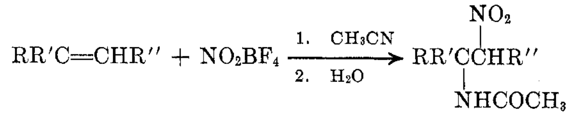
media with hydrogen cyanide or nitriles. Treatment of olefins with halogens in nitrile solvents leads to α-halogenated amides;[3] other modifications of the Ritter reaction with *N*,*N*-dichlorosulfonamides or peracids in nitrile media have also been reported.[4]

We wish to report an extension of the Ritter reaction in which the electrophilic reagent is nitronium or nitryl fluoroborate, NO_2BF_4. This salt is known to nitrate and to initiate the polymerization of olefins.[5] These nitrative polymerizations are effected when NO_2BF_4 is contacted with neat olefins in the liquid state. We have found that olefins react with NO_2BF_4 in anhydrous acetonitrile at −15° to give products which on hydrolytic work-up afford vicinal nitroacetamido derivatives **1**. The products from primary, secondary, and tertiary olefins are acyclic, in contrast to the results with nitrosyl fluoroborate.[4b] Side products such as unsubstituted amides formed by simple Ritter reactions are easily separated by distillation at low pressure.



$$RR'C{=}CHR'' + NO_2BF_4 \xrightarrow[2.\ \ H_2O]{1.\ \ CH_3CN} RR'\underset{NHCOCH_3}{\underset{|}{C}}\overset{NO_2}{\overset{|}{C}}HR''$$

In this manner, propylene is converted to 1-nitro-2-acetamidopropane (**1a**, $R = CH_3$; $R' = R'' = H$)[6] (50%), isobutylene to 1-nitro-2-methyl-2-acetamidopropane (**1b**, $R = R' = CH_3$; $R'' = H$) (23%), and butene-2 to 2-nitro-3-acetamidobutane (**1c**, $R = R'' = CH_3$; $R' = H$) (13%). In the latter case, the identical product was obtained from either the cis or trans olefin. Although it was ascertained that no isomerization of the olefin occurred prior to reaction, other details of the work-up procedure during which isomerization of the nitroacetamide might occur preclude any definitive conclusions of the structure of the reaction intermediate.

Experimental Section

Melting points are uncorrected. Elemental analyses, nmr, and mass spectroscopy were performed by AID laboratory of Esso Research and Engineering Co. Acetonitrile was purified by distillation from P_2O_5. Nitryl fluoroborate was purchased from Alfa Inorganics.

A solution of 13.3 g (0.1 mol) of NO_2BF_4 in 200 ml of anhydrous acetonitrile was treated with 0.2 mol of olefin at −25° under nitrogen with stirring. Upon completion of the addition of olefin, 10 ml of water was introduced. The reaction was stirred for 0.5 hr and gradually warmed to ambient temperature under nitrogen. The mixture was diluted with 50 ml of benzene and the solvent was removed by evaporation at reduced pressure. The residue was extracted with methylene chloride and washed free of acid with aqueous sodium bicarbonate solution, then with brine, dried ($MgSO_4$), evaporated, and distilled under reduced pressure.

Propylene gave 7 g (50% yield) of 1-nitroacetamidopropane (**1a**): mp 103–104° (lit.[6] mp 104°); nmr (acetone-d_6) δ 1.25 (d, 3, CH_3CH, J = 6.5 Hz), 1.9 (s, 3, CH_3CO), 4.7 (m, 3, NCH_2CHN), and 7.5 ppm (broad, 1, NH). *Anal.* Calcd for $C_5H_{10}N_2O_3$: C, 41.08; H, 6.83; N, 19.29; mol wt, 146. Found: C, 41.04; H, 7.07; N, 18.92; mol wt, 146 (mass spectrum).

Isobutylene gave 3.7 g (23%) of 1-nitro-2-methyl-2-acetamidopropane (**1b**): mp 86° ($CHCl_3$–hexane); nmr ($CDCl_3$) δ 1.5 [s, 6, $(CH_3)_2C$], 2.0 (s, 3, CH_3CO), 4.9 (s, 2, CH_2), and 6.6 ppm (broad, 1, NH). *Anal.* Calcd for $C_6H_{12}N_2O_3$: C, 44.94; H, 7.55; N, 17.49. Found: C, 44.55; H, 17.52; N, 17.17.

Both *cis*- and *trans*-butene-2 afforded the same product, but there was no isomerization of unreacted olefin observed during the course of reaction, as indicated by vpc. The brown oil obtained (7.3 g) was distilled to give a fraction, bp 70–75° (0.2 Torr), 1.5 g (12%), which was *N*-*sec*-butylacetamide: $n^{25}D$ 1.437 (lit.[7] $n^{25}D$ 1.436); ir ($CHCl_3$) 3260, 1650, 1545, and 870 cm^{-1}; nmr ($CDCl_3$) δ 0.90 (t, 3, CH_3CH_2), 1.10 (d, 3, CH_3CH), 1.45 (q, 2, CH_2), 1.98 (s, 3, $COCH_3$), 3.88 (q, 1, CH), and 7.0 ppm (broad, 1, NH). The second fraction, bp 105–106° (0.2 Torr), 2.1 g (13%), was 3-nitro-2-acetamidobutane (**1c**): mp 50–52° (ether, hexane), white crystals, mp 53.5° (sublimation, 30°, 0.2 Torr); ir ($CHCl_3$) 3260, 1650, 1545, 1385, and 1370 cm^{-1}; nmr ($CDCl_3$) δ 1.12 (q, 3, CH_3CHNH, J = 6.5 and 1.5 Hz), 1.55 (d, 3, CH_3CHNO_2), 2.0 (s, 3, CH_3CO), and 4.7 ppm (m, 2, CHCH). *Anal.* Calcd for $C_6H_{12}N_2O_3$: C, 44.99; H, 7.55 N, 17.49; mol wt, 160. Found: C, 44.81; H, 7.57; N, 17.57; mol wt, 160 (mass spectrum).

Registry No.—**1a,** 31593-56-3; **1b,** 31662-22-3; **1c,** 31593-57-4; *N*-*sec*-butylacetamide, 1189-05-5; nitronium fluoroborate, 13826-86-3; propylene, 115-07-1; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; isobutylene, 115-11-7.

Acknowledgment.—The authors are indebted to Mr. R. Kelly, Miss M. A. Miciak, and Mr. J. J. Porcelli for experimental assistance.

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Formation of Sulfones in the Thermal Decomposition of Ylides Derived from *p*-Toluenesulfonylhydrazides

J. E. Baldwin*[1] and J. E. Brown

Chemistry Department, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Ylides of the type I were first prepared by Wawzonek and Meyer, who described the thermolysis at 185–195° of the example I (R = Me).[2] They obtained a large amount of a polymer of the *p*-toluenesulfonamide–formaldehyde type, along with *p*-toluenesulfonamide, ammonia, trimethylamine, and formaldehyde. Subsequently Robson and Speakman prepared *N*-trimethylammoniododecanesulfonamidate (II) and demonstrated by suitable trapping experiments that the two products observed on pyrolysis, a trapped nitrene (dimethyl sulfoxide or triphenylphosphine) and dodecanesulfonesulfonamide, were formed by cleavage of the N–N bond to yield a sulfonyl–nitrene intermediate III,[3] which would also account for the products observed in the former case (I, R = Me) (Chart I).

In the course of our investigations of the [2,3] sigmatropic rearrangements of nitrogen ylides,[4,5] we had occasion to prepare ammoniosulfonamidate (I, R = 3-methyl-2-butenyl; mp 138° dec) and have discovered that its thermolysis proceeds in a very different way to

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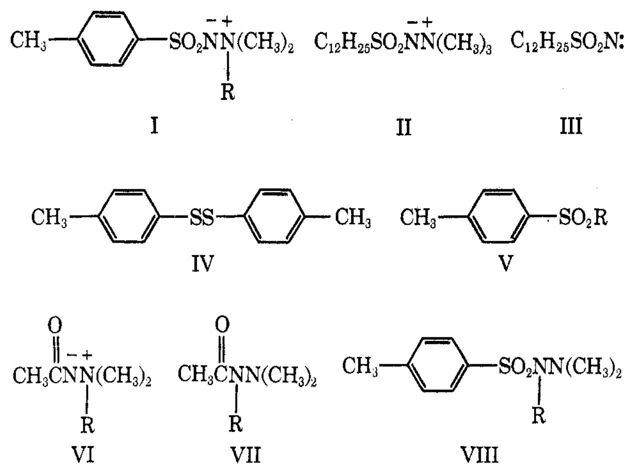
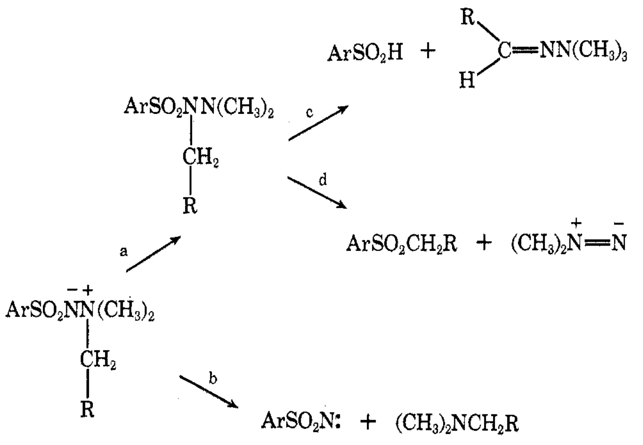
Chart I



Scheme I



those earlier described.[2,3] Thus, pyrolysis at the melting point yielded 4-methylphenyl disulfide (IV, 21%) and sulfone (V, R = 3-methyl-2-butenyl, 22%), along with a volatile fraction which is as yet unidentified but by glpc analysis consists of at least 15 components. Similarly, the benzyl ylide I (R = benzyl) was pyrolyzed to the disulfide IV (4%); sulfone V (R = benzyl, 22%, benzaldehydedimethylhydrazone (5%), *p*-toluenesulfonamide (13%), and a volatile fraction containing *N*,*N*-dimethylbenzylamine (5%). Thus in contrast to the earlier work,[2,3] the pyrolysis of ylides I, in which group R is capable of radical stabilization, leads to major amounts of products, the disulfide IV and sulfone V, formed by complete ejection of the nitrogenous fragment rather than heterolytic cleavage to a nitrene. Since it is known that acylammonioamidates, such as VI (R = benzyl or 3-methyl-2-butenyl), do undergo a facile thermal Stevens rearrangement, by a radical pathway,[4,6] to hydrazides such as VII (R = benzyl or 3-methyl-2-butenyl), it seems likely that in this case also the reaction is prefaced by a similar conversion to the rearrangement product VIII (R = benzyl or 3-methyl-2-butenyl). The hypothetical Scheme I shows how reasonable further transformations *via* paths c and d of this species would yield the hydrazone and sulfone products. Apparently the nitrene route[3] is operative to some extent also, judging by the formation of sulfonamide and amine, path b. The origin of disulfide IV is more difficult to understand, but there is precedence for its formation in the Bamford–Stevens reaction of benzaldehydetosylhydrazone,[7,8] which was rationalized as a deoxygenation of *p*-toluenesulfinate by phenyl carbene. In this series the sulfonylnitrene or dimethyldiazene could be similarly effective deoxygenators, Scheme I.

The product studies noted here suggest that a labile substituent on nitrogen in ylides of type I permits the operation of a previously unobserved pathway in the pyrolytic behavior of such species. They are compatible with the operation of a Stevens type process yielding a substance such as VIII, which may undergo further thermal reactions resulting in complete loss of the nitrogenous portion.

Experimental Section

Melting points were taken on a Thomas-Hoover capillary apparatus and are uncorrected. Elemental analyses were carried out by Midwest Micro-Labs in Indianapolis, Ind. Gas chromatography was performed with a Varian Model 700 equipped with recorder, column temperature 130°, column 30% Carbowax on Chromosorb W (45–60 mesh, 20 ft by 0.375 in.).

Preparation of 1,1-Dimethyl-2-(*p*-toluenesulfonyl)hydrazine.—The procedure of Wawzonek and Meyer[2] was used and the material was obtained as white crystals (57%), mp 78–79° (lit.[2] 79–81°).

Preparation of 1,1-Dimethyl-1-(3-methyl-2-butenyl)-2-(*p*-toluenesulfonyl)hydrazonium Bromide.—1-Bromo-3-methyl-2-butene (20.4 g, 0.136 mol) was added to 26.7 g (0.124 mol) of 1,1-dimethyl-2-(*p*-toluenesulfonyl)hydrazine stirring in 45 ml of acetone. After the solution had been stirred for 24 hr at room temperature and filtered, it yielded 35.9 g (80%) of white solid: mp 107–108°; ir (Nujol) 2700, 1600, 1180 cm^{-1}; nmr ($CDCl_3$) ϵ 1.87 (s, 6), 2.45 (s, 3), 3.07 (s, 1, exchanges), 3.61 (s, 6), 4.71 (d, 2, J = 8 Hz), 5.45 (t, 1, J = 7 Hz), 7.38 (d, 2, J = 8 Hz).

Preparation of 1,1-Dimethyl-1-(3-methylbut-2-enyl)-2-(*p*-toluenesulfonyl)hydrazonium Ylide (I, R = 3-Methyl-2-butenyl).—Potassium *tert*-butoxide (3.46 g, 31.0 mmol) in 22 ml of absolute ethanol was added dropwise to 7.32 g (20.2 mmol) of the hydrazonium bromide stirring in 150 ml of absolute ethanol at room temperature. Stirring for 0.5 hr, followed by filtration and concentration of the filtrate, yielded 5.33 g (93%) of white amorphous solid. Recrystallization from dioxane gave 3.41 (69%) of white prisms: mp 137–138° dec; ir (Nujol) 1270 (s), 1130 (m), 1090 cm^{-1} (m); uv λ_{max} 235 (8600); nmr ($CDCl_3$) ϵ 1.72 (s, 3), 1.80 (s, 3), 2.37 (s, 3), 3.08 (s, 6), 4.03 (d, 1, J = 8 Hz), 5.47 (t, 1, J = 7 Hz), 7.21 (d, 2, J = 8 Hz, 7.79 (d, 2, J = 8 Hz); mass spectrum 70 eV (*m/e*) no molecular ion, 214, 171, 155, 91.

Anal. Calcd for $C_{14}H_{22}O_2S$: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.30; H, 7.70; N, 9.77.

Treatment of this ylide with zinc in water–acetic acid yielded *p*-toluenesulfonamide and *N*,*N*-dimethyl-*N*-(3-methylbut-2-enyl)amine.

Thermolysis of I (R = 3-Methylbut-2-enyl).—Thermolysis was performed by placing 0.951 g of this ylide in a Pyrex 11-mm tube sealed at one end (immersed in an oil bath) and a portion (U shape) immersed in a Dry Ice–acetone bath (−78°). A vacuum (0.04 mm) was applied to the system and the temperature of the oil bath gradually raised. At 140° a vigorous bubbling took place and immediately a yellow condensate, 0.206 g (22%), was collected in the U tube; the nmr indicated *N*-methyl protons, but both glpc and nmr analysis showed little or no *N*,*N*-dimethyl-*N*-(3-methylbut-2-enyl)amine when compared with an authentic sample. The pyrolysis was continued for 20 min and the black residue, 0.705 g, was transferred to a Kügelrohr distillation apparatus and distilled (oven) at 170° (0.05 mm), 0.456 g of yellow oil being collected and 0.192 g of black nonidentifiable tar remaining as residue. Chromatography over alumina of the

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distilled oil (benzene) gave 81 mg of crystalline *p*-tolyl disulfide (IV): mp 43–45° [mp (Eastman *p*-tolyl disulfide IV) 43–45°]; mmp 43–45°; ir and nmr identical. A later fraction (25% $CHCl_3$–75% C_6H_6), 0.132 g, was redistilled, mp 80–81°, white needles. Comparison with authentic *p*-toluene-3-methylbut-2-enyl sulfone prepared by the alkylation of *p*-toluenesulfinic acid with 1-bromo-3-methyl-2-butene showed that the compounds were identical in all respects. Nmr evidence on the crude ylide distillate indicated only the disulfide and sulfone present, and integration yielded weight per cents of 21 and 22%, respectively.

Preparation of 1,1-Dimethyl-1-benzyl-2-(*p*-toluenesulfonyl)-hydrazonium Bromide.—To 12.8 g (59.6 mmol) of 1,1-dimethyl-2-(*p*-toluenesulfonyl)hydrazine in a 50-ml flask was added 20 g (117 mmol) of benzyl bromide. The mixture was warmed on a steam bath until dissolved and allowed to stand for 10 hr at room temperature. The white solid formed was triturated with ether and filtered to yield 14.2 g (62%) of white salt. Recrystallization from ethanol yielded a white powder: mp 105–106°; ir (Nujol) 2750 (broad), 1600, 1700, 1090 cm^{-1}; nmr ($CDCl_3$) δ 2.37 (s, 3), 3.69 (s, 6), 5.52 (s, 2), 7.1–8.1 (m, 9), 9.0–10.5 (broad, 1).

Preparation of 1,1-Dimethyl-1-benzyl-2-(*p*-toluenesulfonyl)-hydrazonium Ylide (I, R = benzyl).—The previously prepared hydrazonium bromide (3.59 g, 9.32 mmol) was dissolved in 20 ml of absolute ethanol and 1.15 g (1.1 equiv) of potassium *tert*-butoxide in 10 ml of ethanol was added while stirring. After the solution was stirred for 4 hr at room temperature, it yielded a white solid, 3.92 g (113%). This was dissolved in hot chloroform and filtered, and the chloroform was removed giving a white solid, 2.12 g (75%). Recrystallization from ethanol yielded white prisms: mp 176–177° dec; ir (Nujol) 1600, 1260, 1130, 1090, 1000 cm^{-1}; nmr ($CDCl_3$) ε 2.30 (s, 3), 3.08 (s, 6), 4.55 (s, 2), 7.0–7.7 (m, 9).

Anal. Calcd for $C_{16}H_{20}N_2O_2S$: C, 63.13; H, 6.62; N, 9.22. Found: C, 63.08; H, 6.49; N, 9.18.

Pyrolysis of the Ylide I (R = Benzyl).—When 1.403 g of this ylide (I, R = benzyl) was pyrolyzed (same manner and apparatus as previously described) at 185° for 15 min, 0.133 g of yellow oil was collected in the trap (−78°). This was not completely characterized, but nmr evidences indicated that *N,N*-dimethylbenzylamine was a major component. The nonvolatile portion, 1.24 g, a black oil, was chromatographed over alumina. Four components were identified: (benzene) 59 mg (4.2%) of *p*-tolyl disulfide; (benzene) 63 mg (4.5%) of benzaldehyde (the dimethylhydrazone was identical with that of the authentic sample); (25% chloroform–75% benzene) 313 mg (22.3%) of *p*-tolyl benzyl sulfone (V, R = benzyl) [recrystallized from carbon tetrachloride; mp 144–145° (lit.[9] 144.5°), nmr ($CDCl_3$) ε 2.40 (s, 3), 4.10 (s, 2) 6.95–7.69 (m, 9)]; and (2% ethyl acetate–98% chloroform) 183 mg (13.1%) of *p*-toluenesulfonamide [mp 136–137° (from water); mixture melting point with the authentic sample was undepressed].

Attempted Preparation of 1,1-Dimethyl-2-benzyl-2-(*p*-toluenesulfonyl)hydrazine (VIII, R = Benzyl).—Reaction of the lithium salt of 1,1-dimethyl-2-(*p*-toluenesulfonyl)hydrazine in ether with benzyl bromide (1 equiv) gave the previously described ylide I (R = benzyl) in 60% yield. With potassium *tert*-butoxide (1 equiv) in ethanol, this ylide also formed. Refluxing potassium *tert*-butoxide (1 equiv) in *tert*-butyl alcohol with the hydrazine (1 equiv) and benzyl bromide (1 equiv) yielded *p*-toluenebenzyl sulfone (V, R = benzyl) as the sole product.

Registry No.—I (R = 3-methyl-2-butenyl), 31529-11-0; I (R = benzyl), 31529-12-1; 1,1-dimethyl-1-(3-methyl-2-butenyl)-2-(*p*-toluenesulfonyl)hydrazonium bromide, 31529-13-2; 1,1-dimethyl-1-benzyl-2-(*p*-toluenesulfonyl)hydrazonium bromide, 31529-14-3.

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Carbomethoxy Radical from Photodecomposition of Carbomethoxymercury Compounds

T. Sakakibara* and Y. Odaira

Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita-shi, Osaka, Japan

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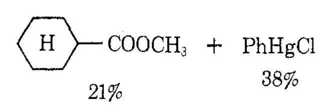
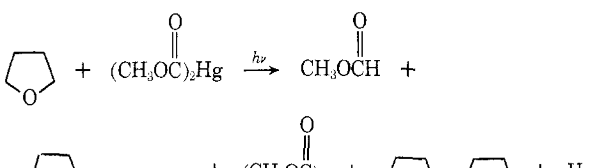
Although many species have been investigated in the study of free-radical chemistry, little work has been reported on carbomethoxy or carbethoxy radicals. These radicals are reportedly unstable and decompose readily to form carbon monoxide and alkoxy radicals or carbon dioxide and alkyl radicals. Gray and Thynne[1] reported that the activation energy of decomposition is only a few kilocalories/mole.

In a course of a study on the photochemical reaction of some mercury compounds,[2] it was found that the photochemical reaction of phenyl(carbomethoxy)mercury with cyclohexyl chloride gave methyl cyclohexylcarboxylate and phenylmercuric chloride, together with some metallic mercury (eq 1).[3] In a similar reaction Fanta[4] found that a photodecomposition of carbomethoxymercuric iodide in benzene produced methyl benzoate and toluene. However, it has not been elucidated whether this carbomethoxylation proceeds *via* formation of a free carbomethoxy radical and can be applied to saturated aliphatic compounds. Thus, we carried out the photochemical reaction of some carbomethoxymercury compounds in tetrahydrofuran (THF).



(1)

In a typical experiment, bis(carbomethoxy)mercury (0.015 mol) was irradiated in THF (82 ml) with a low-pressure mercury lamp for 12 hr under nitrogen. The products formed were methyl formate (50%), methyl tetrahydrofuroate (21%), dimethyl oxalate (5.3%), and α,α′-bistetrahydrofuranyl (43%), in addition to metallic mercury (quantitative yield) (eq 2). The results of photolysis of some organomercury compounds in THF are shown in Table I.



(2)

In the photolysis of carbomethoxymercury compounds, the formation of the esters may be evidence for the carbomethoxy radical and successful carbomethoxyl-

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