solvent evaporated in air leaving 0.18 g. of pale yellow solid, m.p. 175–210°. Crystallization from benzene–petroleum ether (b.p. 80–100°) gave 0.16 g. of crystals m.p. 218–220°. This material did not depress the melting point of an authentic sample of 4-benzenesulfonamido-5-methoxyacenaphthene (X). The infrared spectra of these materials were superimposable.

The reaction of 4-benzenesulfonimido-5-methoxy-5-acenaphthenequinol acetate and hydrochloric acid. 4-Benzenesulfonimido-5-methoxy-5-acenaphthenequinol acetate (XI), 1.4 g. (0.00352 mole), was suspended in 75 ml. of glacial acetic acid and 7 ml. of concd. hydrochloric acid was added with stirring. The yellow suspension slowly changed to a deeper yellow solution over a period of 40 min. and then a yellow-orange solid began to separate. The reaction mixture was stirred for a total of 10 hr. and then allowed to stand overnight at room temperature. The yellow-orange solid was collected on a filter and dried yielding 0.85 g. Chromatographic purification using 2% methyl alcohol in chloroform as eluent followed by crystallization from benzene chloroform gave 0.8 g. of 4,4′-dibenzenesulfonamido-5,5′-dimethoxy-2,1′-biacenaphthylidine (XII) as yellow-orange crystals, m.p. 264–265°, with darkening.

Anal. Calcd. for $C_{35}H_{30}N_2S_2O_6$: C, 67.64; H, 4.48. Found: C, 67.54; H, 4.57.

The acetic acid–hydrochloric acid filtrate from the above reaction was diluted with a large volume of water and 0.30 g. of a yellow substance, m.p. 145–155° precipitated. This was not identified.

Biacenaphthylidine (XIV). Six g. (0.0394 mole) of acenaphthylene was dissolved in 300 ml. of glacial acetic acid and 21 ml. of concd. hydrochloric acid was added with stirring. The solution became more orange and after 10 hr. stirring the yellow solid formed was collected on a filter and washed well with water. There was obtained 5.0 g. of XIV, m.p. 230–250°. A small sample was crystallized from benzene giving yellow-orange prisms, m.p. 275–277° (lit.[18] m.p. 277°).

Boulder, Colo.

[Contribution from the Research Department, Diamond Alkali Co.]

Novel Polyacetylenic Diols[1] and Polyacetylenic Polyurethanes

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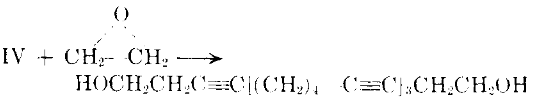
Three novel polyacetylenic-α,ω-diols were prepared by the reaction of formaldehyde, ethylene oxide and trimethylene oxide, respectively, with the α,ω-diGrignard reagent of 1,7,13,19-eicosatetrayne. The diols were converted to the corresponding biscarbanilates and reduced to the known saturated compounds. Reaction of the diols with five different diisocyanates gave a series of polyurethanes. Replacing polypropylene glycol with a polyacetylenic diol in an elastomeric polyurethane formulation gave a polyurethane with a 6.5% greater density and a 20% greater (calories/ml.) heat of combustion.

The preparation of elastomeric polyurethanes by the reaction of polyester glycols or of polyether glycols with diisocyanates is well known.[2] We believed that the use of a long-chain polyacetylenic α,ω-diol, such as could be prepared from 1,7,13,19-eicosatetrayne,[3] should result in a polyurethane having a greater density and energy content than an otherwise similar polyurethane prepared from a polyalkylene ether glycol such as polypropylene glycol (PPG). This paper describes the preparation of several novel polyacetylenic diols, their conversion to polyurethanes and an examination of some mechanical and thermal properties of these polyurethanes.

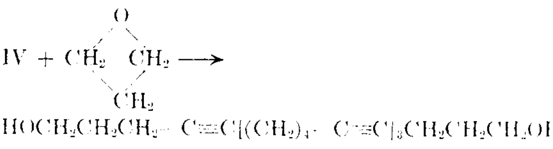
The preparation of 2,8,14,20-docosatetrayne-1,22-diol (I), 3,9,15,21-tetracosatetrayne-1,24-diol (II), and of 4,10,16,22-hexacosatetrayne-1,26-diol (III) was carried out by the reaction of the α,ω-diGrignard reagent of 1,7,13,19-eicosatetrayne with formaldehyde, ethylene oxide, and trimethylene oxide (oxetane) respectively. Treatment of the diols with phenylisocyanate gave the corresponding α,ω-biscarbanilates as derivatives. Catalytic reduction of the polyacetylenic diols gave the corresponding known[4] saturated diols.

$$H-C\equiv C[(CH_2)_4-C\equiv C]_3H + C_2H_5MgBr \longrightarrow BrMgC\equiv C[(CH_2)_4-C\equiv C]_3MgBr \quad (IV)$$

$$IV + CH_2O \longrightarrow HOCH_2-C\equiv C[(CH_2)_4-C\equiv C]_3CH_2OH \quad (I)$$



$$IV + CH_2{-}CH_2O \longrightarrow HOCH_2CH_2C\equiv C[(CH_2)_4-C\equiv C]_3CH_2CH_2OH \quad (II)$$



$$IV + CH_2CH_2CH_2O \longrightarrow HOCH_2CH_2CH_2-C\equiv C[(CH_2)_4-C\equiv C]_3CH_2CH_2CH_2OH$$

(III)

Reaction of the diols with tolylene diisocyanate (TDI), diphenylmethane 4,4′-diisocyanate (MDI), hexamethylene diisocyanate (HMDI), 5,11-hexadecadiyne 1,16-diisocyanate ($OCN[(CH_2)_4C\equiv C]_2(CH_2)_4NCO$) (HDDI)[5] and hexadecane-1,16 diisocyanate (HDI),[5] without a cross-linking agent, gave the simple polyurethanes whose properties

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[1] Presented in part at the 138th Meeting of the American Chemical Society, New York, September 15, 1960, Abstracts of Papers, p. 74-P.

[2] B. A. Dombrow, *Polyurethanes*, Reinhold, New York, 1957, Chapter 6.

[3] J. H. Wotiz, R. F. Adams, and C. G. Parsons, *J. Am. Chem. Soc.*, 83, 373 (1961).

[4] K. E. Murry and R. Schoenfeld, *Australian J. Chem.*, 8, 432–436 (1955); *Chem. Abstr.*, 49, 16472e (1955).

[5] J. H. Wotiz and F. Huba, unpublished results, and also ref. 1.

TABLE I

PROPERTIES OF SIMPLE POLYACETYLENIC POLYURETHANES

Diisocyanate	Diol	Reaction Time, Hr.	Reaction Temp.	η_{inh} 25°, DMF[g]	Softening Range °C.	Shore D Hardness
TDI[a]	I	0.5	78[d]	0.65	274–287	72
TDI	II	12	110[e]	0.31	235–245	—
TDI	III	5	110	0.41	226–238	—
MDI[a]	I	22	98[f]	0.45	133–190	58
MDI	II	18	98	0.70	274–277	74
MDI	III	17	98	0.41	136–150	65
HMDI[a]	I	20	98	0.37	250–283	43
HMDI	II	19	98	0.62	150–280	50
HMDI	III	19	98	0.38	126–138	65
HDDI[b]	I	18	98	—	<50	—
HDDI	II	18	98	0.17	70–75	—
HDDI	III	18	98	0.19	70–80	—
HDI[a]	I	72	110[e]	0.26[h,i]	280–300	—
HDI	II	72	110	0.23[h,i]	335–345	—
HDI	[c]	72	110	0.62[h]	160–360	—

[a] 99.7+% pure. [b] 87% pure. [c] 1,24-Tetracosanediol. [d] Benzene. [e] Toluene. [f] Heptane. [g] Dimethylformamide. [h] *m*-Cresol. [i] Did not all dissolve.

TABLE II

POLYURETHANES OF POLYPROPYLENE GLYCOL[a] AND OF POLYACETYLENIC DIOLS WITH HEXAMETHYLENE DIISOCYANATE[b] AND TRIMETHYLOLPROPANE

	A	B	C	D	E
Diol	PPG[e]	PPG[e]	I	II	II
Cure temp.	60	60	80	80	100
Cure time (days)	3	4	3	4	3
Avg. tensile strength (p.s.i.)	1,300	1,250	3,490	3,650	2,140
Avg. tensile modulus (p.s.i.)	450[f]	425[f]	—	12,400	5,650
Avg. elongation at break (%)	1,380	1,120	1,200	95	160
Test speed (in./min.)	5.0	5.0	20.0	0.5	0.5
No. specimens tested	3	3	1	3	3
Hardness—shore A	40	40	77	100	98
shore D	—	—	—	73	54
Avg. B.t.u./lb.[c]	13,230	13,190	14,650	14,860	14,625
Avg. calories/g.[d]	7,351	7,328	8,140	8,256	8,126
Avg. density (26°)	1.022	1.022	1.094	1.094	1.092
Avg. calories/ml.	7,513	7,489	8,905	9,032	8,874

[a] Polyoxypropylene glycol 2025 from Union Carbide Chemicals Co., South Charleston, W. Va. was used as received. [b] HMDI from Mobay Chemical Co., New Martinsville, W. Va. was distilled prior to use. [c] Average of two values of gross heat of combustion including hydrogen to liquid water and nitrogen to nitric acid dissolved in water. Cosma Testing Laboratories, Cleveland, Ohio. [d] Average B.t.u./lb. × 0.5556. [e] Catalyzed by 10 mg. of ferric acetylacetonate per 0.01 mole of diol, and containing 1% *N*-phenyl-2-naphthylamine as antioxidant based on the combined weight of diol and triol. [f] 100% modulus.

are summarized in Table I. With the exception of the 5,11-hexadecadiyne 1,16-diisocyanate-I product, which was soft and waxy, all the polyurethanes shown were hard and generally tough materials.

A polyurethane similar to that prepared by Smith and Magnusson[6] from polypropylene glycol, hexamethylene diisocyanate and trimethylolpropane was chosen to represent a typical elastomeric composition. Analogous compositions containing I and II in place of the polypropylene glycol were prepared to demonstrate the effect of the triple bonds. The mechanical and thermal properties of those polymers are summarized in Table II.

The polyurethanes based on the polyacetylenic diols have about a 6.5% greater density and about a 20% greater heat of combustion (cal./ml.) than those polyurethanes based on polypropylene glycol. The data also indicate that the use of I results in a more elastomeric polyurethane than does the use of II. I and II were sufficiently more reactive towards the diisocyanate than was polypropylene glycol that the use of a catalyst in the polyacetylenic diol compositions was not needed.

No attempt was made to develop a procedure leading to the optimum mechanical properties of the polyacetylene containing elastomers. Useful elastomeric properties were obtained and presumably could be improved by appropriate formulation studies.

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(6) T. L. Smith and A. B. Magnusson, *J. Polymer Sci.*, **42**, 391 (1960).

TABLE III

BISCARBANILATES OF POLYACETYLENIC DIOLS

Product	Yield, %	M.P.	Empirical Formula	Calcd. C	Calcd. H	Found C	Found H
2,8,14,20-Docosatetrayne-1,22-biscarbanilate	72	106.5–108	$C_{36}H_{40}N_2O_4$	76.7	7.1	76.8	7.2
3,9,15,21-Tetracosatetrayne-1,24-biscarbanilate	78	116	$C_{38}H_{44}N_2O_4$	77.2	7.5	77.2	7.5
4,10,16,22-Hexacosatetrayne-1,26-biscarbanilate	69	85	$C_{40}H_{48}N_2O_4$	77.4	7.8	77.4	7.9

EXPERIMENTAL[7]

1,7,13,19-Eicosatetrayne-α,ω-diGrignard reagent (IV). A solution of 3.2 moles of ethylmagnesium bromide in 3 l. of tetrahydrofuran was placed into a 5-l. flask fitted with a good stirrer, reflux condenser, dropping funnel, and thermometer. 1,7,13,19-Eicosatetrayne (399 g., 1.5 moles) was added with stirring during 30 min. while the temperature rose to a reflux. Refluxing was continued, with the application of external heat, for about 2 hr. until the ethane evolution ceased.

2,8,14,20-Docosatetrayne-1,22-diol (I). The addition funnel of the flask containing IV was replaced with a gas inlet tube dipping below the surface of the liquid. Paraformaldehyde (100 g., 3.33 moles), which had been dried over phosphorus pentoxide, was placed into a flask fitted with a nitrogen inlet tube and a gas outlet tube connected to the Grignard solution flask. A fine stream of dry nitrogen was passed over the paraformaldehyde, while the latter was heated to 170–200°, and the liberated formaldehyde was passed into the Grignard solution until the original black solution had become light tan, usually after 93 g. (3.1 moles) of formaldehyde had been introduced. As the reaction progressed, the mixture became very viscous and stirring became difficult. After all the formaldehyde had been added, the mixture was refluxed an additional 30 min. and then was poured, with stirring, into 12 l. of ice and water to which 1 l. of concd. hydrochloric acid had been added. The solid was filtered off, dried and recrystallized three times from 1-l. portions of carbon tetrachloride to give 300 g. (61%) of I melting at 67–68.5°.

Anal. Calcd. for $C_{22}H_{30}O_2$: C, 81.0; H, 9.2; Hydroxyl No. 346. Found: C, 80.1; H, 9.2; Hydroxyl No. 345.

3,9,15,21-Tetracosatetrayne-1,24-diol (II). A solution of IV (0.086 mole) in 200 ml. of tetrahydrofuran was placed into a 500-ml. flask fitted as before. Ethylene oxide (11.2 g., 0.256 mole) was passed, with the aid of a nitrogen stream, through the stirred, refluxing Grignard solution during 3 hr. The exceptionally viscous mixture was refluxed an additional 30 min. and hydrolyzed by pouring into a dilute hydrochloric acid–ice mixture. The crude solid was dissolved in carbon tetrachloride, dried with anhydrous magnesium sulfate, two-thirds of the solvent removed, and the solution chilled. The resulting product was recrystallized from carbon tetrachloride to give 18.6 g. (57%) of II melting at 74.5–75.0°.

Anal. Calcd. for $C_{24}H_{34}O_2$: C, 81.3; H, 9.6; Hydroxyl No. 317. Found: C, 80.4; H, 9.6; Hydroxyl No. 304.

4,10,16,22-Hexacosatetrayne-1,26-diol (III). A solution of IV (0.586 mole) in 620 ml. of tetrahydrofuran was placed into a 1-l. flask furnished with a stirrer, thermometer, reflux condenser, and an addition funnel. Trimethylene oxide (58 g., 1 mole) was added during 1.2 hr. while the stirred solution was heated at a reflux. After an additional 4-hr. reflux period, the mixture was cooled and then hydrolyzed by pouring into 4 l. of ice and water containing 200 ml. of concd. hydrochloric acid. The solids were filtered off and dissolved in 1 l. of hot carbon tetrachloride, the solution dried with anhydrous magnesium sulfate, concentrated to 650 ml. and cooled and the resulting solid recrystallized from 400 ml. of carbon tetrachloride to give 30 g. (13%) of III melting at 65–66°.

Anal. Calcd. for $C_{26}H_{38}O_2$: C, 81.6; H, 10.0; Hydroxyl No. 294. Found: C, 81.4; H, 10.0; Hydroxyl No. 274.

Biscarbanilates of I–III. A solution of diol (0.05 mole) in 35 ml. of toluene was prepared in a 100-ml. flask fitted with a reflux condenser. Phenyl isocyanate (12 ml., 0.108 mole) was added and the solution was refluxed 30 min., cooled and the product was recrystallized from toluene to give the biscarbanilates whose yields and properties are summarized in Table III.

Catalytic reduction of the polyacetylenic diols. The polyacetylenic diol (5–15 g.) in ethyl acetate (125 ml.) containing about 0.1 g. of platinum dioxide as catalyst was hydrogenated at 60 p.s.i. and at room temperature in a Parr low-pressure, shaker-type hydrogenation apparatus. Hydrogen uptake was essentially complete in 30 min. The mixture was heated to dissolve the product, filtered to remove the catalyst, decolorized with carbon and cooled to separate the saturated diols. The results are summarized in Table IV.

TABLE IV

SATURATED DIOLS FROM POLYACETYLENIC DIOLS

Product	Yield,[a] %	M.P. Found	M.P. Reported[b]
1,22-Docosanediol	90	104–105	105.6–105.7
1,24-Tetracosanediol	75	106–107.5	108.3–108.6
1,26-Hexacosanediol	85	110–110.5	110.4–110.5

[a] No attempt was made to obtain maximum yields. [b] See ref. 4.

Preparation of polyacetylenic polyurethanes. All polyurethanes were prepared by weighing 0.01 mole of the diol into an 18-mm. test tube placed into a vapor bath polymerizer.[8] The diols were melted and degassed at about 30 mm. for 30 min. The diisocyanate (0.01 mole) was weighed into the test tube and mixing was accomplished with bubbling dry high-purity nitrogen. The nitrogen stream was then passed over the melt during the polymerization which was carried out for the time and at the temperature indicated in Table I.

Preparation of elastomeric polyurethanes. The mole ratio of ingredients used was 7.5 diisocyanate:5 diol: 1-trimethylolpropane. All ingredients except the diisocyanate were weighed into a flask fitted with a stirrer, thermometer and a vacuum take-off tube. The flask was immersed in an oil bath kept at 80–90° and the stirred mixture was degassed

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[7] All melting points are uncorrected. Elemental analyses by the Diamond Alkali Co., Research Analytical Laboratory.

[8] P. J. Flory, *J. Am. Chem. Soc.*, 62, 1057 (1940).

in vacuo for 3–5 hr. The diisocyanate was added, stirring was continued for an additional 30 min. and the melt was poured into 4″ × 8″ × 0.075″ polyethylene lined molds and oven cured at 60–100° for 3 or 4 days. After removal from the mold, the polyurethane sheet was cut into 4″ × 0.5″ × 0.075″ strips for physical testing. The results are summarized in Table II.

Acknowledgment. The authors wish to thank Mr. R. F. Adams for the catalytic hydrogenation data and Dr. C. A. Neros and Mr. A. A. Klann for the mechanical testing data.

PAINESVILLE, OHIO

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE GIVAUDAN CORP.]

A New Synthesis of Irones. II. The Synthesis of 4-(2-*p*-Cymyl)-2-butanone

H. E. ESCHINAZI

Received January 26, 1961

In the synthesis of irones by the acid rearrangement of 2-(2,2,3-trimethylcyclobutyl)-hepta-2,4-dien-6-one a substantial amount of 4-(2-*p*-cymyl)-2-butanone is formed as a result of a hydrogen transfer reaction.

In a previous paper[1] describing a new synthesis of irones from α-pinene involving five steps we also reported the formation of a high boiling isomer in 16% yield, 4-phenylsemicarbazone, m.p. 144°.[2]

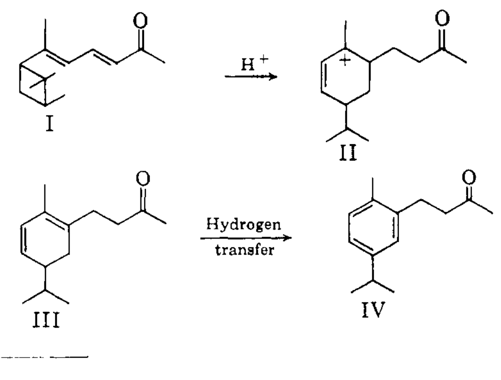
We wish to report the isolation of 4-(2-*p*-cymyl)-2-butanone (IV) as the presumed isomer from the irone-containing mixture resulting from the acid treatment of 2-(2,2,3-trimethylcyclobutyl)-hepta 2,4-dien-6-one.

The unknown ketone reacts readily in the cold with an aqueous alcoholic solution of semicarbazide acetate and gives an immediate precipitate of semicarbazone, m.p. 158–159°, from which the pure ketone is obtained: b.p. 105–106° at 1.5 mm. pressure, n_D^{20} 1.5077, α_D^{25} 0°, 2,4-dinitrophenylhydrazone, m.p. 122°.

The NMR spectrum[3] of the new ketone taken in carbon tetrachloride solution, with tetramethylsilane added as an internal standard, showed six peaks (A to F) in the spectra which corresponded well with the following groups: (A) aromatic; (B) methylene adjacent to aromatic ring, methylene adjacent to ketone and methine (—$\overset{|}{\underset{|}{\mathrm{C}}}$—H) adjacent to an aromatic ring; (C) an isopropyl group on an aromatic ring; (D) methyl ketone; (E and F) methyls of an isopropyl group on an aromatic ring. The interpretation of these data in terms of an aromatic ring substituted by methyl and isopropyl groups and a butanone side chain was furthermore confirmed by the absence of optical rotation, and, by chemical and spectroscopic evidence. In contradistinction with irone which was smoothly hydrogenated to tetrahydroirone in the presence of palladium catalyst, the ketone was unaffected by this treatment thus pointing to the absence of alkene linkages and the possible presence of an aromatic ring. The summation of the above evidence and the Wolff-Kishner reduction of the ketone to 2-butyl-*p*-cymene confirm its structure as that of 4-(2-*p*-cymyl)-2-butanone (IV).

The synthesis of 2-butyl-*p*-cymene was achieved in a single step through the Grignard reaction between carvone and butyl magnesium bromide.[4] The infrared and ultraviolet spectra of the two hydrocarbons were identical in every respect.

The formation of 4-(2-*p*-cymyl)-2-butanone (IV) may be rationalized by assuming that a protonated form of 2-(2,2,3-trimethylcyclobutyl)-hepta-2,4-dien-6-one (I) would first undergo a cyclization accompanied by the splitting of the cyclobutane ring as in II; then the *p*-menthadiene conjugated derivative III obtained from II would, through dis-



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[1] H. E. Eschinazi, *J. Am. Chem. Soc.*, **81**, 2905 (1959).

[2] The elementary analysis gave: C, 74.03; H, 8.18. Calcd. for irone 4-phenylsemicarbazone, $C_{21}H_{29}N_3O$, mol. wt., 339.45: C, 74.29; H, 8.61; N, 12.38. Calcd. for 4-(2-*p*-cymyl)-2-butanone, 4-phenylsemicarbazone, $C_{21}H_{27}N_3O$, mol. wt., 337.42: C, 74.74; H, 8.07; N, 12.45.

[3] We wish to express our sincere thanks to Dr. Martin Saunders of Yale University, New Haven, Conn., for the NMR spectra as well as the constructive suggestions in connection with the elucidation of the structure of the ketone IV.

[4] The Grignard reaction between various alkyl halides and carvone has been described by several workers to give at first the 2-alkyl-*p*-menthatriene which rearranges to 2-alkyl-*p*-cymene under acetic-hydrochloric acid treatment, *cf.* A. Klage, *Ber.*, **39**, 2310 (1906); H. Ruppe and coworkers, *Ber.*, **39**, 1120 (1906); **47**, 3068 (1914); F. W. Semmler, K. Jonas, and P. Roenish, *Ber.*, **50**, 1835 (1917).