942).
19. Hall, H. K., Jr., J. Am. Chem. Soc. *78*, 2717–2719 (1956).
20. Coppinger, G. M., J. Am. Chem. Soc. *76*, 1372–1373 (1954).

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