sion free radical polymerization recipes. *cis*-1,4-Polyisoprene, *cis*-1,4-polybutadiene, and piperylene were prepared by Ziegler catalysts.

Hydrogenation of Simple Olefins (Table I).—Into a 100-ml. steel autoclave was placed 0.5 mole of the olefin to be reduced (cyclohexene, caprylene, or octene-1) together with 7.5 ml. (0.03 mole) of the triisobutylborane. The autoclave was purged with nitrogen, charged to 2500 p.s.i. with hydrogen, and heated at 235° for 5 hr. Under these conditions, quantitative reduction was realized as shown by infrared spectroscopy and gas phase chromatography. Extensive hydrogenation of simple olefins has also been observed at lower temperatures (180–190°) but the reaction may usually be driven rapidly to completion at the higher temperature.

Hydrogenation of *cis*-1,4-Polyisoprene (Table III).—Into a 4500-ml. steel autoclave was placed a 5% benzene solution of *cis*-1,4-polyisoprene (42 g. of polymer), 16.5 ml. (0.067 mole) of triisobutyl borane, and 205 g. (2.5 moles) of cyclohexene. The autoclave was purged with nitrogen, charged to 2500 p.s.i. with hydrogen at room temperature, and heated at 190° for 48 hr. There was no further decrease in hydrogen pressure after 24 hr. and a total pressure drop of 500 p.s.i. was observed. The polymer was precipitated from the reaction mixture by addition of methanol and dried in a vacuum oven at 45° for 7 hr. An infrared spectrum of the tough rubbery product closely resembled that of a random copolymer of ethylene and propylene (B).

Hydrogenation of Other Olefinic Polymers (Table IV).—Exploratory experiments were carried out as indicated below. Into a 2960-ml. steel autoclave was placed a 5.6% benzene solution of styrene–butadiene rubber (100 g. of polymer) and 7.0 ml. (0.028 mole) of triisobutylborane. The autoclave was purged with nitrogen, charged to 2000 p.s.i. with hydrogen at room temperature, and heated at 225° for 5 hr. The polymer was precipitated from the cooled reaction mixture by addition of methanol and dried in a vacuum oven. The product was a semisolid whose infrared spectrum showed that the aliphatic double bonds had been completely saturated.

1,2-Polybutadiene.—The product was a liquid whose infrared spectrum was essentially identical to that of polybutene.

1,4-Polybutadiene.—Complete reduction gave a severely degraded liquid polymer.

***cis*-1,4-Polybutadiene.**—The product was insoluble in benzene and was recrystallized from hot xylene. The infrared spectrum and melt characteristics were those of a high density polyethylene of moderate molecular weight (A).

Polypiperylene.—A liquid product resulted. The infrared spectrum closely resembled that of completely hydrogenated *cis*-1,4-polyisoprene (C).

***cis*-Polyisoprene-3*d*.**—A completely saturated *cis*-1,4-polyisoprene whose infrared spectrum showed that extensive deuterium exchange had occurred.

A Facile Conversion of Aldehydes to Nitriles

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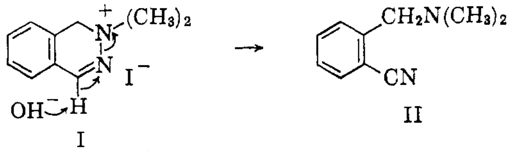
Aldehydes were conveniently converted to the corresponding N,N,N-trimethylhydrazonium salts [$RCH{=}NN(CH_3)_3{}^+X^-$]. These salts underwent a beta elimination reaction when treated with methanolic sodium methoxide to give high yields of the corresponding nitriles.

The recent observation[1] in these laboratories that 2,2-dimethyl-1,2-dihydrophthalazinium iodide (I) is transformed to α-N,N-dimethylamino-*o*-toluonitrile (II) on treatment with aqueous sodium hydroxide suggested that N,N,N-trimethylhydrazonium salts derived from aldehydes (III) might also undergo an analogous beta elimination reaction to give the corresponding nitriles.[2]



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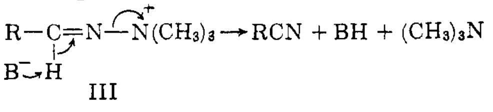

$$R{-}\underset{\underset{B^-\ H}{|}}{C}{=}N{-}\overset{+}{N}(CH_3)_3 \rightarrow RCN + BH + (CH_3)_3N$$

III

It was found that quaternary salts of type III (Table I) could be simply prepared by the reaction of either methyl iodide or methyl *p*-toluenesulfonate with solutions of the N,N-dimethylhydrazones[3] which were obtained by refluxing the aldehyde and N,N-dimethylhydrazine in either benzene or alcohol.

The crude quaternary salts were smoothly converted to the corresponding nitriles by methanolic sodium methoxide. Fifteen different nitriles were synthesized by this method (Table II). Benzonitrile and *p*-methoxybenzonitrile were obtained in excellent yields by employing methanolic potassium hydroxide as the basic medium in the elimination reaction, but this method gave only poor yields of *p*-nitrobenzonitrile. However, the use of methanolic sodium methoxide afforded *p*-nitrobenzonitrile in 92% yield.

The nitrile synthesis described in this paper resembles the base-catalyzed conversion of aromatic chloroimines ($ArCH{=}NCl$) to nitriles reported by Hauser and Gillaspie[4] with our beta elimination differing only in the nature of the leaving group.

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[1] R. F. Smith and E. D. Otremba, *J. Org. Chem.*, **27**, 879 (1962).

[2] For other recently reported methods of converting aldehydes to nitriles and leading references on older methods see: (a) H. M. Blatter, H. Lukaszewski, and G. de Stevens, *J. Am. Chem. Soc.*, **83**, 2203 (1961); (b) J. H. Hunt, *Chem. Ind.* (London), 1873 (1961); (c) J. H. Pomeroy and C. A. Craig, *J. Am. Chem. Soc.*, **81**, 6340 (1959).

[3] (a) D. Todd, *ibid.*, **71**, 1353 (1949); (b) R. H. Wiley, S. C. Slaymaker, and H. Kraus, *J. Org. Chem.*, **22**, 204 (1957).

[4] C. R. Hauser and A. G. Gillaspie, *J. Am. Chem. Soc.*, **52**, 4517 (1930).

TABLE I

PREPARATION AND PROPERTIES OF QUATERNARY HYDRAZONIUM SALTS

$RCH{=}NN(CH_3)_3^+X^-$

	Aldehyde	X^-	Preparation solvent	Recrystallization solvent	M. p., °C.[a]	Crude yield, %	Formula	% N Calcd.	% N Found
1.	Benz-	I^-	EtOH	MeOH	233–235	92	$C_{10}H_{15}N_2I$	[b]	
2.	*o*-Chlorobenz-	I^-	C_6H_6	MeOH	208–210	72	$C_{10}H_{14}N_2ClI$	8.63	8.63
3.	*m*-Chlorobenz-	TsO^-[c]	C_6H_6	EtOH	222–224	77	$C_{17}H_{21}N_2O_3ClS$	7.60	7.42
4.	*p*-Chlorobenz-	TsO^-	C_6H_6	MeOH	227–228	64	$C_{17}H_{21}N_2O_3ClS$	7.60	7.67
5.	*p*-Chlorobenz-	TsO^-	EtOH			76			
6.	*p*-Methoxybenz-	TsO^-	MeOH	EtOH	194–196	88	$C_{18}H_{24}N_2O_4S$	7.69	7.69
7.	Veratric	TsO^-	MeOH	EtOH	175–177	72	$C_{19}H_{26}N_2O_5S$	7.10	6.69
8.	*p*-Dimethylaminobenz-	I^-	C_6H_6	MeOH	262–265 dec.	70[d]	$C_{12}H_{20}N_3I$	12.61	12.54
9.	Salicyl-	I^-	C_6H_6	MeOH	201–204	57	$C_{10}H_{15}N_2OI$	9.15	9.23
10.	Salicyl-	TsO^-	EtOH	*n*-PrOH	184–187	84	$C_{17}H_{22}N_2O_4S$	8.00	8.04
11.	*p*-Nitrobenz-	TsO^-	EtOH	MeOH	242–243	68	$C_{17}H_{21}N_3O_5S$	11.07	11.02
12.	*m*-Nitrobenz-	TsO^-	C_6H_6	EtOH	207–209	70	$C_{17}H_{21}N_3O_5S$	11.07	11.21
13.	*m*-Nitrobenz-	I^-	EtOH	DMF[e]	212–214	73	$C_{10}H_{14}N_3O_2I$	12.54	12.81
14.	*o*-Nitrobenz-	TsO^-	EtOH	EtOH	149–151	67	$C_{17}H_{21}N_3O_5S$	11.07	11.02
15.	*o*-Nitrobenz-	I^-	C_6H_6	MeOH		15	$C_{10}H_{14}N_3O_2I$		
16.	*o*-Nitrobenz-	I^-	MeOH	MeOH	202–205	60	$C_{10}H_{14}N_3O_2I$	12.54	12.50
17.	*n*-Valer-	I^-	C_6H_6	EtOAc	105–107	81	$C_8H_{19}N_2I$	10.26	10.37
18.	Hydrocinnam-	I^-	C_6H_6	EtOH	189–190	85	$C_{12}H_{19}N_2I$	8.81	9.05
19.	*n*-Hept-	I^-	C_6H_6	EtOAc	108–109	92	$C_{10}H_{23}N_2I$	9.40	9.43
20.	Cinnam-	I^-	C_6H_6	MeOH	199–201	82	$C_{12}H_{17}N_2I$	8.86	9.12

[a] Melting points of analytical samples. [b] Calcd.: C, 41.39; H, 5.21; I, 43.74. Found: C, 41.58; H, 4.96; I, 43.92. [c] *p*-Toluenesulfonate. [d] Yield based on pure hydrazone[8b] obtained in 90% yield by the benzene solvent procedure (see Experimental). [e] Dimethylformamide.

TABLE II

PREPARATION AND PROPERTIES OF NITRILES OBTAINED FROM QUATERNARY HYDRAZONIUM SALTS

Nitrile	Crude yield, %	Salt used	Crude m.p. or b.p., °C. Found	Lit.
Benzo-[a]	85	1	B 188–190	191[b]
o-Chlorobenzo-	88	2	M 40–42	44[c]
m-Chlorobenzo-	54	3	M 37–39	40–41[c]
p-Chlorobenzo-	80	4	M 82–86	94[d]
p-Chlorobenzo-	68	5	M 80–85	
p-Methoxybenzo-[a]	74	6	M 56–59	61–62[e]
Veratro-	55	7	M 62–64	67[f]
p-Dimethylamino-benzo-	93	8	M 66–69	76[g]
Salicylo-[h]	90	9	M 94–98	98[i]
p-Nitrobenzo-	92	11	M 146–148	147[b]
m-Nitrobenzo-	68	12	M 98–107	118[b]
m-Nitrobenzo-	77	13	M 115–117	
o-Nitrobenzo-	73	14	M 107–108	111[j]
o-Nitrobenzo-	59	16	M 98–102	
n-Valero-	51	17	B 139–141	141[b]
Hydrocinnamo-	78	18	B 122–124 (11 mm.)	125 (11 mm.)[k]
n-Heptano-	62	19	B 182–186	182[k]
Cinnamo-	83	20	B 136–140 (17 mm.)	137 (16 mm.)[l]

[a] Potassium hydroxide used as the base in the elimination reaction. [b] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley & Sons, New York, N.Y., p. 321. [c] R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley & Sons, New York, N.Y., 1953, p. 618. [d] "Dictionary of Organic Compounds," I. M. Heilbron, ed., 1st ed. revised, Oxford University Press, p. 472. [e] Ref. *d*, p. 178. [f] Ref. *c*, p. 620. [g] Ref. *d*, p. 276. [h] Two equivalents of sodium methoxide used, product isolated after acidification of the diluted reaction mixture. [i] Ref. *d*, p. 342. The benzoyl derivative had m.p. 103–105° (lit., 106°). [j] Ref. *d*, p. 642. [k] Ref. *c*, p. 611. [l] Ref. *c*, p. 616.

Hauser, Le Maistre, and Rainsford[5] later made a kinetic study of the chloroimine→nitrile reaction and established the reaction to be second order.

A survey of the literature revealed that the only other reported study of quaternary hydrazonium salts is the recent work of Smith and Most.[6] These workers carried out a thorough investigation of the N,N,N-trimethylhydrazonium salts derived from ketones and found that Beckmann-type rearrangements could not be obtained on heating but base-catalyzed Neber-type rearrangements could be realized with salts possessing alpha hydrogens.

A brief study was made of the behavior of the quaternary hydrazonium salts of aldehydes in aqueous solution. It was found that quaternary hydrazonium salts derived from aromatic aldehydes substituted with electron-withdrawing substituents underwent a slow elimination reaction on refluxing their aqueous solutions for six to eight hours. Under these conditions, the trimethylhydrazonium iodides derived from *o*-nitro, *m*-nitro, and *o*-chlorobenzaldehyde were converted to the corresponding nitriles in yields of 75, 45, and 82%, respectively. On the other hand, it was found that treatment of the benzaldehyde derivative under analogous conditions resulted in the recovery of 47% of the starting material and a mixture of benzaldehyde and benzonitrile. On treatment of the benzaldehyde derivative with 1 *N*

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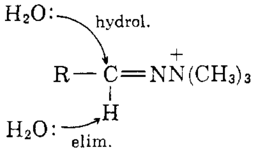
[5] C. R. Hauser, J. W. Le Maistre, and A. E. Rainsford, *J. Am. Chem. Soc.*, **57**, 1056 (1935).

[6] P. A. S. Smith and E. E. Most, Jr., *J. Org. Chem.*, **22**, 358 (1957).

sodium hydroxide at room temperature, an oil separated immediately which also consisted of a mixture of benzonitrile and benzaldehyde. Smith and Most[6] noted that the hydrolysis of the ketone derivatives was markedly accelerated by base. The quaternary hydrazonium iodide of *p*-dimethylaminobenzaldehyde also underwent simultaneous elimination and hydrolysis when its aqueous solution was refluxed.

From the observations described above, it is felt that the elimination reaction in water alone also takes place *via* an E_2 mechanism with water functioning as the base.[7] The electron-withdrawing substituents enhance the acidity of the beta hydrogen thus facilitating the elimination reaction. It is interesting to note in this regard that Hauser and co-workers[5] obtained relative rates of 1.0:7.7:540 for the sodium hydroxide-catalyzed decomposition of the chloroimines derived from benzaldehyde, *o*-chlorobenzaldehyde, and *o*-nitrobenzaldehyde, respectively. With the unsubstituted compound and the *p*-dimethylamino compound, elimination and hydrolysis can compete more favorably because of the lower acidity of the beta hydrogen.



It should be noted that this nitrile synthesis is suitable for the preparation of both aromatic and aliphatic nitriles. This versatility, coupled with the simplicity of the experimental procedure, should establish this method as one of considerable utility.

Experimental

Melting points and boiling points are uncorrected. Analyses are by Mr. Kenneth Fleischer and his staff of the Sterling-Winthrop Research Institute.

Preparation of N,N,N-Trimethylhydrazonium Salts. Procedure A.—Solutions consisting of 0.10 mole of the aldehyde, 0.10 mole (7.6 ml.) of N,N-dimethylhydrazine,[8] and 100 ml. of dry benzene were prepared and refluxed under a Dean-Stark water separator until the collection of water was complete. The solutions were then concentrated to half volume by continued heating with the trap open. After cooling the hydrazone solutions, 0.10 mole of either methyl iodide of methyl *p*-toluenesulfonate was added, and the solutions were refluxed for 2-4 hr. although in many instances separation of the product started immediately. After the addition of an equal volume of dry ether, the crude products were filtered and dried in a vacuum desiccator.

Procedure B.—Solutions consisting of 0.10 mole of the aldehyde, 0.10 mole of dimethylhydrazine, and 50 ml. of methanol or ethanol were prepared and refluxed for 4-6 hr. One tenth of a mole of the quaternizing agent was added to the cooled solutions and refluxing was continued for an additional 2-4 hr. The crude salts were isolated by concentration of the solutions followed by dilution with ether.

With the exception of the *o*-nitrobenzaldehyde derivative (no. 15), procedure A was generally found to be superior to procedure B for the preparation of these compounds. The crude quaternary salts prepared by procedure A usually had melting points fairly close to those found for the analytical samples while the salts prepared by procedure B frequently had wide melting ranges and required several recrystallizations for analysis.

Preparation of Nitriles.—The crude, dry quaternary salts were added to solutions of sodium methoxide in methanol (150 ml./0.10 g.-atom). A vigorous evolution of trimethylamine was usually observed and the reaction mixtures were refluxed until the amine odor was no longer detectable. After dilution of the reaction mixtures with a large volume of water, the nitriles were isolated by extraction with ether or filtration.

Table II records the crude melting points and boiling points of the prepared nitriles. Recrystallization of the crude solids resulted in the formation of pure products which had melting points that were in excellent agreement with the reported values. The infrared spectra of the liquid nitriles were obtained and all showed the presence of a nitrile band and the absence of absorption in the carbonyl region. The spectrum of benzonitrile was identical with that of an authentic sample. Many of the solid nitriles were hydrolyzed to the corresponding carboxylic acids, and in all cases the resultant acids had melting points that were in excellent agreement with reported values.

Reactions of N,N,N-Trimethylhydrazonium Iodides in Aqueous Solution.—A. One gram of the *m*-nitrobenzaldehyde derivative (no. 13, Table I) in 20 ml. of water was refluxed for 6 hr. On cooling, 0.20 g. (45%) of *m*-nitrobenzonitrile crystallized, m.p. 115-116°.

B. One gram of the *o*-nitrobenzaldehyde derivative (no. 15) in 100 ml. of water was refluxed for 4 hr. On cooling, 0.33 g. (75%) of *o*-nitrobenzonitrile crystallized, m.p. 109-110°.

C. A solution consisting of 6.5 g. of the *o*-chlorobenzaldehyde derivative (no. 2) and 100 ml. of water was refluxed for 6 hr. On cooling, 2.3 g. (82%) of *o*-chlorobenzonitrile crystallized, m.p. 39-41°.

D. A solution consisting of 5.8 g. of the benzaldehyde derivative (no. 1) in 90 ml. of water was refluxed for 7 hr. On cooling, a solid and an oil separated. The oil was removed by extraction with ether and the solid was identified as starting material, 2.7 g. (47%), m.p. 233-235°. The infrared spectrum of the ether soluble oil (1.2 g.) indicated that it consisted of a mixture of benzonitrile and benzaldehyde (nitrile band at 2240 cm.$^{-1}$, carbonyl band at 1700 cm.$^{-1}$). The crude 2,4-dinitrophenylhydrazone of benzaldehyde, m.p. 224-230°, was obtained in 70% yield from the mixture.

Treatment of the benzaldehyde derivative with one equivalent of 1 *N* sodium hydroxide resulted in the immediate formation of an oil (b.p. 184-186°) which was also found to be a mixture of benzonitrile and benzaldehyde by examination of the infrared spectrum.

E. A solution consisting of 3.3 g. of the *p*-dimethylaminobenzaldehyde derivative (no. 8) in 75 ml. of water was refluxed for 8 hr. Work-up of the reaction mixture in a manner analogous to that described in part D afforded 0.5 g. of starting material and 1.5 g. of ether-soluble material, m.p. 47-53°. The infrared spectrum of the ether soluble material showed a very weak nitrile band and a strong carbonyl band.

Acknowledgment.—This work was supported by a Grant-in-Aid from the Research Foundation of the State University of New York. The senior

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(7) Elimination under these conditions may be considered to be mechanistically similar to the decomposition of the trimethyl-β-(*p*-nitrophenyl)ethylammonium ion to *p*-nitrostyrene in aqueous solution, E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 659 (1941).

(8) Purchased from Distillation Products Industries, Rochester, New York.

author also wishes to express his thanks to the Foundation for a Summer Fellowship. We also wish to acknowledge gratefully the kindness of the staff of the Sterling-Winthrop Research Institute for the analytical determinations and the use of library facilities.

The Acid-catalyzed Thermal Decomposition of Some N,N'-Diaryl-α,ω-diaminoalkanes

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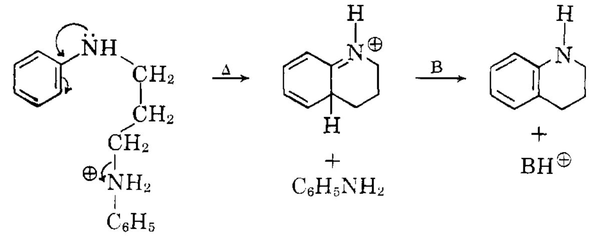
The acid-catalyzed cyclization reported[1] for diphenyltrimethylenediamine (I) has been examined further. When positions *ortho* to the amino nitrogen are vacant, julolidines are formed. Diphenyl- and dinaphthylethylenediamines give piperazine derivatives and the tetramethylene analog of (I) gives N-phenylpyrrolidine.

It has been reported[1] that N,N'-diphenyltrimethylenediamine (I) breaks down smoothly at 230–250°, in the presence of hydrobromic acid, to give anilines and 1,2,3,4-tetrahydroquinoline (II). The following mechanism (Scheme I) was suggested for the formation of these products:

Scheme I



The yield of aniline, based on Scheme I, was almost quantitative, while that of II was *ca.* 50%. An analogous reaction occurred with N,N'-di-*o*-tolyltrimethylenediamine, but here the yield of primary amine was slightly greater than that required by the simple reaction scheme.

We now report further data on the behavior of diamines, of the general formula ArNH(CH$_2$)$_n$NHAr, when heated in the presence of 0.1 mole of hydrobromic acid.

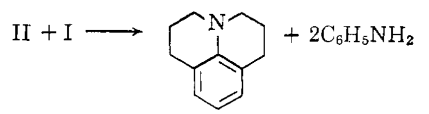
N,N'-Diaryltrimethylenediamines (*n* = **3**).—We examined the breakdown of six such diamines, including the diphenyl and di-*o*-tolyl compounds. In all cases the amount of released primary amine was roughly in accord with Scheme I. However, in at least half of these cases, such approximation must be fortuitous because in each of these instances, further treatment of the residue left after distillation of the tetrahydroquinoline resulted in the isolation of significant quantities of a julolidine (III). For each of the trimethylenediamines examined, the average product composition (over two experiments) is listed in Table I.

Table I

Yields from ArNH(CH$_2$)$_3$NHAr (+0.1 Mole HBr) at 230–260° (in Moles Product from 1 Mole Diamine)

Ar	Primary amine	(II) derivative	(III) derivative
Phenyl	1.02	0.46	0.17
o-Tolyl	1.05	.57	...
m-Tolyl	1.02	.37	.23
p-Tolyl	1.13	.28	.21
1-Naphthyl	1.04	.69	...
2-Naphthyl	0.85	.62	...

The julolidine may arise from the tetrahydroquinoline:



On this, as on other reasonable schemes, the over-all production of julolidine from diamine requires the release of three moles of primary amine from two moles of diamine.

Of the three diamines failing to yield julolidines, the *o*-tolyl and the 1-naphthyl compounds cannot do so. With the 2-naphthyl compound, neither the formation of 5,6-benzo-1,2,3,4-tetrahydroquinoline (to the exclusion of the 6,7-benzo product) nor the failure to yield a julolidine is surprising. Julolidine formation, or 5,6-benzo-1,2,3,4-tetrahydroquinoline formation, would involve ring closure at the unreactive 3-position of a naphthalene nucleus. On the other hand, the *m*-tolyl compound affords not only 8-methyljulolidine, but the expected pair of tetrahydroquinolines, in the ratio of three parts of 7-methyl isomer to two parts of 5-methyl isomer. This favoring of the 7-derivative by an electron-rich substituent is similar to the known trend in the Skraup closure, although the latter synthesis gives rise to no appreciable proportion of 5-isomer.[2]

N,N'-Diphenyltetramethylenediamine (*n* = **4**).—This compound was found to break down smoothly

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[1] A. Fischer, R. D. Topsom, and J. Vaughan, *J. Org. Chem.*, **25**, 463 (1960).

[2] L. Bradford, T. J. Elliott, and F. M. Rowe, *J. Chem. Soc.*, 437 (1947).